Pesticides in tomatoes

Proficiency Testing Program

IAAC T 009 2012

DRAFT FINAL REPORT

May 8, 2013

Organized by

Standards Council of Canada in partnership the Centre d'expertise en analyse environnementale du Québec (CEAEQ)

Under the Auspices of

The Inter-American Accreditation Cooperation

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Conseil canadien des normes

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Acknowledgements

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Standards Council of Canada (SCC) wishes to gratefully acknowledge the support provided by the IAAC secretariat and express our sincere thanks to the Inter American Accreditation Cooperation (IAAC) members and their laboratories for their participation and cooperation. We would also like to acknowledge Sylvie Boisvenue for coordinating this program. Also our thanks to Luc Levert and his team of the Centre d'expertise en analyse environnementale du Québec (CEAEQ) for collaborating the supply, packaging, pre-testing of the samples, the data analysis and assisting in preparing the final report.

CEAEQ is accredited as a proficiency testing provider (CAN-P-1593 and CAN-P-43) by the Standards Council of Canada (SCC) and is presently on the list of approved Proficiency Testing providers for SCCs PSA Environmental Testing program. Their accreditation scope covers the PT projects of the current program. The CEAEQ also has extensive expertise and is an ISO/IEC 17025 accredited laboratories by the SCC since December 1999.

CEAEQ would like to warmly acknowledge the support provided by La *Direction du laboratoire d'expertise et d'analyse alimentaire (DLEAA)* of the *Ministère de l'agriculture, des pêcheries et de l'alimentation du Québec (MAPAQ)* for the product development and validation.

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Summary of Results

1. The proficiency testing (PT) programme, IAAC T009, was conducted from December 2012 to February 2013

2. A total of 24 laboratories from 6 economies (7 accreditation bodies) participated in the program and 18 laboratories submitted their results.

3. The program was specifically designed to evaluate some pesticides from two different families; organochlorinated and organophosphates pesticides. The PT program consisted of three 3,0 grams samples of freeze-dried and ground tomatoes with no preservative. The bottles used were 15 ml amber glass with PTFE lined caps.

4. Z-scores were used to evaluate the performance of the participants.

Table 1: Summary of the results for the Proficiency Testing Study

Pesticides (mg/kg)	Sample No.	Assigned value (Mean)	Total number of reported results
Cypermethrin	1 2 3	2,00 3,27 2,06	15
p,p'-DDT	1 2 3	0,674 0,950 0,721	15
Dimethoate	1 2 3	0,191 0,431 0,248	17
Carbaryl	1 2 3	0,906 1,19 1,00	17
Carbofuran	1 2 3	0,979 0,994 1,23	17
Diazinon	1 2 3	0,176 0,174 0,254	14
Endosulfan I	1 2 3	0,428 0,339 0,536	16
Endosulfan II	1 2 3	0,848 0,829 1,11	16
Malathion	1 2 3	0,614 0,686 0,712	16

1: Foreword

This report summarizes the results of the ***IAAC T009 - Pesticides in tomatoes - Proficiency Testing Program*** for testing laboratories on behalf of the *Inter-American Accreditation Cooperation (IAAC)*. The Standards Council of Canada coordinated the program in cooperation with our collaborator, the Centre d'Expertise en Analyse Environnementale du Québec. The validation of the material used in the Proficiency Testing study was made in collaboration with La *Direction du Laboratoire d'Expertises et d'Analyses Alimentaire (DLEAA)* of *Ministère de l'alimentation, des pêches et de l'agriculture du Québec (MAPAQ)* which is ISO/IEC 17025 accredited by the SCC. The program covered the analysis of cypermethrin, p,p'-DDT, dimethoate, carbaryl, carbofuran, diazinon, endosulfan I, endosulfan II and matlathion in tomatoes.

2: Introduction

2.1 Objectives for the Evaluation

The use of pesticides is prevalent throughout the world. Although this use can be an asset for agricultural producers, it is now proven that it is also a threat to public health. It can also affect animals and plants by leaching into soils and surface water. Pesticide pollution can also have a significant impact on the economy.

In recent years, many nations have realized the problem with pesticide pollution and are taking steps to control or clean up the polluted waters and soils. Organic farming has become a huge trend. People all over the world are better informed about the risk associated with pesticide pollution. Comparable results from laboratories of each country are essential. Even more when we know that it represents several public health concerns, especially for children.

The objective of this inter laboratory testing program was to evaluate a few compounds of two large pesticides families; organochlorinated and organophosphates pesticides. As it is crucial for human, animal and environmental health to make sure that food can be tested around the world with similar results. The PT program consisted of three 3.0 grams samples of freeze-dried ground tomatoes with no preservative. The bottles used were 15 ml amber glass with PTFE lined caps.

2.2 Participants in the Evaluation

In August 2012, the SCC sent a proposal detailing the study. It has been discussed and accepted at the IAAC General Assembly by the IAAC Laboratory Subcommittee. IAAC accrediting bodies were requested to nominate laboratories in their respective economies to participate in this study. Included in the invitation was a description of the samples (matrix, concentration range) and measurands to be analyzed and a nomination form to be completed for each participant. Information provided was used to register the laboratories and assigned a unique identification for reporting PT results. The deadline for returning the nomination form was October 15th 2012.

A total of 24 laboratories from 6 economies (7 accreditation bodies) participated in the program. IAAC member laboratory accreditation bodies were invited to participate. 18 laboratories submitted their results. The details of the participating economies, accreditation bodies and number of laboratories for each one are presented in Annex A.

3: Design and Implementation

3.1 Sample Preparation and Distribution

For each samples, a large batch of tomatoes was obtained from a local provider. A mixture of pesticides was added to the material. The final product was a homogeneous powder. This powder was designed to be combined with water prior to the analysis.

The 3 samples had concentrations that were unique, within 0.1 and 30 mg/kg for each pesticide (dry weight basis).

3.2 Homogeneity and Stability Testing

Homogeneity was evaluated for each sample with the analysis of 10 replicates randomly selected among the bottles. All of the pesticides were analysed for each sample by the DLEAA. The between-samples standard deviation (S_s) was compared to the inter laboratory standard deviation (σ_{pt}). The samples were considered adequately homogeneous if

$$S_s \leq 0.3\sigma_{pt}$$

The individual test results for each sample and pesticide for the homogeneity verification is found in Annex F.

All the pesticides were analysed for each sample by the DLEAA. The samples were considered stable if the difference between the stability results (X) with the reference value (Y) from homogeneity testing is lower than $0.3\sigma_{pt}$.

$$|X - Y| \leq 0.3\sigma_{pt}$$

The individual results for each sample and pesticide from the stability verification is found in Annex F.

The homogeneity and stability testing of the samples were not always acceptable according to *ISO 13528:2005, Annex B*. In that case, the guideline suggests that the proficiency testing provider check its preparation and storage procedures in order to look for any improvement, which will be the case.

3.3 Samples distribution

The samples were labelled as IAAC T 009 2012 – Tomatoes samples #1, #2 and #3 with identification of the parameter and a serial number. The serial numbers were randomly assigned to the participants.

A package was prepared and labelled for each participating laboratory. Hardcopies of the "*IAAC T009 2012 instruction letter for laboratory.doc*", "*IAAC T009 2012 receipt of samples acknowledgement form (for laboratories).doc*", "*IAAC T009 2012 – Information – Analysis Conditions.doc*" as well as a reporting form spreadsheet customized for each laboratory *"lab number.xls"* were enclosed in each individual package. Each participating laboratory was identified with a unique confidential laboratory code number.

A bulk package containing individually labelled packages for the participating laboratories was prepared for each Accreditation Body. A hardcopy of the "*IAAC T009 2012 instruction letter (for AB).doc*" and "*IAAC T009 2012 receipt of samples acknowledgement form (for AB).doc*" was enclosed in each bulk package.

There were also some packages sent directly to the laboratories, according to their shipment's preferences. In that case, the packages did not include letters to the accreditations bodies

An electronic copy of all the documents and report files was also sent to each laboratory by email on December 14th 2012 with detailed instructions and unique reporting spreadsheet. Refer to Annex D for these documents and forms.

The packages with the PT samples were sent via courier on December 12th 2012. In the case that the packages were not sent directly to the laboratories, each AB was responsible to distribute the individually labelled packages to their participating laboratories. Each AB or laboratory had to acknowledge via email the receipt of the samples to the Coordinator of the IAAC T009 2012 program before December 26th 2012.

The laboratories had to return their results before January 31st 2013 employing the customized *"lab number.xls"* spreadsheet along with their completed "*IAAC T009 2012 – Information – Analysis Conditions.doc*". On January 8th 2013, an important notice was sent to the laboratories regarding the report of the results. Refer to the Annex E for this email. On January 21st 2013, this deadline was extended to February 14th 2013 via email. You may also refer to the Annex E for this email.

3.4 Sample results reception

Each of the participants was randomly allocated a unique confidential code number and provided their own uniquely numbered *"lab number.xls"* spreadsheet. All reference to the participants in this report is via the code they were allocated. The laboratories reported their results with the associated uncertainty, where available. Additional information on the analysis method used for each measurand was also reported by the participants on the supplied "*IAAC T009 2012 – Information – Analysis Conditions.doc*". All results were registered in a database used for the statistical analysis. Before performing the statistical analysis, an email

was sent to every laboratory who submitted results. The objective was to let us know if any result needed to be changed because of a typing error or else. Refer to Annex E.

Six laboratories did not analyse or report results for any of the PT samples.

The results with associated uncertainty values reported by each laboratory are shown in Annex B.

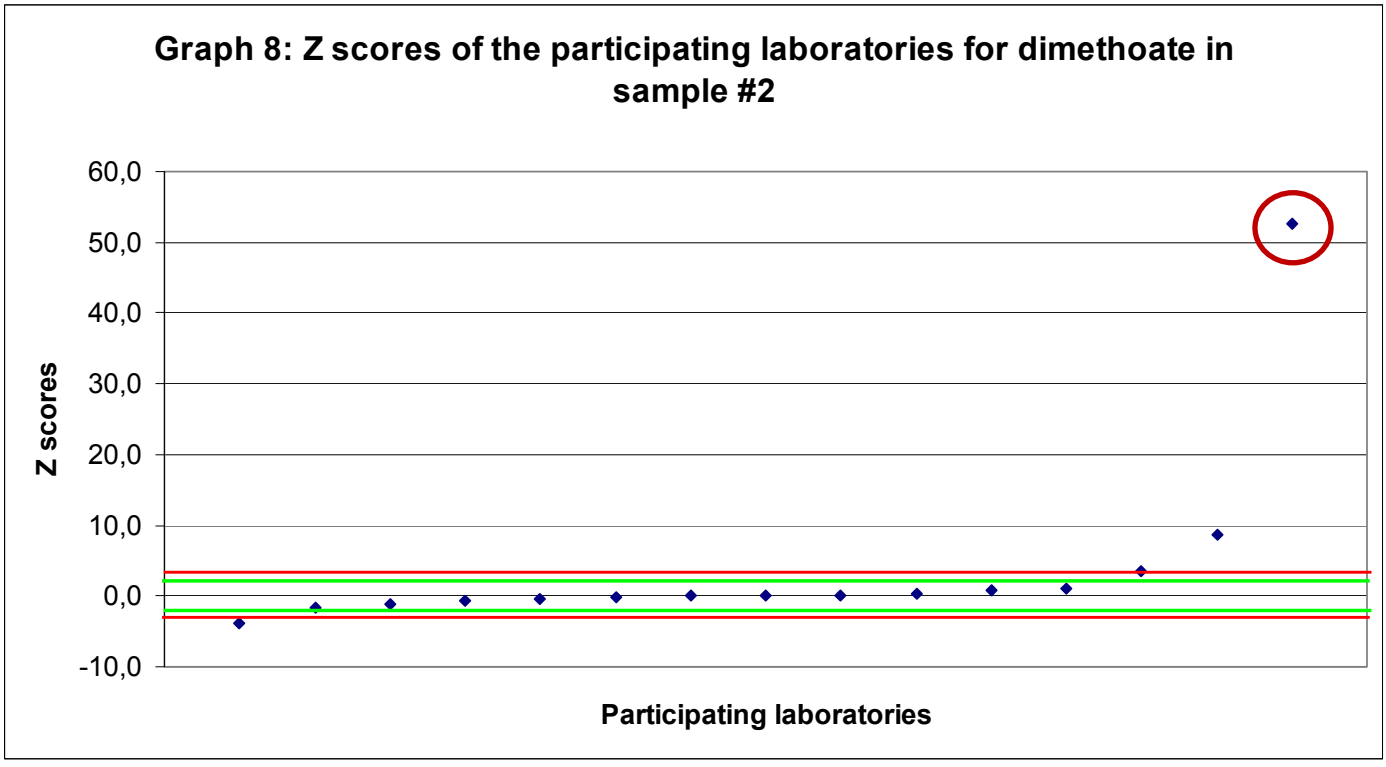
4: Statistical Evaluation of Results

Proficiency testing by inter laboratory comparisons is used to determine the performance of individual laboratories for specific tests or measurements. This IAAC T009 2012 PT program used the ISO/IEC 17043 requirements. All statistical methods used for the assessment of the laboratories are described in the ISO 13528:2005, *"Statistical methods for use in proficiency testing by inter laboratory comparisons"*, Geneva, Switzerland.

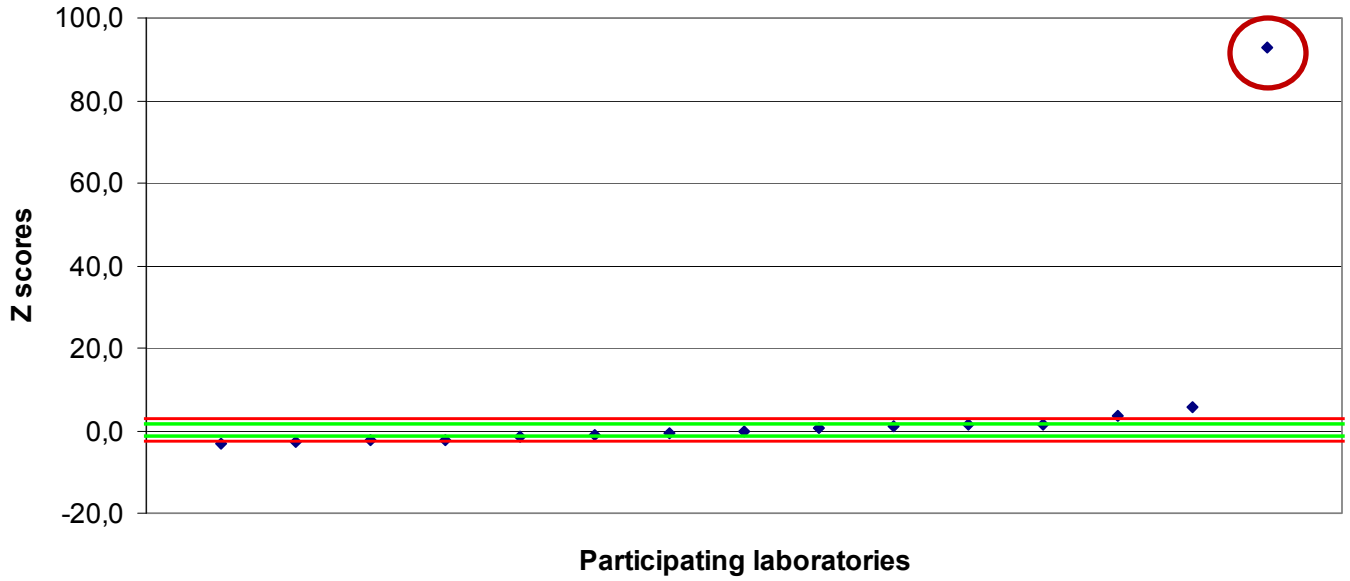
4.1 Determination of the assigned values and standard deviations:

The assigned value was calculated employing the consensus value from participants and is the robust average of the results reported by all participants in the round using robust statistics as determined by Algorithm A in ISO 13528. With this robust method the outliers have no influence on the values of the robust estimates.

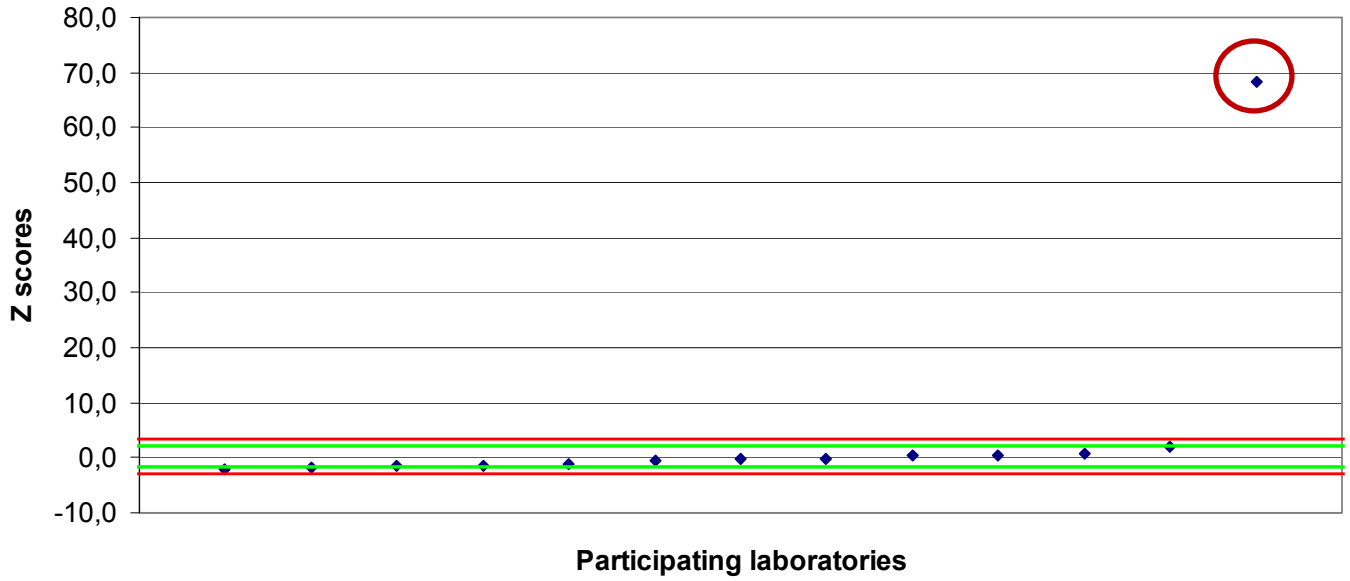
However, before proceeding with the statistical analysis, some obvious outliers were intentionally removed. See the examples below:



Graph 19: Z scores of the participating laboratories for endosulfan I in sample #1



Graph 25: Z scores of the participating laboratories for malathion in sample #1



4.2 Determination of the uncertainty of the assigned value

Statistically, the assigned value from any PT round has a standard uncertainty μ_x that depends on the method that is used to derive it, and also, when it is derived from tests in several laboratories, on the number of laboratories and perhaps on other factors. If the standard uncertainty μ_x of the assigned value is too large in comparison with the standard deviation for proficiency testing σ_{pt}, then there is a risk that some laboratories will receive action and warning signals because of inaccuracy in determination of the assigned value, not because of any cause within the laboratories.

When the assigned value is derived as a robust average calculated using Algorithm A, the standard uncertainty of the assigned value *X* is estimated as:

$$\mu x = 1.25 \times s^* / \sqrt{p}$$

Where s* is the robust standard deviation of the results calculated using Algorithm A.

If:

$$\mu x \leq 0.3 \sigma pt$$

Where, σ_{pt} is the standard deviation used to assess proficiency.

Then the uncertainty of the assigned value is negligible it not need be included in the interpretation of the results of the proficiency test.

The standard deviation σ_{pt} used to assess the proficiency of participants could have been derived from the results reported by the participants in the round. However, according to point 6.2 of the ISO 13528:2005 norm, it is possible to prescribe the standard deviation that should be used for the proficiency testing. In this study, the standard deviation given by the Algorithm A would have been too large in order to compare laboratories between them. Also, as it is a human health concern, it would have been illogical to allow as much as 50 or 60 % of expected deviation. The allowed expected deviation has been fixed to 20%, which is reasonable according to the standard deviations of the samples that are always under 10%. (see Annex F)

According to *Health Canada* the Maximum Residue Limits (MRLs) in food can be as low as 0.001 mg/kg, depending on the pesticide and the food. As an example, for tomatoes the MRL for cypermethrin is 0.3 mg/kg. Therefore, a high expected deviation would lead to a possible effect on human. For additional information about MRLs, refer to *Health Canada*'s website: http://www.hc-sc.gc.ca/dhp-mps/vet/mrl-lmr/index-eng.php.

4.3 Z-score calculation

The Z-scores were calculated using the assigned value and the standard deviation calculated from the results of the participants as:

$$Z = |x - X| / \sigma_{pt}$$

Where σ_{pt} is the standard deviation for proficiency assessment, X is the assigned value and x the laboratory result.

The z-scores can be interpreted and evaluated as follows:

(a) $|z| \leq 2$ Satisfactory
(b) $2 < |z| < 3$ Questionable
(c) $|z| \geq 3$ Unsatisfactory

The z-scores and their evaluations are found in Annex C.

Laboratories having a z-score > 3 or < -3 should thoroughly investigate their results. Also, the laboratories having a z-score in the range $2 < |z| < 3$ are encouraged to review the results.

The points allocated for every Z Score in are attributed as follows:

Z Score	Score
$\|Z\| \leq 1$	5
$1 < \|Z\| \leq 2$	4
$2 < \|Z\| \leq 3$	3
$\|Z\| > 3$	0

The graphic representations of the results are found in Annex C.3. On these charts, laboratory's z-score are shown in order of magnitude.

An interim report containing the participant's results was issued to participants and their on March 22nd 2013. Participants were requested to check the correctness of their submitted data and to inform the organizers of any transcription errors as soon as possible.

5: Technical comments and discussion

The z-scores of the individual participants and their evaluations are presented in the tables in Annex C and the ordered z-scores charts of the results are in Graph 1' to 27' within Annex C. The z-score performance of the participants is summarized as follows:

Table 2 : Z Scores repartition for each sample of every pesticide

Pesticides (mg/kg)	Sample No.	Total number of reported results	|z| ≤ 2		2 < |z| < 3		|z| ≥ 3	
			No.	%	No.	%	No.	%
Cypermethrin	1	15	4		1		10	
	2	15	5		1		9	
	3	15	5		1		9	
	Total :	45	14	**31,1**	3	**6,7**	28	**62,2**
p,p'-DDT	1	15	3		5		7	
	2	16	7		4		5	
	3	16	5		7		4	
	Total :	47	15	**31,9**	16	**34,0**	16	**34,0**
Dimethoate	1	17	11		3		3	
	2	17	11		0		6	
	3	17	12		1		4	
	Total :	51	34	**66,7**	4	**7,8**	13	**25,5**
Carbaryl	1	17	14		1		2	
	2	17	10		4		3	
	3	17	14		1		2	
	Total :	51	38	**74,5**	6	**11,8**	7	**13,7**
Carbofuran	1	17	14		2		1	
	2	17	13		3		1	
	3	17	13		3		1	
	Total :	51	40	**78,4**	8	**15,7**	3	**5,9**
Diazinon	1	14	12		1		1	
	2	14	12		0		2	
	3	14	10		1		3	
	Total :	42	34	**81,0**	2	**4,8**	6	**14,3**
Endosulfan I	1	16	10		2		4	
	2	16	8		3		5	
	3	16	7		2		7	
	Total :	48	25	**52,1**	7	**14,6**	16	**33,3**
Endosulfan II	1	16	10		4		2	
	2	16	12		1		3	
	3	16	9		3		4	
	Total :	48	31	**64,6**	8	**16,7**	9	**18,8**
Malathion	1	16	11		2		3	
	2	16	10		3		3	
	3	16	12		1		3	
	Total :	48	33	**68,8**	6	**12,5**	9	**18,8**

By looking to the "*Table 2: Z Scores repartition for each sample of every pesticide"*, it is obvious that only a small percentage of laboratories reported results within two sigma (i.e. 2 x 20%) for cypermethrin and p,p'-DDT.

For cypermethrin, it could be due to the complexity of the chromatograph. There are four detectable isomers for this substance (*alpha*, *beta*, *theta* and *zeta-cypermethrin*). Therefore not only the integration can be

harder but also the calibration. It has been reported by some laboratories that only one or two of the isomers were tested.

About p,p'-DDT, the main problem may reside in the injection. It is really important to be careful with this analyte as it tends to degrade in the injection port. This degradation leads to the presence of other analytes such as DDD and DDE. A few of the participants mentioned the problem.

Participating laboratories were asked to describe the analytical methods used in the IAAC T009 program using the "*IAAC T009 2012 – Information – Analysis Conditions.doc*" form. At least 60 % of the participating laboratories used the *QuEChERS* or a *QuEChERS*-like method. At least 80 % used a GC column of 30 m. No statistical assessments were made regarding methods performance. Since some of the methods (such as *Soxhlet extraction*) were used only by a small number of laboratories, no conclusion can be made on the real performance of the method (e.g. If only 1 laboratories used method X and all of them failed, we would find that, for this study, 100% of laboratories that used method X have an unsatisfactory results).

Difficulties of some laboratories in order to get a satisfying performance can be related to the choice of method but could be induced by some deficiencies in the assurance quality program and maintenance of equipment. In general, good practices like instrument calibration and maintenance, the use of reference material in real matrices (when it is possible), fortified samples and different sources of reference material in addition of the use of standards are very important.

6: Conclusion

In general, the laboratories participating in IAAC T009 proficiency testing program performed well. Technical factors such as lack in instruments calibration and maintenance, the absence of reference material in real matrices (when it is possible), fortified samples and different sources of reference material could explain the difficulties of some laboratories in order to get a satisfying performance. However, some problems concerning the homogeneity and stability of the samples could also be a part of explanation. A good quality assurance program should include the use of reference material, fortified samples, etc. on a regular basis with acceptance criteria. It should also include a calibration and maintenance program of the critical equipments.

Finally, inter laboratory testing is also essential to ensure an effective measurement of water quality by laboratories. This program also highlights the positive effect of a regular and close in time frame proficiency testing participation of laboratories on their analytical performances.

7: Acknowledgments:

An inter laboratory study of this magnitude would not be possible without the help of a team of dedicated people. We thank all the technical staff of the reference material division of the CEAEQ for their excellent work preparing and packaging the samples. We would also like to thank the team of chemists and technicians of our reference laboratory, the Laboratoire d'Expertise et d'Analyse Alimentaire (DLEAA) for their assistance in the verification of the homogeneity and stability and their help for product development.

Annex A: List of participating economies

Table A.1: List of participating economies and their related accreditation bodies

Economy	Accreditation Body	No. of Labs
Canada	Standards Council of Canada (SCC)	4
United States of America	ACLASS, brand of ANSI-ASQ National Accreditation Board	3
United States of America	American Association for Laboratory Accreditation (A2LA)	2
Ecuador	Organismo de Acreditación Ecuatoriano (OAE)	2
Chile	Instituto Nacional de Normalización (INN)	2
Paraguay	Organismo Nacional de Acreditacion (ONA)	1
Colombia	Organismo Nacional de Acreditacion de Colombia (ONAC)	4

Annex B: Data reported by laboratories

Table B1: Results for cypermethrin in tomatoes

Laboratory (confidential number)	**Sample #1** (mg/kg)	**Sample #2** (mg/kg)	**Sample #3** (mg/kg)
22	---	---	---
15	---	---	---
47	2,122	3,789	2,246
5	N,A	N,A	N,A
32	11,06	26,02	14,31
17	1,59	2,42	1,81
16	10,288	13,202	16,148
40	3,0	4,3	2,6
20	0,3084	0,2667	0,1754
7	3,67	5,75	3,86
34	1,158	3,872	1,262
10	2,07	3,10	2,24
38	0,72	1,24	0,87
14	1,99	3,24	2,46
35	3,33	4,76	3,41
6	3,87	6,76	3,75
28	0,531	0,210	0,158
9	4,279	6,876	4,321

Table B2: Results for p,p'-DDT in tomatoes

Laboratory (confidential number)	**Sample #1** (mg/kg)	**Sample #2** (mg/kg)	**Sample #3** (mg/kg)
22	---	---	---
15	0,87	1,23	1,01
47	1,086	1,540	0,992
5	N,A	N,A	N,A
32	Nodetectable	21,34	23,26
17	0,36	0,61	0,55
16	2,528	3,166	2,770
40	1,4	1,6	1,3
20	0,1580	0,4152	0,1689
7	0,988	1,43	1,06
34	0,165	0,375	0,300
10	0,49	0,63	0,58
38	0,30	0,42	0,38
14	1,08	1,29	1,10
35	0,960	1,24	1,13
6	1,16	1,64	1,12
28	0,597	0,91	0,690
9	1,058	1,152	0,840

Table B3: Results for dimethoate in tomatoes

Laboratory (confidential number)	**Sample #1** (mg/kg)	**Sample #2** (mg/kg)	**Sample #3** (mg/kg)
22	---	---	---
15	<15	<15	<15
47	0,110	0,388	0,152
5	0,147	0,405	0,189
32	6,36	5,11	4,08
17	0,28	0,75	0,43
16	0,104	0,293	0,119
40	0,2	0,4	0,2
20	0,2280	0,1105	0,2862
7	0,187	0,467	0,233
34	0,190	0,452	0,235
10	0,14	0,34	0,20
38	0,21	0,53	0,29
14	0,19	0,45	0,24
35	0,192	0,431	0,261
6	0,21	0,51	0,28
28	0,806	1,208	1,332
9	0,181	0,44	0,241

Table B4: Results for carbaryl in tomatoes

Laboratory (confidential number)	**Sample #1** (mg/kg)	**Sample #2** (mg/kg)	**Sample #3** (mg/kg)
22	1,07	1,42	1,16
15	---	---	---
47	0,883	1,208	1,009
5	1,101	1,498	1,287
32	0,43	0,52	0,67
17	1,10	3,22	1,05
16	0,957	0,977	0,798
40	1,8	1,8	0,8
20	0,1942	0,3031	0,2740
7	1,17	1,79	1,31
34	0,974	1,252	1,066
10	0,84	0,83	0,99
38	1,25	1,86	1,52
14	0,93	1,03	0,95
35	0,826	0,926	0,945
6	0,57	0,74	0,68
28	0,910	1,86	1,34
9	1,158	1,475	1,311

Table B5: Results for carbofuran in tomatoes

Laboratory (confidential number)	**Sample #1** (mg/kg)	**Sample #2** (mg/kg)	**Sample #3** (mg/kg)
22	0,78	0,79	1,00
15	---	---	---
47	1,046	1,115	1,335
5	1,121	1,204	1,530
32	0,74	0,87	1,09
17	1,30	1,54	1,87
16	1,084	0,859	0,789
40	1,3	1,4	1,4
20	0,5455	0,7210	0,6784
7	1,23	1,41	1,53
34	1,253	1,210	1,688
10	0,86	0,76	1,11
38	1,32	1,41	1,68
14	1,06	0,95	1,30
35	0,817	0,754	1,05
6	0,70	0,70	0,85
28	5,56	5,93	10,98
9	1,212	1,212	1,533

Table B6: Results for diazinon in tomatoes

Laboratory (confidential number)	**Sample #1** (mg/kg)	**Sample #2** (mg/kg)	**Sample #3** (mg/kg)
22	---	---	---
15	---	---	---
47	0,244	0,225	0,223
5	N,A	N,A	N,A
32	0,94	1,17	1,66
17	n/a	n/a	n/a
16	0,145	0,108	0,297
40	0,2	0,15	0,2
20	0,1487	0,1044	0,0960
7	0,194	0,177	0,313
34	0,154	0,154	0,256
10	0,15	0,12	0,210
38	0,23	0,21	0,33
14	0,12	0,11	0,25
35	0,200	0,240	0,326
6	0,19	0,19	0,29
28	0,17	0,36	0,17
9	0,253	0,238	0,386

Table B7: Results for endosulfan I in tomatoes

Laboratory (confidential number)	**Sample #1** (mg/kg)	**Sample #2** (mg/kg)	**Sample #3** (mg/kg)
22	---	---	---
15	0,57	0,44	0,87
47	0,357	0,250	0,503
5	N,A	N,A	N,A
32	8,81	10,60	14,27
17	0,30	0,26	0,45
16	0,968	0,714	1,373
40	0,8	0,5	0,8
20	0,3872	0,5585	0,2053
7	0,434	0,283	0,667
34	0,770	0,335	0,675
10	0,26	0,17	0,40
38	0,16	0,12	0,24
14	0,23	0,14	,041
35	0,543	0,460	0,874
6	0,52	0,33	0,70
28	0,210	0,188	0,354
9	0,592	0,385	0,815

Table B8: Results for endosulfan II in tomatoes

Laboratory (confidential number)	**Sample #1** (mg/kg)	**Sample #2** (mg/kg)	**Sample #3** (mg/kg)
22	---	---	---
15	0,93	0,95	1,35
47	0,768	0,685	1,051
5	N,A	N,A	N,A
32	9,56	18,01	13,51
17	0,79	0,81	1,17
16	2,477	2,026	3,220
40	1,1	0,5	0,9
20	0,7813	0,8901	0,3895
7	1,03	0,895	1,41
34	0,630	0,890	0,795
10	0,66	0,52	0,97
38	0,39	0,36	0,58
14	0,60	,042	0,96
35	1,27	1,12	1,73
6	1,30	1,15	1,65
28	0,591	0,515	0,797
9	1,243	0,982	1,538

Table B9: Results for malathion in tomatoes

Laboratory (confidential number)	**Sample #1** (mg/kg)	**Sample #2** (mg/kg)	**Sample #3** (mg/kg)
22	---	---	---
15	<15	<15	<15
47	0,629	0,945	0,887
5	N,A	N,A	N,A
32	9,37	1,36	4,56
17	0,58	0,71	0,76
16	0,385	0,399	0,387
40	2,3	3,0	2,4
20	0,9063	0,6367	0,6342
7	0,683	0,893	0,975
34	<0,1	<0,1	<O,1
10	0,43	0,45	0,56
38	0,47	0,62	0,59
14	0,44	0,41	0,61
35	0,630	0,852	0,824
6	0,75	0,97	0,93
28	,506	0,545	0,605
9	0,679	0,854	0,876

Annex C: Summarized and Detailed Results, Z-Score charts

Annex C.1: Summary of the results for each parameter

In this section, the tables are presenting the overall scores for each pesticide, by laboratories. Reported in percentage, it represents the average of the z-scores for the three samples.

The overall scores should be interpreted in the same way than the z-scores. When the absolute value of a z-score is under 2, it is judged satisfactory. Therefore, an overall score over 80 % should also be interpreted as satisfactory. An overall score between 60 and 80 % can be interpreted as questionable. Finally, an overall score under 60% could be interpreted as unsatisfactory.

	5	6	7	9	10	14	15	16	17	20	22	28
Cypermethrin	---	0	0	0	100	100	---	0	87	0	---	0

	32	34	35	38	40	47
Cypermethrin	0	80	20	20	0	100

Number of participants : 15

	5	6	7	9	10	14	15	16	17	20	22	28
p.p DDT	---	20	60	80	87	47	73	0	73	20	---	100

	32	34	35	38	40	47
p.p DDT	---	20	67	60	20	27

Number of participants : 15

	5	6	7	9	10	14	15	16	17	20	22	28
Dimethoate	87	100	100	100	87	100	0	67	20	67	---	0

	32	34	35	38	40	47
Dimethoate	0	100	100	93	67	80

Number of participants : 17

	5	6	7	9	10	14	15	16	17	20	22	28
Carbaryl	80	80	73	80	93	100	---	93	60	0	100	80

	32	34	35	38	40	47
Carbaryl	67	100	93	67	0	100

Number of participants : 17

	5	6	7	9	10	14	15	16	17	20	22	28
Carbofuran	87	80	73	80	93	100	---	93	67	67	87	0

	32	34	35	38	40	47
Carbofuran	93	80	93	73	67	100

Number of participants : 17

	5	6	7	9	10	14	15	16	17	20	22	28
Diazinon	---	100	93	67	93	87	---	93	---	60	---	60

	32	34	35	38	40	47
Diazinon	0	100	87	80	60	87

Number of participants : 14

	5	6	7	9	10	14	15	16	17	20	22	28
Endosulfane I	---	87	93	80	73	40	53	0	87	33	---	67

	32	34	35	38	40	47
Endosulfane I	0	60	53	20	33	93

Number of participants : 16

	5	6	7	9	10	14	15	16	17	20	22	28
Endosulfane II	---	67	87	80	87	60	93	0	100	67	---	80

	32	34	35	38	40	47
Endosulfane II	0	87	67	60	67	100

Number of participants : 16

	5	6	7	9	10	14	15	16	17	20	22	28
Malathion	---	73	87	87	80	80	0	67	100	87	---	93

	32	34	35	38	40	47
Malathion	0	0	93	93	87	87

Number of participants : 16

Annex C.2: Detailed results

Parameter : Cypermethrin
Units : mg/kg (dry weight basis)

	Sample 1			Sample 2			Sample 3		
Lab #	Result	Z score	Pt	Result	Z score	Pt	Result	Z score	Pt
5	---			---			---		
6	3,87	+4,7	0	6,76	+5,3	0	3,75	+4,1	0
7	3,67	+4,2	0	5,75	+3,8	0	3,86	+4,4	0
9	4,279	+5,7	0	6,876	+5,5	0	4,321	+5,5	0
10	2,07	+0,2	5	3,10	-0,3	5	2,24	+0,4	5
14	1,99	0,0	5	3,24	0,0	5	2,46	+1,0	5
15	---			---			---		
16	10,288	+21	0	13,202	+15	0	16,148	+34	0
17	1,59	-1,0	4	2,42	-1,3	4	1,81	-0,6	5
20	0,3084	-4,2	0	0,2667	-4,6	0	0,1754	-4,6	0
22	---			---			---		
28	0,531	-3,7	0	0,210	-4,7	0	0,158	-4,6	0
32	11,06	+23	0	26,02	+35	0	14,31	+30	0
34	1,158	-2,1	3	3,872	+0,9	5	1,262	-1,9	4
35	3,33	+3,3	0	4,76	+2,3	3	3,41	+3,3	0
38	0,72	-3,2	0	1,24	-3,1	0	0,87	-2,9	3
40	0,3084	-4,2	0	0,2667	-4,6	0	0,1754	-4,6	0
47	2,122	+0,3	5	3,789	+0,8	5	2,246	+0,5	5
Expected value	2,00			3,27			2,06		
Expected deviation	0,400	20%		0,654	20%		0,412	20%	

Parameter : p.p DDT
Units : mg/kg (dry weight basis)

Lab #	Sample 1			Sample 2			Sample 3		
	Result	Z score	Pt	Result	Z score	Pt	Result	Z score	Pt
5	---			---			---		
6	1,16	+3,6	0	1,64	+3,6	0	1,12	+2,8	3
7	0,988	+2,3	3	1,43	+2,5	3	1,06	+2,4	3
9	1,058	+2,8	3	1,152	+1,1	4	0,840	+0,8	5
10	0,49	-1,4	4	0,63	-1,7	4	0,58	-1,0	5
14	1,08	+3,0	0	1,29	+1,8	4	1,10	+2,6	3
15	0,87	+1,5	4	1,23	+1,5	4	1,01	+2,0	3
16	2,528	+14	0	3,166	+12	0	2,770	+14	0
17	0,36	-2,3	3	0,61	-1,8	4	0,55	-1,2	4
20	0,1580	-3,8	0	0,4152	-2,8	3	0,1689	-3,8	0
22	---			---			---		
28	0,597	-0,6	5	0,91	-0,2	5	0,690	-0,2	5
32	---			21,34	+107	0	23,26	+156	0
34	0,165	-3,8	0	0,375	-3,0	0	0,300	-2,9	3
35	0,960	+2,1	3	1,24	+1,5	4	1,13	+2,8	3
38	0,30	-2,8	3	0,42	-2,8	3	0,38	-2,4	3
40	0,1580	-3,8	0	0,4152	-2,8	3	0,1689	-3,8	0
47	1,086	+3,1	0	1,540	+3,1	0	0,992	+1,9	4
Expected value	0,674			0,950			0,721		
Expected deviation	0,1348	20%		0,190	20%		0,1442	20%	

Parameter : Dimethoate
Units : mg/kg (dry weight basis)

Lab #	Sample 1			Sample 2			Sample 3		
	Result	Z score	Pt	Result	Z score	Pt	Result	Z score	Pt
5	0,147	-1,2	4	0,405	-0,3	5	0,189	-1,2	4
6	0,21	+0,5	5	0,51	+0,9	5	0,28	+0,6	5
7	0,187	-0,1	5	0,467	+0,4	5	0,233	-0,3	5
9	0,181	-0,3	5	0,44	+0,1	5	0,241	-0,1	5
10	0,14	-1,3	4	0,34	-1,1	4	0,20	-1,0	5
14	0,19	0,0	5	0,45	+0,2	5	0,24	-0,2	5
15	<15	-5,0	0	<15	-5,0	0	<15	-5,0	0
16	0,104	-2,3	3	0,293	-1,6	4	0,119	-2,6	3
17	0,28	+2,3	3	0,75	+3,7	0	0,43	+3,7	0
20	0,2280	+1,0	5	0,1105	-3,7	0	0,2862	+0,8	5
22	---			---			---		
28	0,806	+16	0	1,208	+9,0	0	1,332	+22	0
32	6,36	+161	0	5,11	+54	0	4,08	+77	0
34	0,190	0,0	5	0,452	+0,2	5	0,235	-0,3	5
35	0,192	+0,0	5	0,431	+0,0	5	0,261	+0,3	5
38	0,21	+0,5	5	0,53	+1,1	4	0,29	+0,8	5
40	0,2280	+1,0	5	0,1105	-3,7	0	0,2862	+0,8	5
47	0,110	-2,1	3	0,388	-0,5	5	0,152	-1,9	4
Expected value	0,191			0,431			0,248		
Expected deviation	0,0382	20%		0,0862	20%		0,0496	20%	

Parameter : Carbaryl
Units : mg/kg (dry weight basis)

Lab #	Sample 1			Sample 2			Sample 3		
	Result	Z score	Pt	Result	Z score	Pt	Result	Z score	Pt
5	1,101	+1,1	4	1,498	+1,3	4	1,287	+1,4	4
6	0,57	-1,9	4	0,74	-1,9	4	0,68	-1,6	4
7	1,17	+1,5	4	1,79	+2,5	3	1,31	+1,6	4
9	1,158	+1,4	4	1,475	+1,2	4	1,311	+1,6	4
10	0,84	-0,4	5	0,83	-1,5	4	0,99	-0,1	5
14	0,93	+0,1	5	1,03	-0,7	5	0,95	-0,3	5
15	---			---			---		
16	0,957	+0,3	5	0,977	-0,9	5	0,798	-1,0	4
17	1,10	+1,1	4	3,22	+8,5	0	1,05	+0,3	5
20	0,1942	-3,9	0	0,3031	-3,7	0	0,2740	-3,6	0
22	1,07	+0,9	5	1,42	+1,0	5	1,16	+0,8	5
28	0,910	+0,0	5	1,86	+2,8	3	1,34	+1,7	4
32	0,43	-2,6	3	0,52	-2,8	3	0,67	-1,7	4
34	0,974	+0,4	5	1,252	+0,3	5	1,066	+0,3	5
35	0,826	-0,4	5	0,926	-1,1	4	0,945	-0,3	5
38	1,25	+1,9	4	1,86	+2,8	3	1,52	+2,6	3
40	0,1942	-3,9	0	0,3031	-3,7	0	0,2740	-3,6	0
47	0,883	-0,1	5	1,208	+0,1	5	1,009	+0,0	5
Expected value	0,906			1,19			1,00		
Expected deviation	0,1812	20%		0,238	20%		0,200	20%	

Parameter : Carbofuran
Units : mg/kg (dry weight basis)

Lab #	Sample 1			Sample 2			Sample 3		
	Result	Z score	Pt	Result	Z score	Pt	Result	Z score	Pt
5	1,121	+0,7	5	1,204	+1,1	4	1,530	+1,2	4
6	0,70	-1,4	4	0,70	-1,5	4	0,85	-1,5	4
7	1,23	+1,3	4	1,41	+2,1	3	1,53	+1,2	4
9	1,212	+1,2	4	1,212	+1,1	4	1,533	+1,2	4
10	0,86	-0,6	5	0,76	-1,2	4	1,11	-0,5	5
14	1,06	+0,4	5	0,95	-0,2	5	1,30	+0,3	5
15	---			---			---		
16	1,084	+0,5	5	0,859	-0,7	5	0,789	-1,8	4
17	1,30	+1,6	4	1,54	+2,7	3	1,87	+2,6	3
20	0,5455	-2,2	3	0,7210	-1,4	4	0,6784	-2,2	3
22	0,78	-1,0	4	0,79	-1,0	4	1,00	-0,9	5
28	5,56	+23	0	5,93	+25	0	10,98	+40	0
32	0,74	-1,2	4	0,87	-0,6	5	1,09	-0,6	5
34	1,253	+1,4	4	1,210	+1,1	4	1,688	+1,9	4
35	0,817	-0,8	5	0,754	-1,2	4	1,05	-0,7	5
38	1,32	+1,7	4	1,41	+2,1	3	1,68	+1,8	4
40	0,5455	-2,2	3	0,7210	-1,4	4	0,6784	-2,2	3
47	1,046	+0,3	5	1,115	+0,6	5	1,335	+0,4	5
Expected value	0,979			0,994			1,23		
Expected deviation	0,1958	20%		0,1988	20%		0,246	20%	

Parameter : Diazinon
Units : mg/kg (dry weight basis)

	Sample 1			Sample 2			Sample 3		
Lab #	Result	Z score	Pt	Result	Z score	Pt	Result	Z score	Pt
5	---			---			---		
6	0,19	+0,4	5	0,19	+0,5	5	0,29	+0,7	5
7	0,194	+0,5	5	0,177	+0,1	5	0,313	+1,2	4
9	0,253	+2,2	3	0,238	+1,8	4	0,386	+2,6	3
10	0,15	-0,7	5	0,12	-1,6	4	0,210	-0,9	5
14	0,12	-1,6	4	0,11	-1,8	4	0,25	-0,1	5
15	---			---			---		
16	0,145	-0,9	5	0,108	-1,9	4	0,297	+0,8	5
17	---			---			---		
20	0,1487	-0,8	5	0,1044	-2,0	4	0,0960	-3,1	0
22	---			---			---		
28	0,17	-0,2	5	0,36	+5,3	0	0,17	-1,7	4
32	0,94	+22	0	1,17	+29	0	1,66	+28	0
34	0,154	-0,6	5	0,154	-0,6	5	0,256	+0,0	5
35	0,200	+0,7	5	0,240	+1,9	4	0,326	+1,4	4
38	0,23	+1,5	4	0,21	+1,0	4	0,33	+1,5	4
40	0,1487	-0,8	5	0,1044	-2,0	4	0,0960	-3,1	0
47	0,244	+1,9	4	0,225	+1,5	4	0,223	-0,6	5
Expected value	0,176			0,174			0,254		
Expected deviation	0,0352	20%		0,0348	20%		0,0508	20%	

Parameter : Endosulfane I
Units : mg/kg (dry weight basis)

	Sample 1			Sample 2			Sample 3		
Lab #	Result	Z score	Pt	Result	Z score	Pt	Result	Z score	Pt
5	---			---			---		
6	0,52	+1,1	4	0,33	-0,1	5	0,70	+1,5	4
7	0,434	+0,1	5	0,283	-0,8	5	0,667	+1,2	4
9	0,592	+1,9	4	0,385	+0,7	5	0,815	+2,6	3
10	0,26	-2,0	4	0,17	-2,5	3	0,40	-1,3	4
14	0,23	-2,3	3	0,14	-2,9	3	,041	-4,6	0
15	0,57	+1,7	4	0,44	+1,5	4	0,87	+3,1	0
16	0,968	+6,3	0	0,714	+5,5	0	1,373	+7,8	0
17	0,30	-1,5	4	0,26	-1,2	4	0,45	-0,8	5
20	0,3872	-0,5	5	0,5585	+3,2	0	0,2053	-3,1	0
22	---			---			---		
28	0,210	-2,5	3	0,188	-2,2	3	0,354	-1,7	4
32	8,81	+98	0	10,60	+151	0	14,27	+128	0
34	0,770	+4,0	0	0,335	-0,1	5	0,675	+1,3	4
35	0,543	+1,3	4	0,460	+1,8	4	0,874	+3,2	0
38	0,16	-3,1	0	0,12	-3,2	0	0,24	-2,8	3
40	0,3872	-0,5	5	0,5585	+3,2	0	0,2053	-3,1	0
47	0,357	-0,8	5	0,250	-1,3	4	0,503	-0,3	5
Expected value	0,428			0,339			0,536		
Expected deviation	0,0856	20%		0,0678	20%		0,1072	20%	

Parameter : Endosulfane II
Units : mg/kg (dry weight basis)

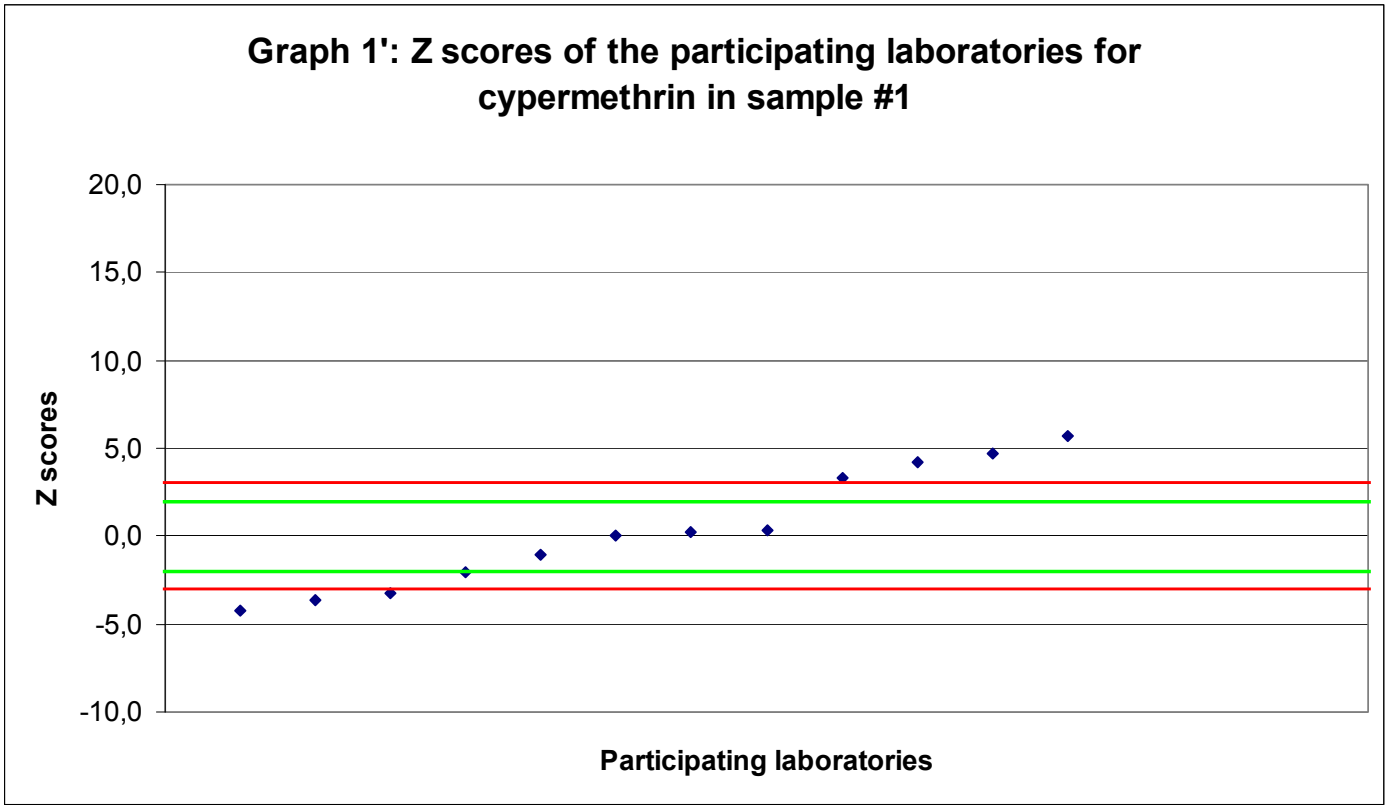
	Sample 1			Sample 2			Sample 3		
Lab #	Result	Z score	Pt	Result	Z score	Pt	Result	Z score	Pt
5	---			---			---		
6	1,30	+2,7	3	1,15	+1,9	4	1,65	+2,4	3
7	1,03	+1,1	4	0,895	+0,4	5	1,41	+1,4	4
9	1,243	+2,3	3	0,982	+0,9	5	1,538	+1,9	4
10	0,66	-1,1	4	0,52	-1,9	4	0,97	-0,6	5
14	0,60	-1,5	4	,042	-4,7	0	0,96	-0,7	5
15	0,93	+0,5	5	0,95	+0,7	5	1,35	+1,1	4
16	2,477	+9,6	0	2,026	+7,2	0	3,220	+9,5	0
17	0,79	-0,3	5	0,81	-0,1	5	1,17	+0,3	5
20	0,7813	-0,4	5	0,8901	+0,4	5	0,3895	-3,2	0
22	---			---			---		
28	0,591	-1,5	4	0,515	-1,9	4	0,797	-1,4	4
32	9,56	+51	0	18,01	+104	0	13,51	+56	0
34	0,630	-1,3	4	0,890	+0,4	5	0,795	-1,4	4
35	1,27	+2,5	3	1,12	+1,8	4	1,73	+2,8	3
38	0,39	-2,7	3	0,36	-2,8	3	0,58	-2,4	3
40	0,7813	-0,4	5	0,8901	+0,4	5	0,3895	-3,2	0
47	0,768	-0,5	5	0,685	-0,9	5	1,051	-0,3	5
Expected value	0,848			0,829			1,11		
Expected deviation	0,1696	20%		0,1658	20%		0,222	20%	

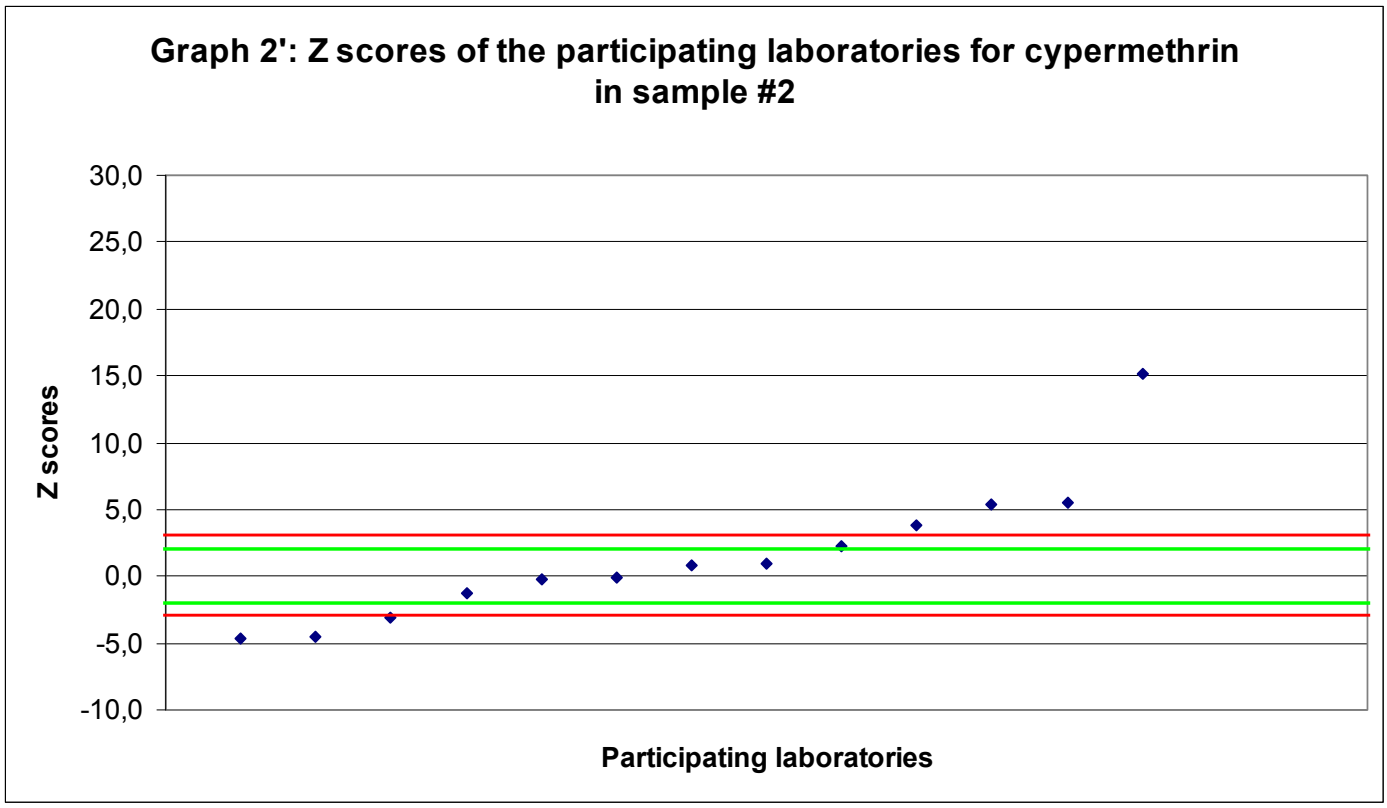
Parameter : Malathion
Units : mg/kg (dry weight basis)

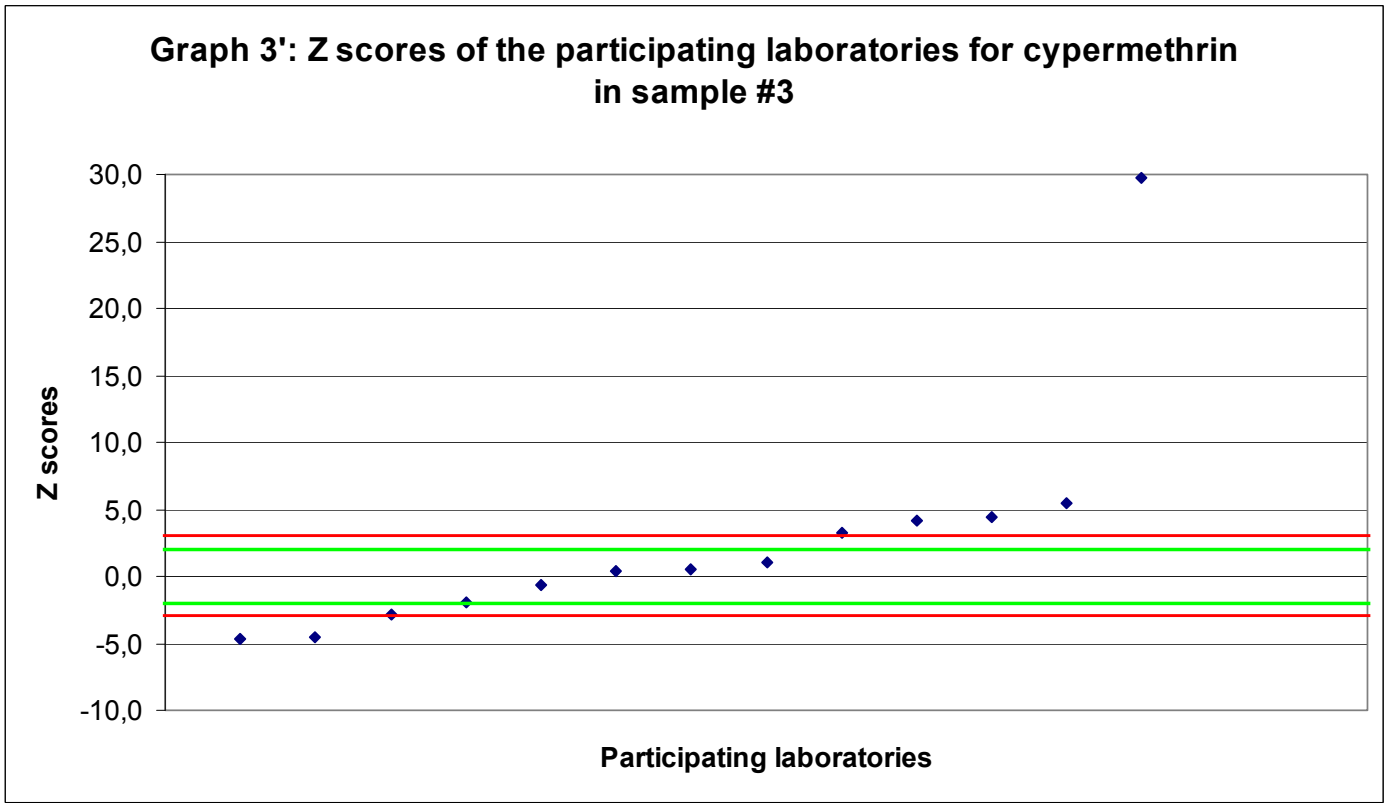
	Sample 1			Sample 2			Sample 3		
Lab #	Result	Z score	Pt	Result	Z score	Pt	Result	Z score	Pt
5	---			---			---		
6	0,75	+1,1	4	0,97	+2,1	3	0,93	+1,5	4
7	0,683	+0,6	5	0,893	+1,5	4	0,975	+1,8	4
9	0,679	+0,5	5	0,854	+1,2	4	0,876	+1,2	4
10	0,43	-1,5	4	0,45	-1,7	4	0,56	-1,1	4
14	0,44	-1,4	4	0,41	-2,0	3	0,61	-0,7	5
15	<15	-5,0	0	<15	-5,0	0	<15	-5,0	0
16	0,385	-1,9	4	0,399	-2,1	3	0,387	-2,3	3
17	0,58	-0,3	5	0,71	+0,2	5	0,76	+0,3	5
20	0,9063	+2,4	3	0,6367	-0,4	5	0,6342	-0,5	5
22	---			---			---		
28	,506	-0,9	5	0,545	-1,0	4	0,605	-0,8	5
32	9,37	+71	0	1,36	+4,9	0	4,56	+27	0
34	<0,1	-5,0	0	<0,1	-5,0	0	<O,1	-5,0	0
35	0,630	+0,1	5	0,852	+1,2	4	0,824	+0,8	5
38	0,47	-1,2	4	0,62	-0,5	5	0,59	-0,9	5
40	0,9063	+2,4	3	0,6367	-0,4	5	0,6342	-0,5	5
47	0,629	+0,1	5	0,945	+1,9	4	0,887	+1,2	4
Expected value	0,614			0,686			0,712		
Expected deviation	0,1228	20%		0,1372	20%		0,1424	20%	

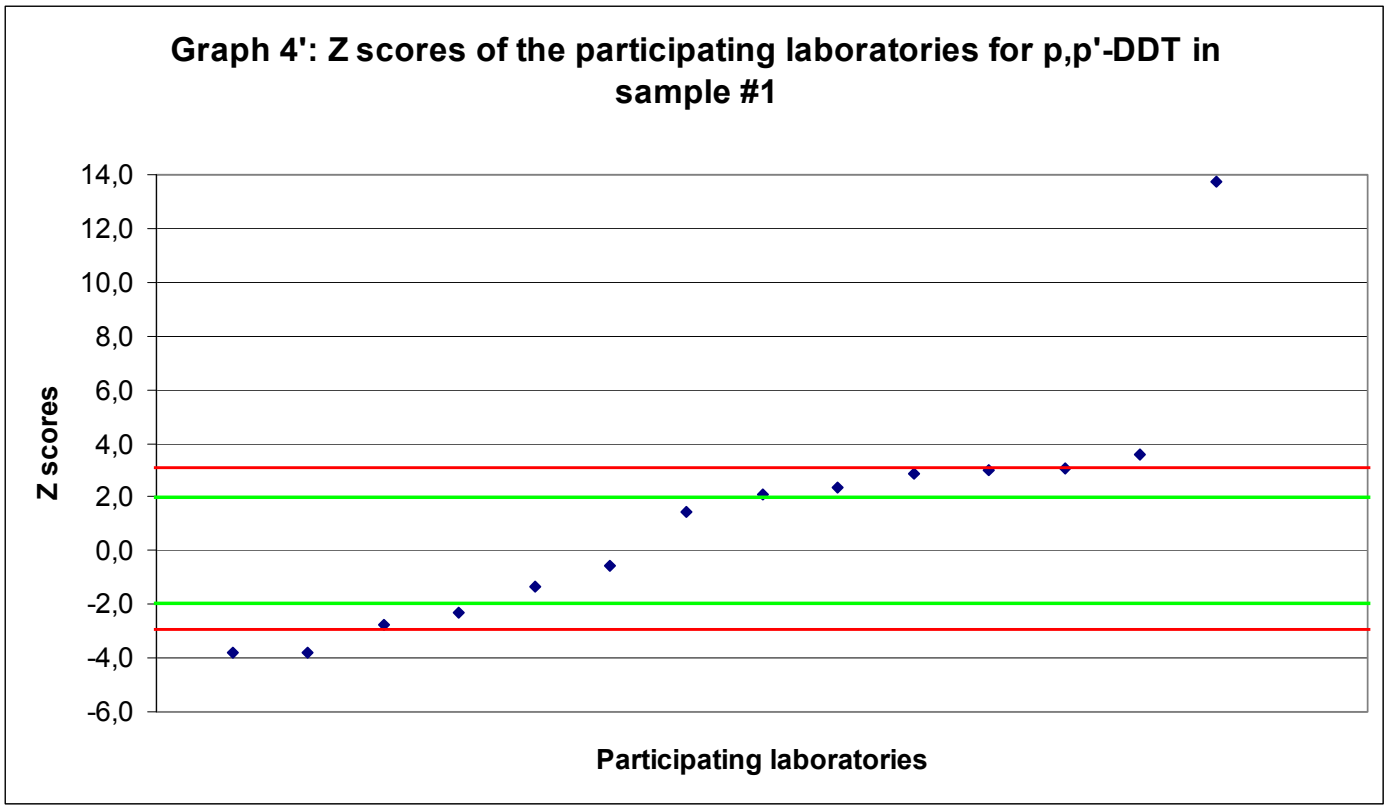
Annex C.3: Graphic representation of the Z scores

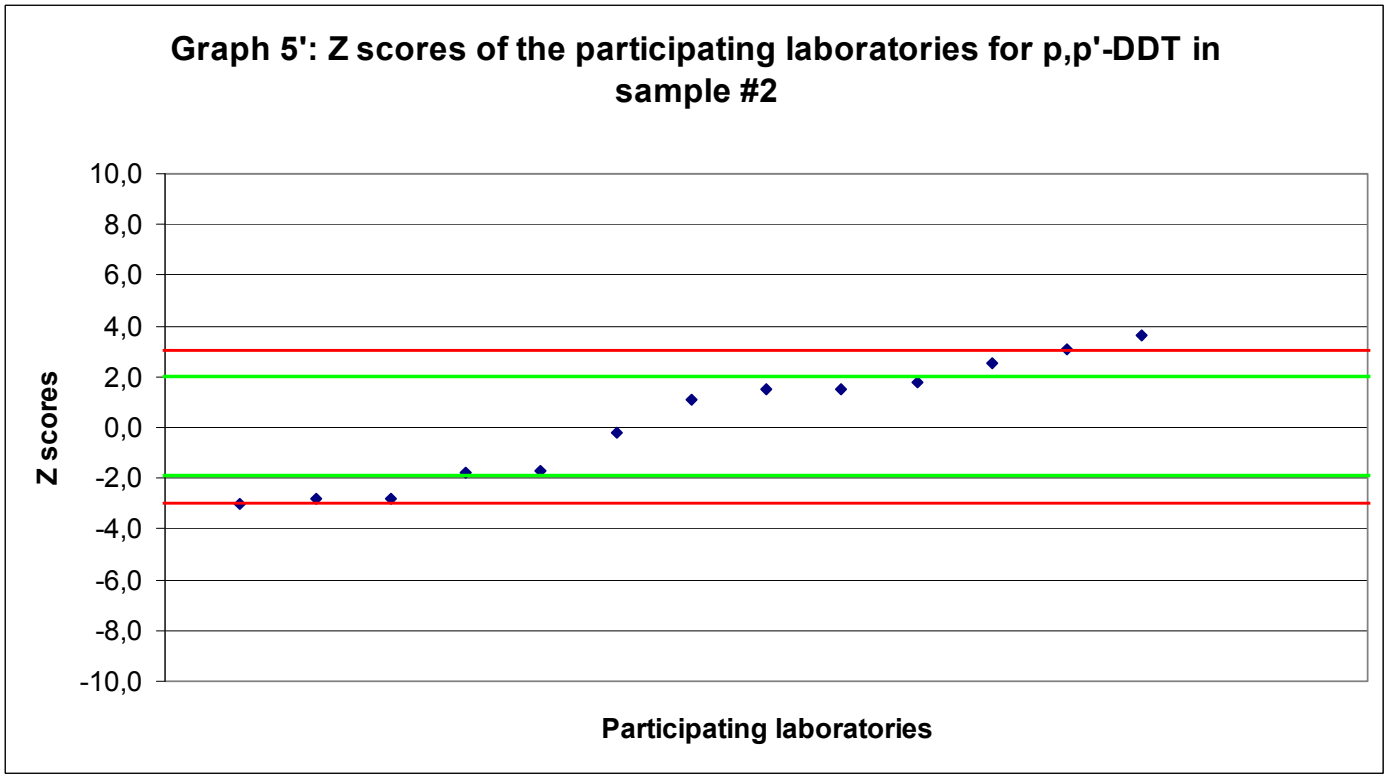
This section shows a z-score graphic representation for each pesticide of every sample. The red line represents the unsatisfactory limit and the green line is the satisfactory limit. They area between the two lines is the range where the results are questionable. The results from this area may require an investigation or not, depending on the case.

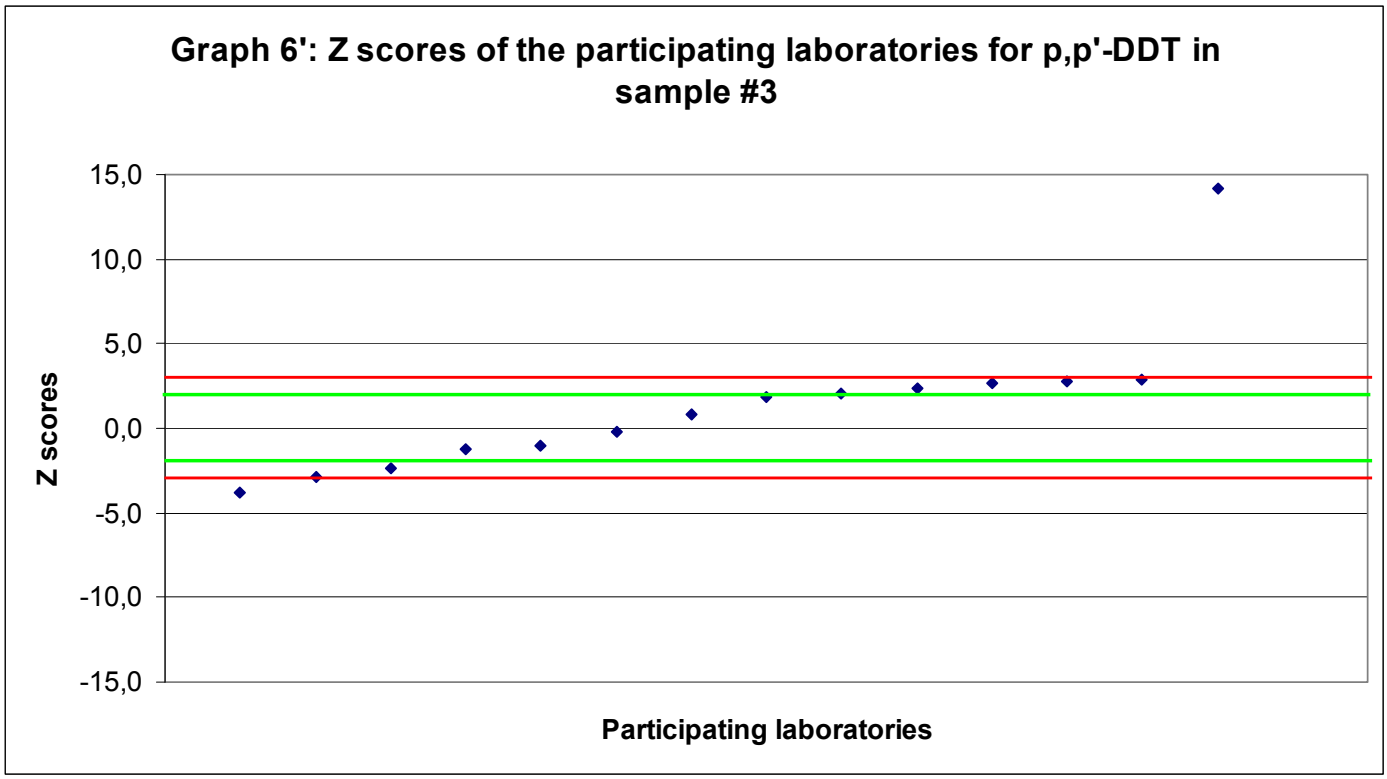


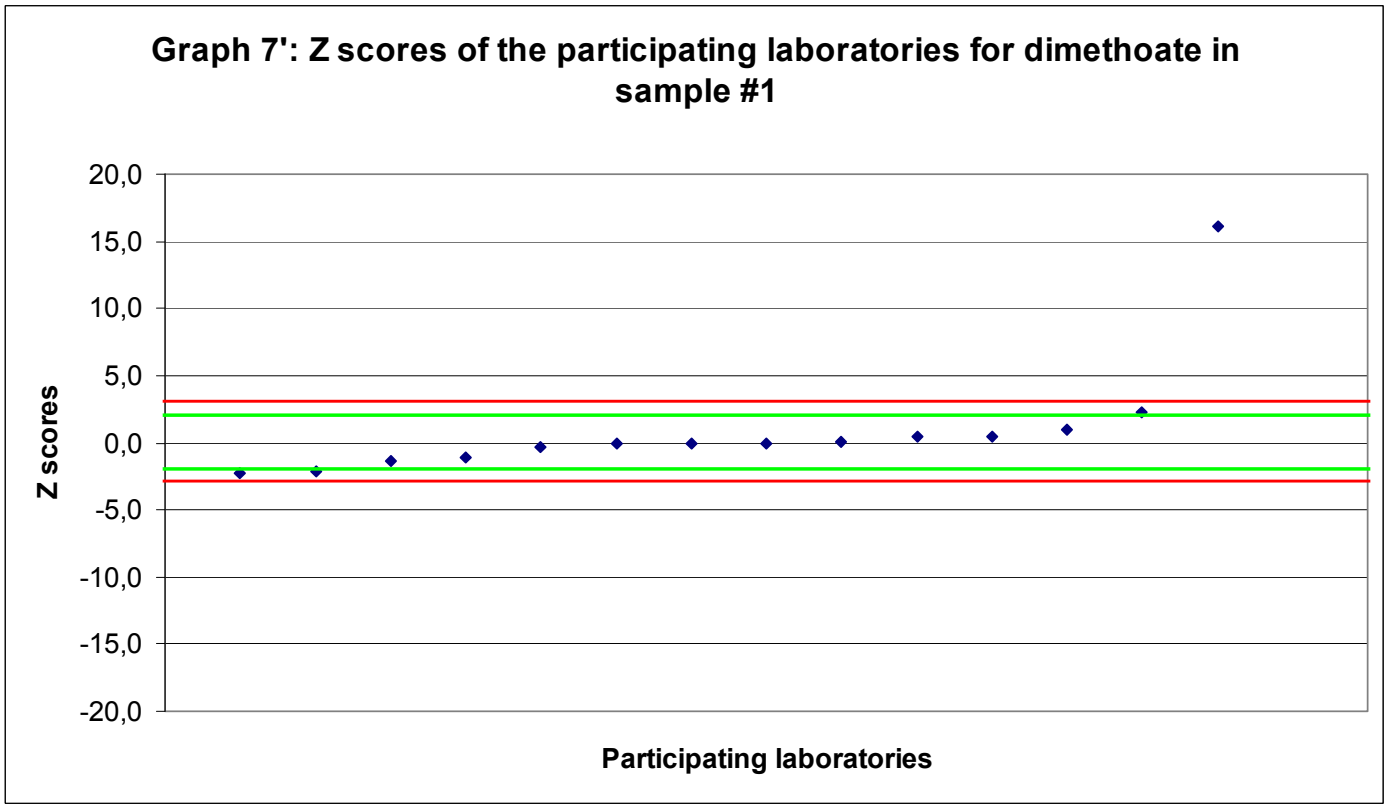

Graph 2': Z scores of the participating laboratories for cypermethrin in sample #2
30,0
25,0
20,0
15,0
10,0
5,0
0,0
-5,0
-10,0
Z scores
Participating laboratories

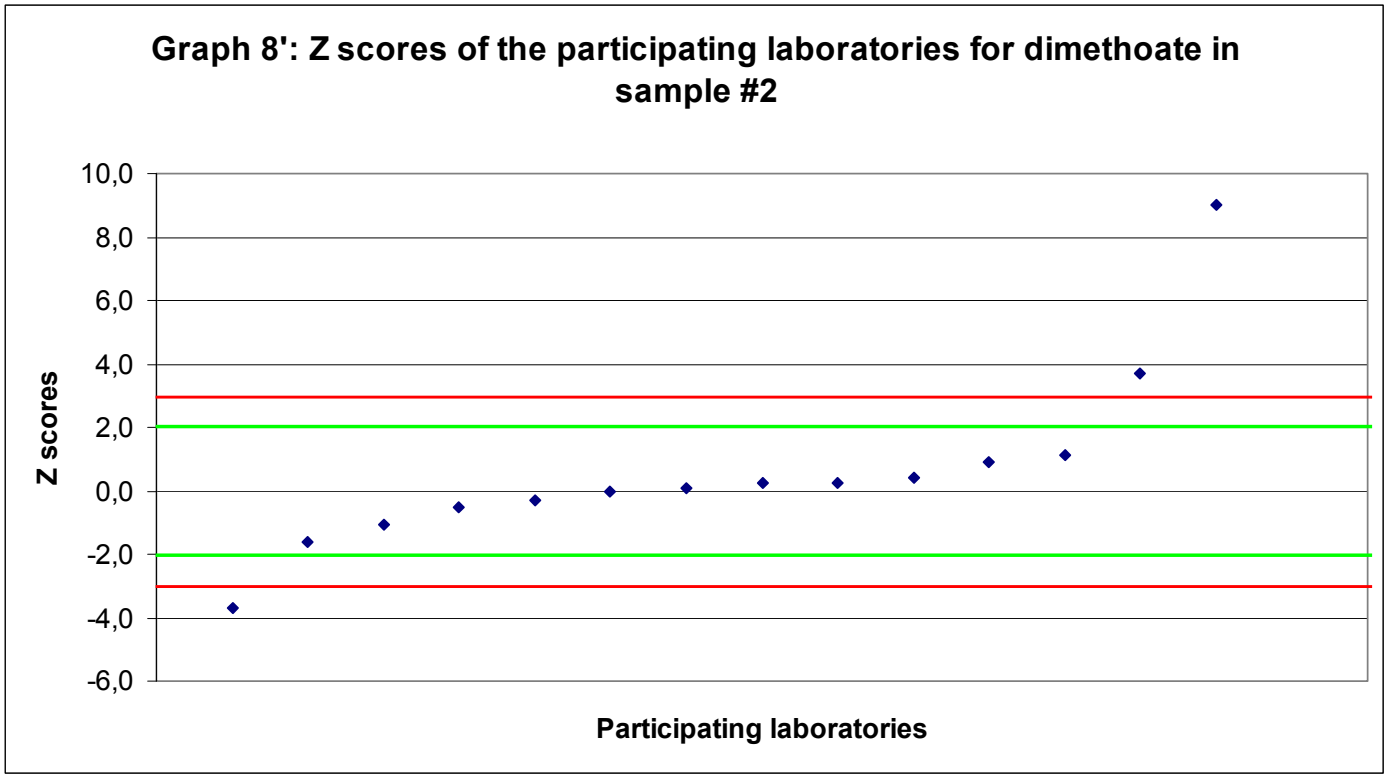

Graph 3': Z scores of the participating laboratories for cypermethrin in sample #3
30,0
25,0
20,0
15,0
10,0
5,0
0,0
-5,0
-10,0
Z scores
Participating laboratories

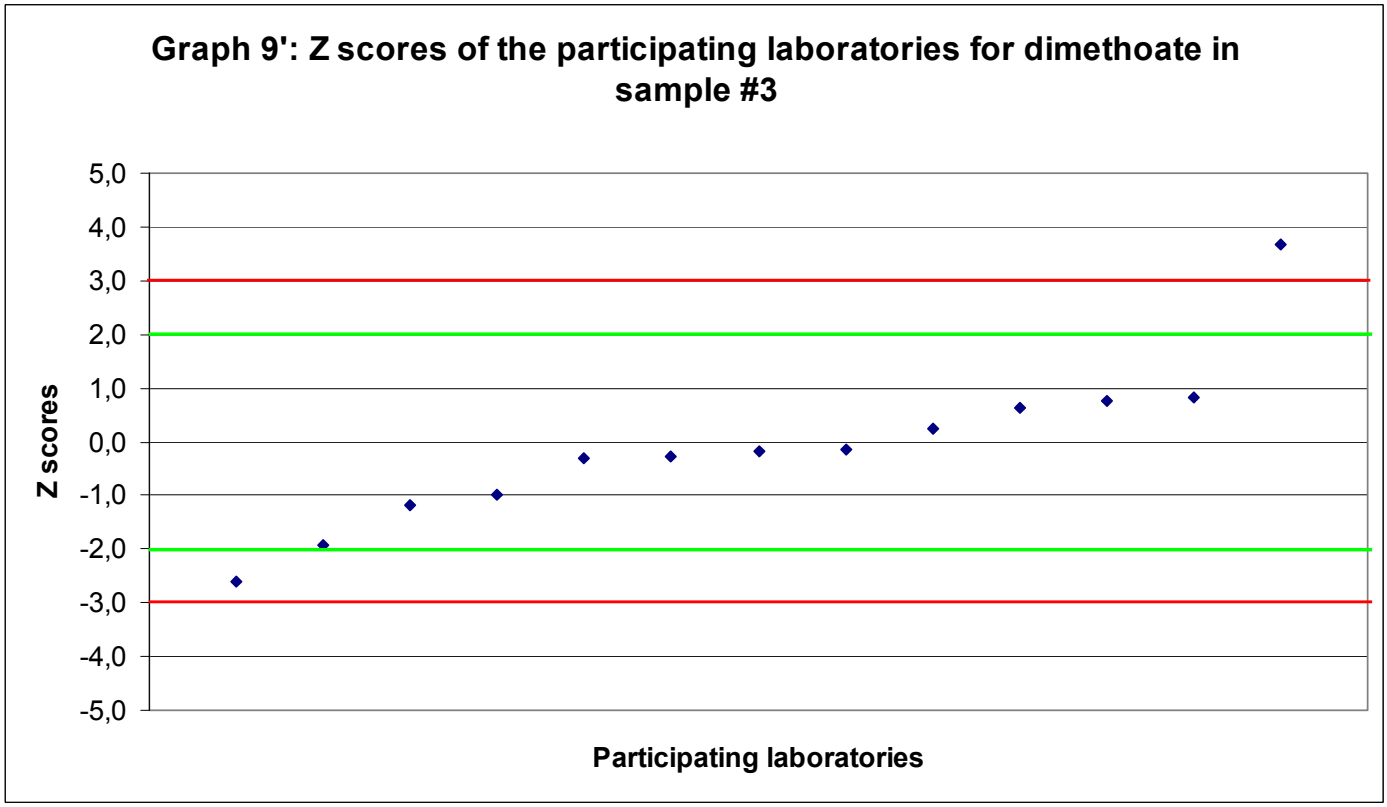

Graph 4': Z scores of the participating laboratories for p,p'-DDT in sample #1
14,0
12,0
10,0
8,0
6,0
4,0
2,0
0,0
-2,0
-4,0
-6,0
Z scores
Participating laboratories

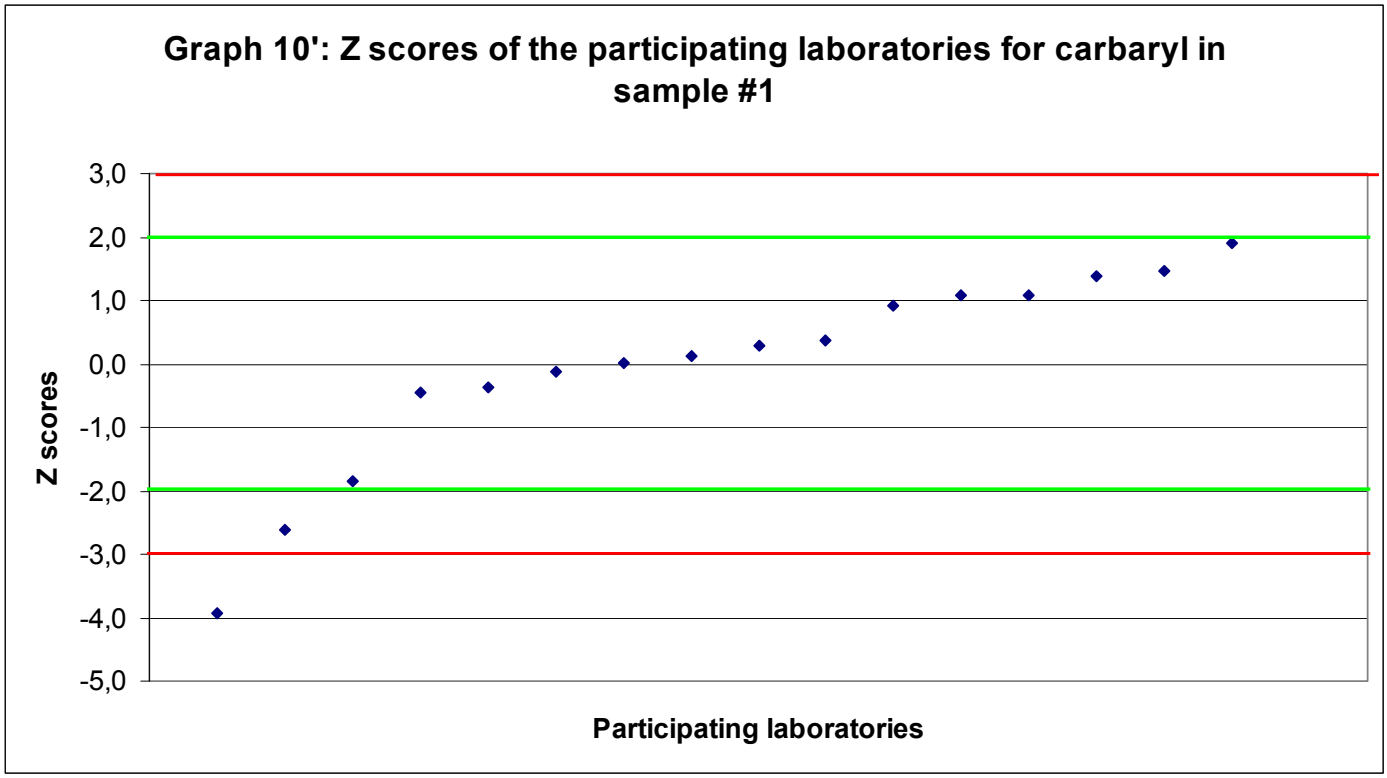

Graph 5': Z scores of the participating laboratories for p,p'-DDT in sample #2
10,0
8,0
6,0
4,0
2,0
0,0
-2,0
-4,0
-6,0
-8,0
-10,0
Z scores
Participating laboratories

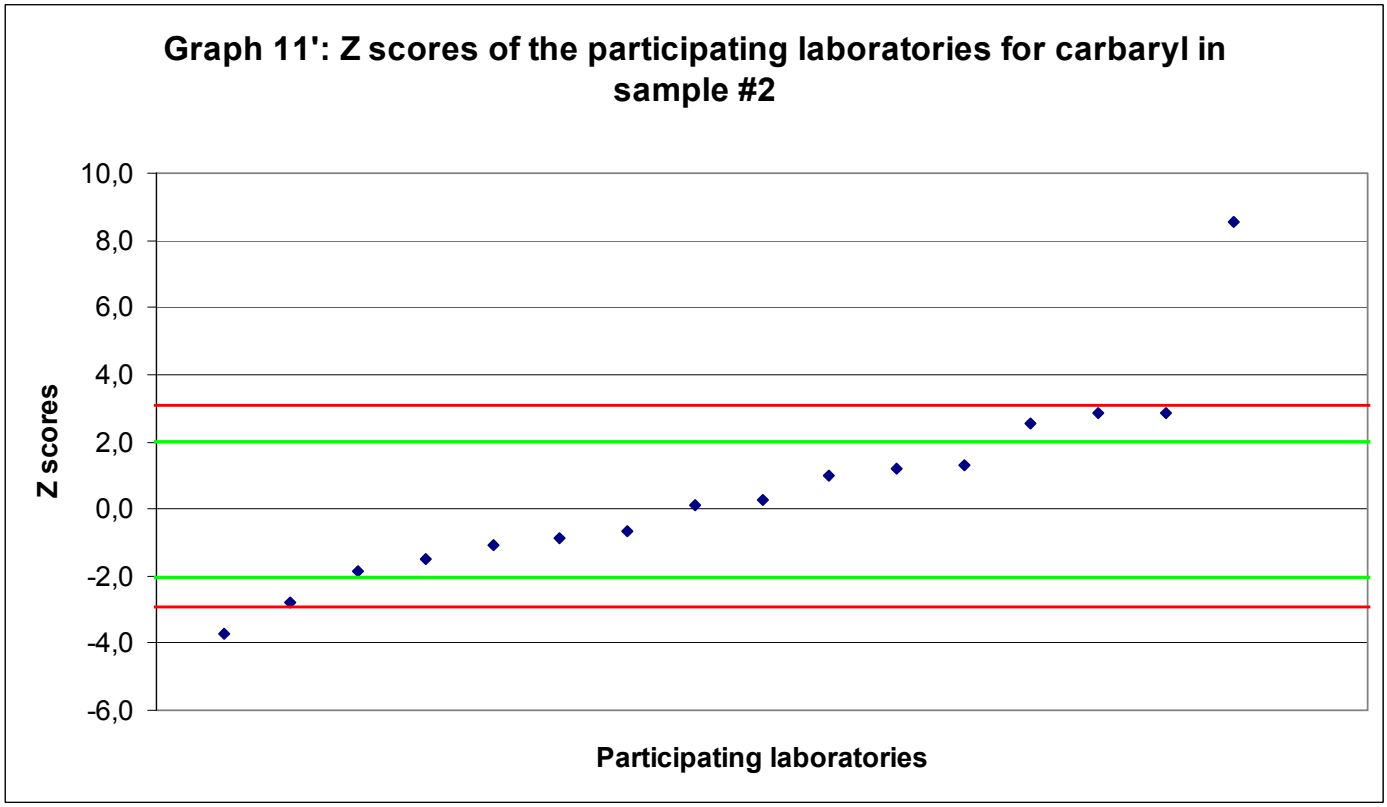

Graph 6': Z scores of the participating laboratories for p,p'-DDT in sample #3
15,0
10,0
5,0
0,0
-5,0
-10,0
-15,0
Z scores
Participating laboratories

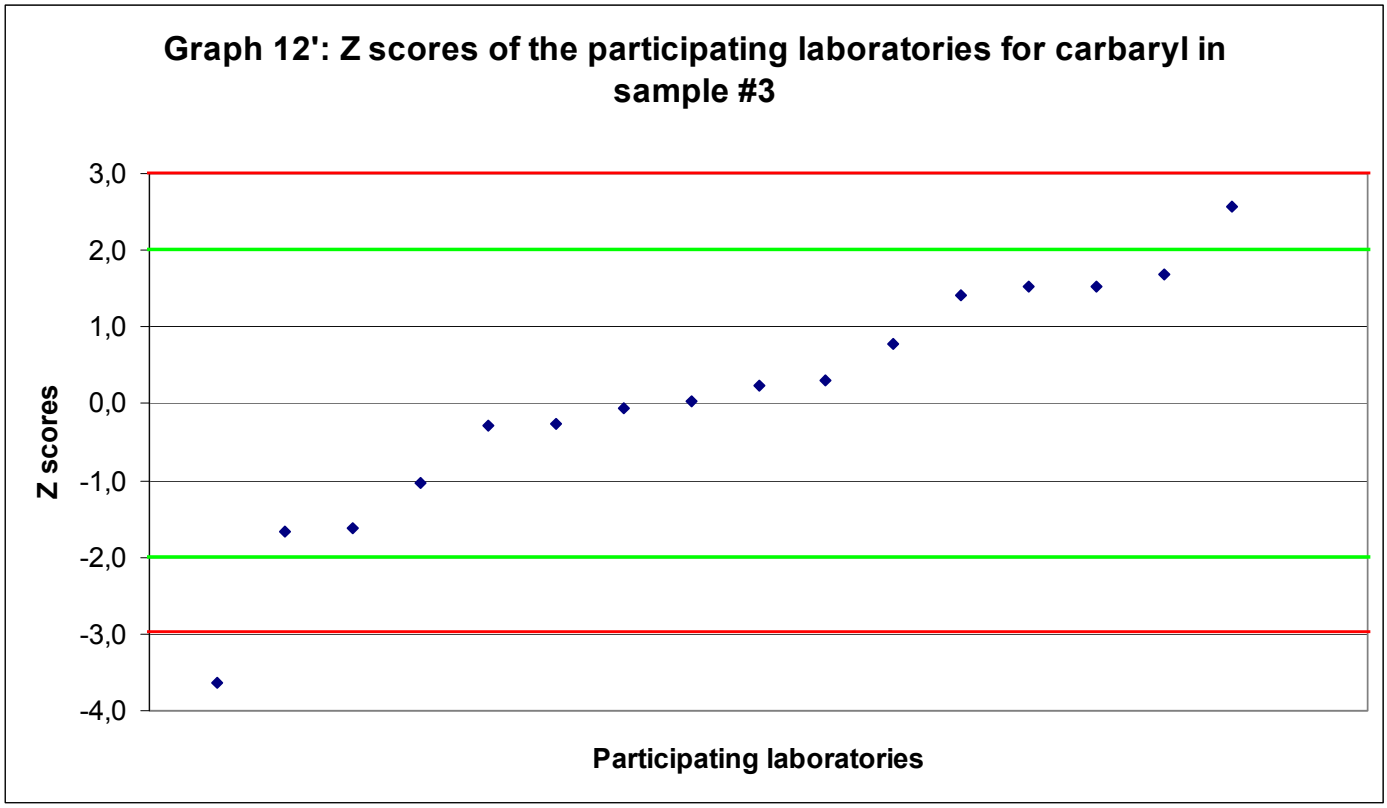

Graph 7': Z scores of the participating laboratories for dimethoate in sample #1
20,0
15,0
10,0
5,0
0,0
-5,0
-10,0
-15,0
-20,0
Z scores
Participating laboratories

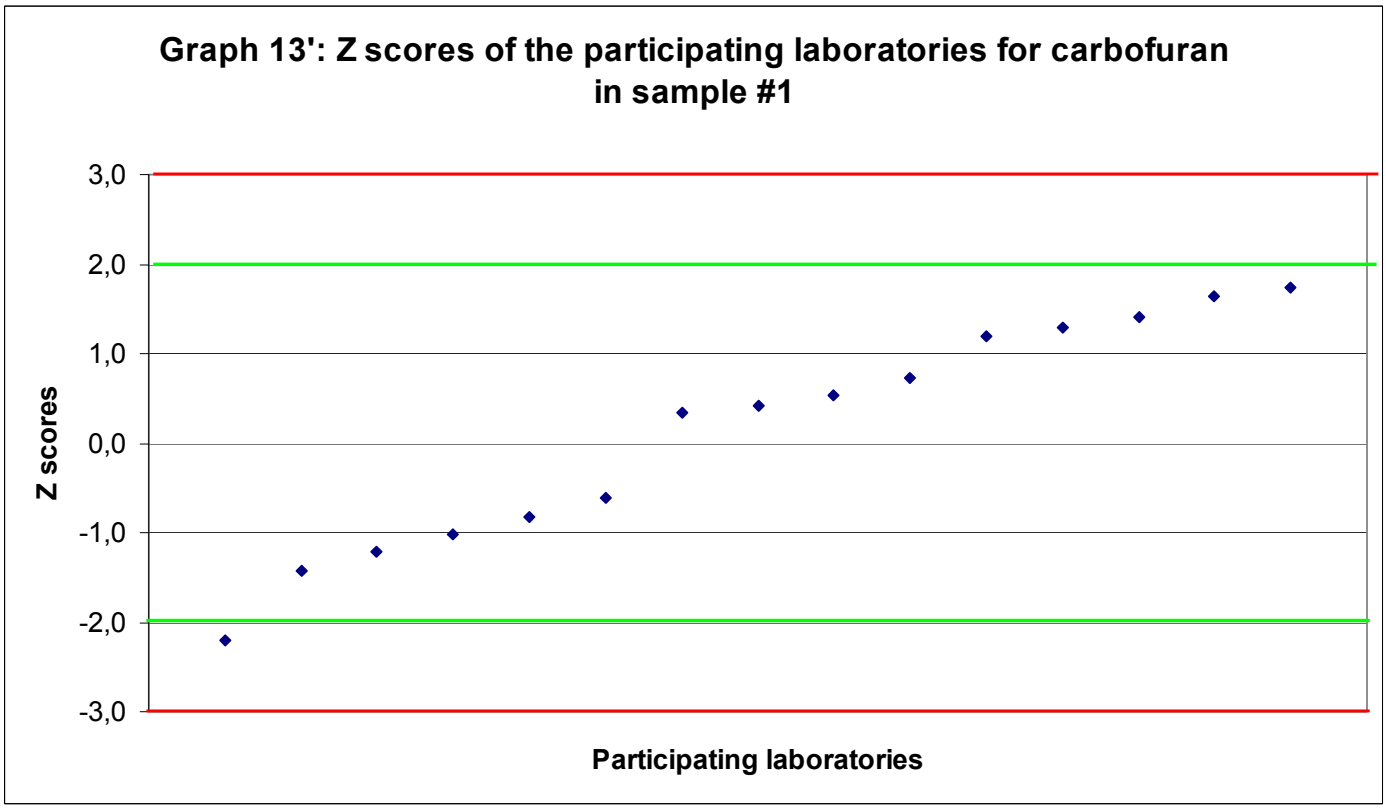

Graph 8': Z scores of the participating laboratories for dimethoate in sample #2
10,0
8,0
6,0
4,0
2,0
0,0
-2,0
-4,0
-6,0
Z scores
Participating laboratories

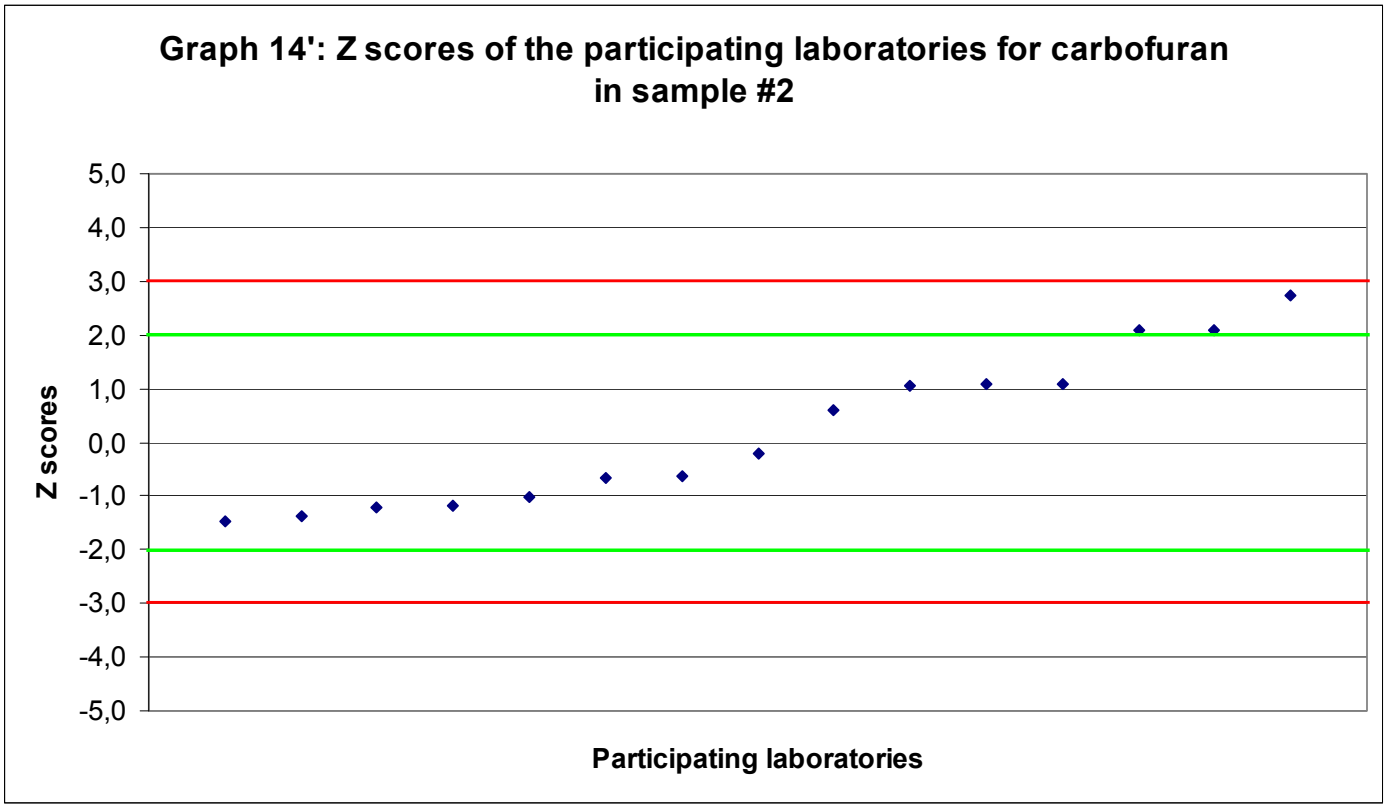

Graph 9': Z scores of the participating laboratories for dimethoate in sample #3
5,0
4,0
3,0
2,0
1,0
0,0
-1,0
-2,0
-3,0
-4,0
-5,0
Z scores
Participating laboratories

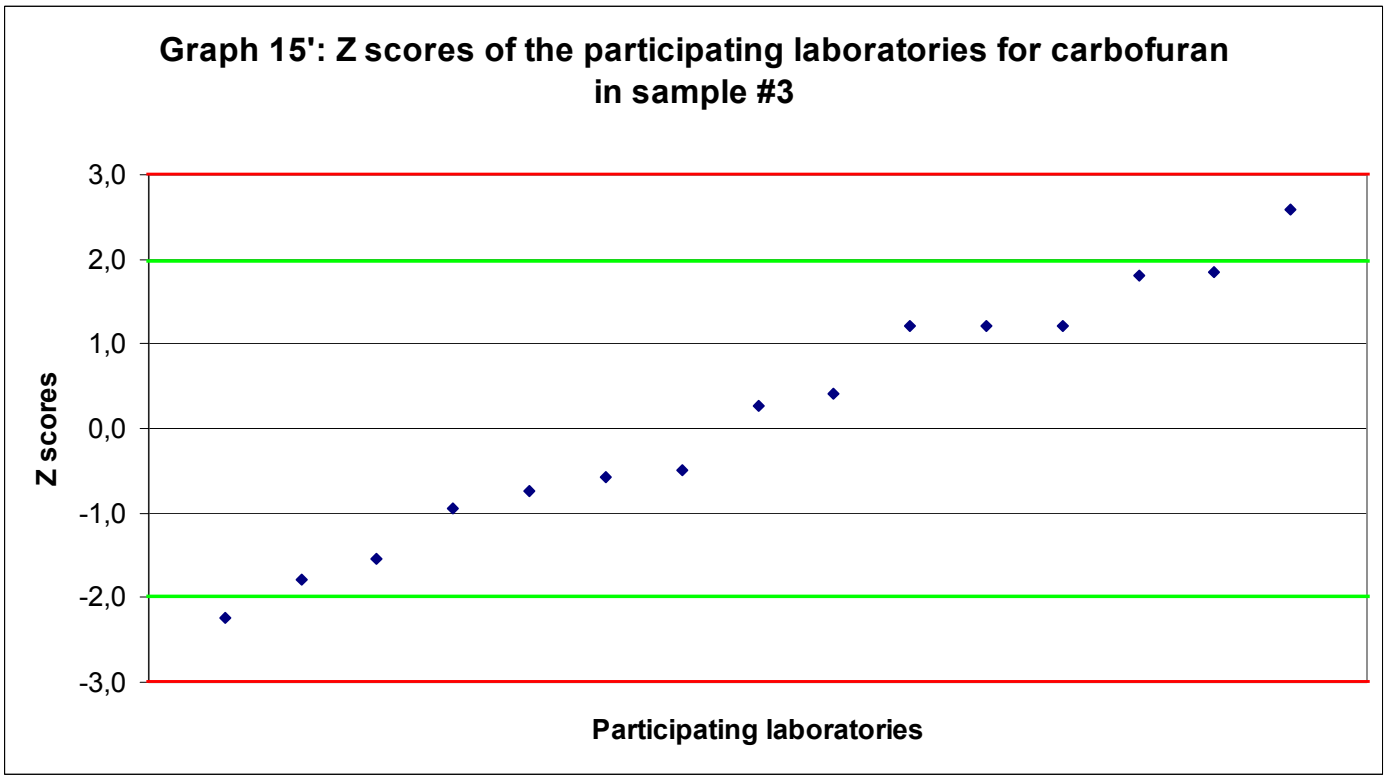

Graph 10': Z scores of the participating laboratories for carbaryl in sample #1
3,0
2,0
1,0
0,0
-1,0
-2,0
-3,0
-4,0
-5,0
Z scores
Participating laboratories

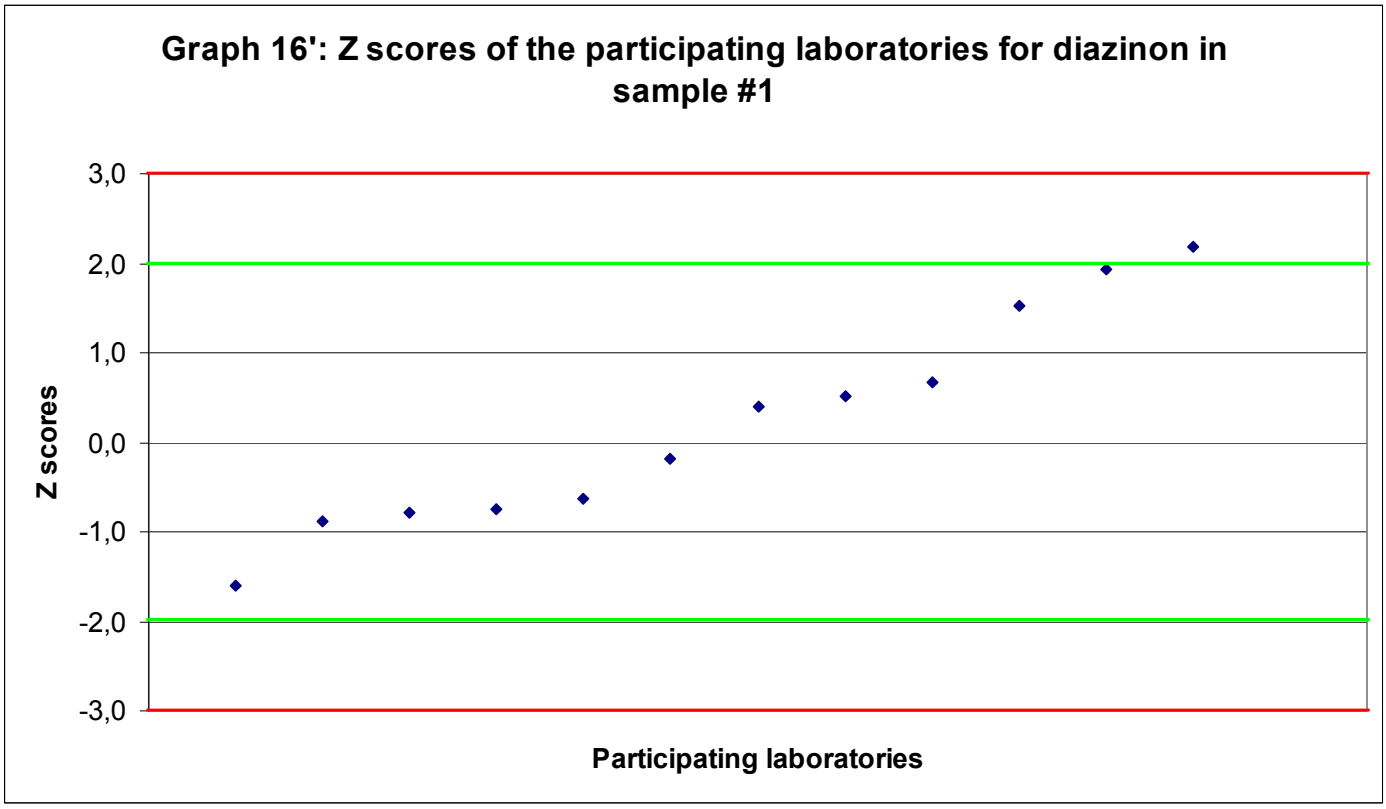

Graph 11': Z scores of the participating laboratories for carbaryl in sample #2
10,0
8,0
6,0
4,0
2,0
0,0
-2,0
-4,0
-6,0
Z scores
Participating laboratories

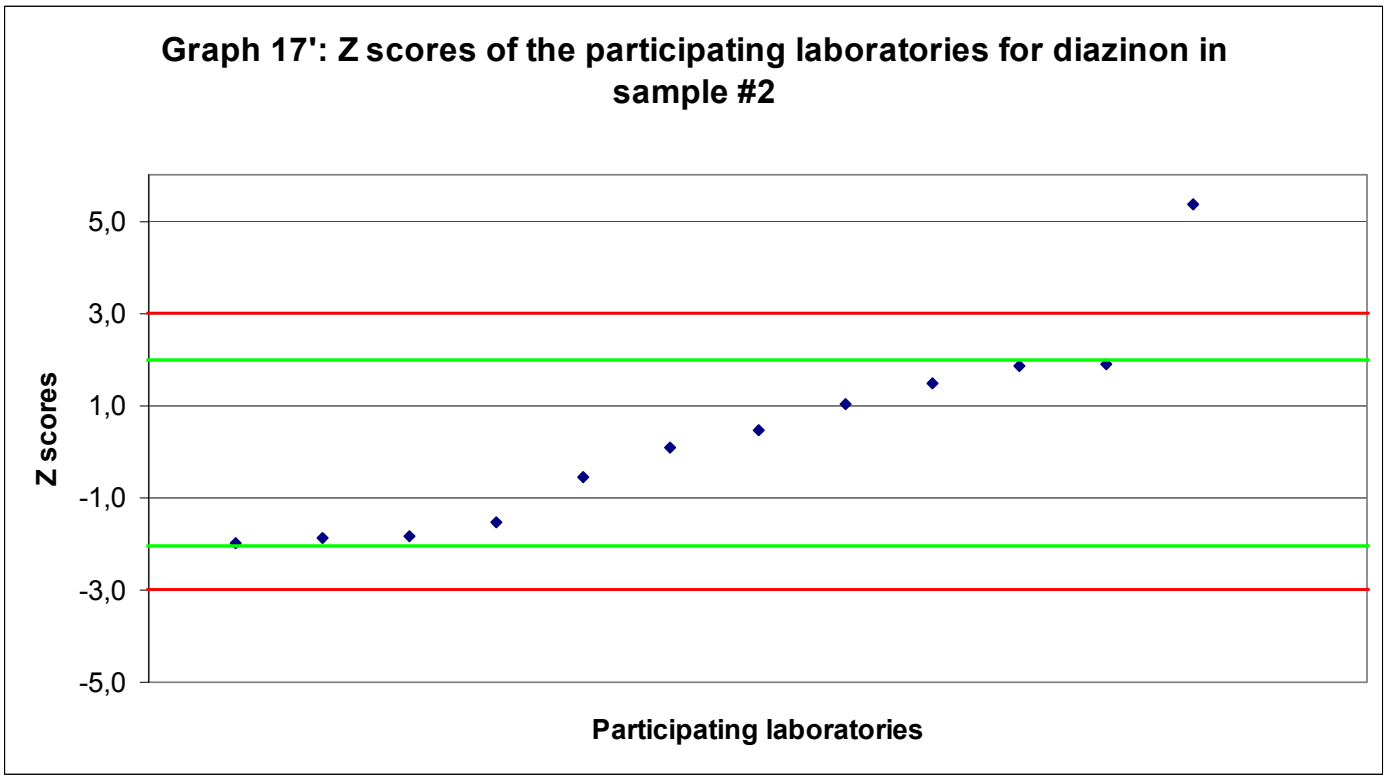

Graph 12': Z scores of the participating laboratories for carbaryl in sample #3
3,0
2,0
1,0
0,0
-1,0
-2,0
-3,0
-4,0
Z scores
Participating laboratories

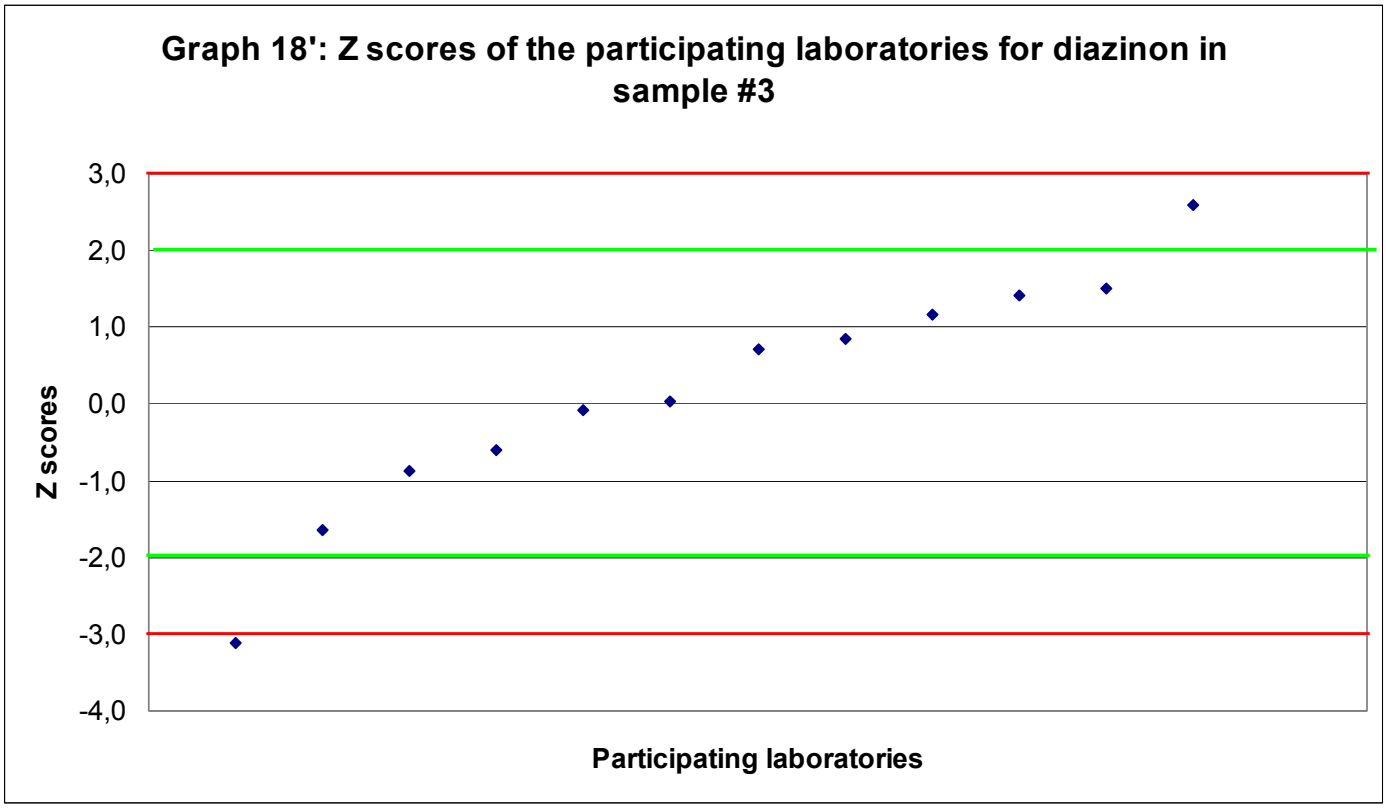

Graph 13': Z scores of the participating laboratories for carbofuran in sample #1
3,0
2,0
1,0
0,0
-1,0
-2,0
-3,0
Z scores
Participating laboratories

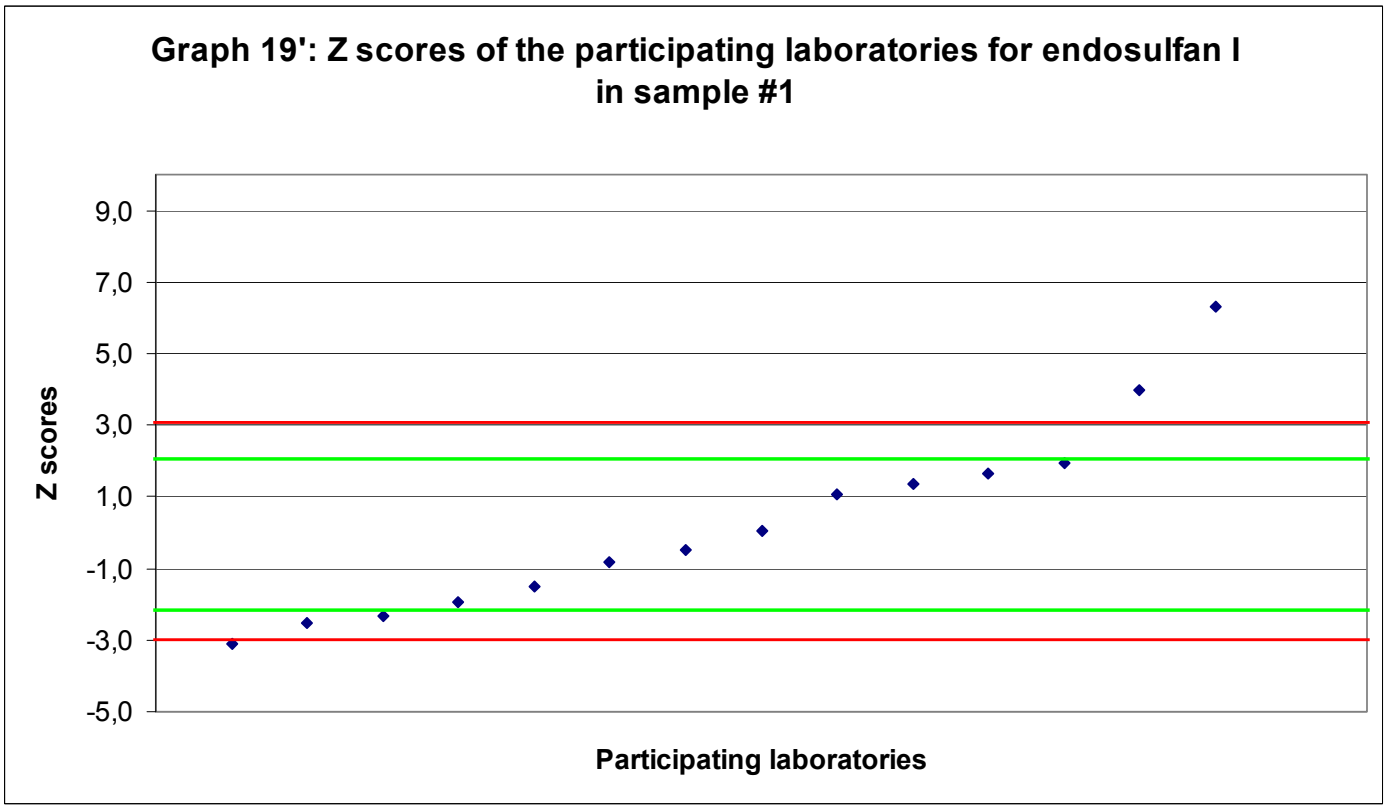

Graph 14': Z scores of the participating laboratories for carbofuran in sample #2
5,0
4,0
3,0
2,0
1,0
0,0
-1,0
-2,0
-3,0
-4,0
-5,0
Z scores
Participating laboratories


Graph 15': Z scores of the participating laboratories for carbofuran in sample #3
3,0
2,0
1,0
0,0
-1,0
-2,0
-3,0
Z scores
Participating laboratories

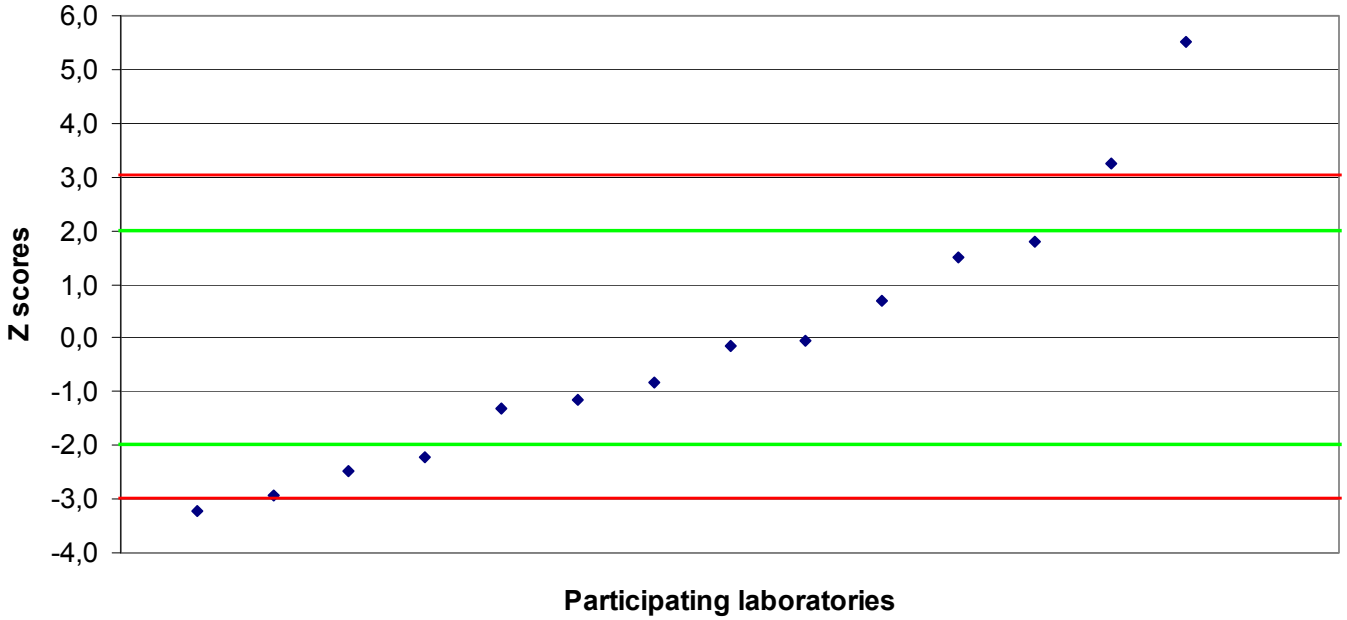

Graph 16': Z scores of the participating laboratories for diazinon in sample #1
3,0
2,0
1,0
0,0
-1,0
-2,0
-3,0
Z scores
Participating laboratories


Graph 17': Z scores of the participating laboratories for diazinon in sample #2
5,0
3,0
1,0
-1,0
-3,0
-5,0
Z scores
Participating laboratories

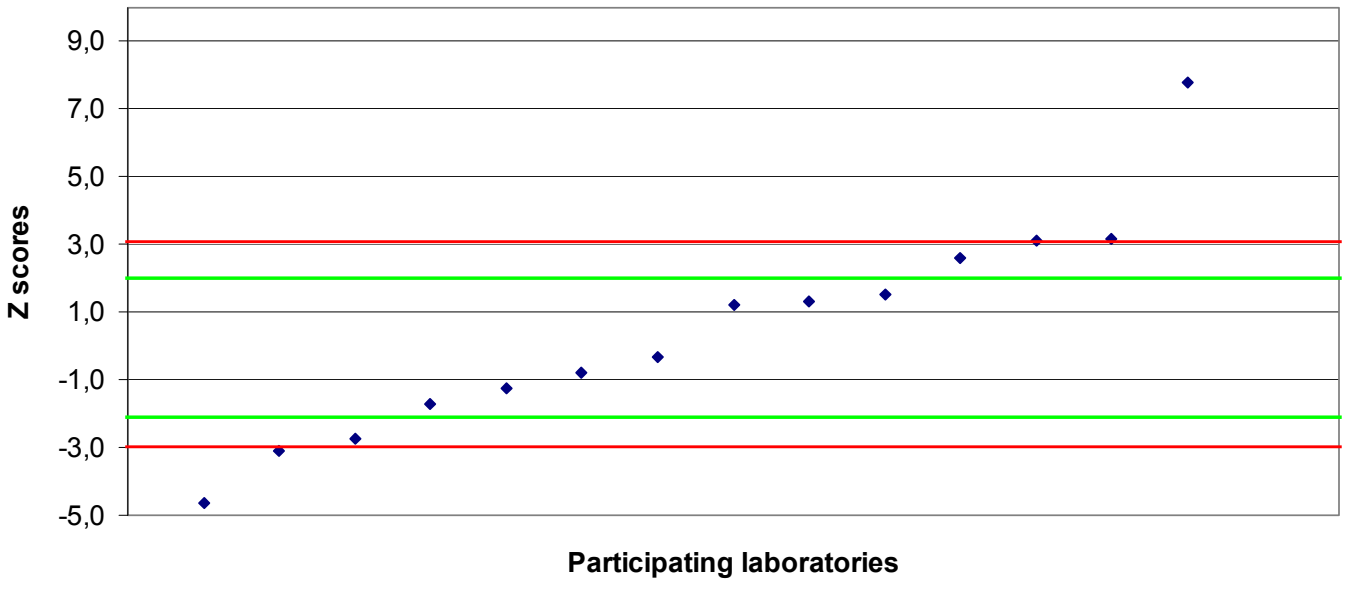

Graph 18': Z scores of the participating laboratories for diazinon in sample #3
3,0
2,0
1,0
0,0
-1,0
-2,0
-3,0
-4,0
Z scores
Participating laboratories


Graph 19': Z scores of the participating laboratories for endosulfan I in sample #1
9,0
7,0
5,0
3,0
1,0
-1,0
-3,0
-5,0
Z scores
Participating laboratories

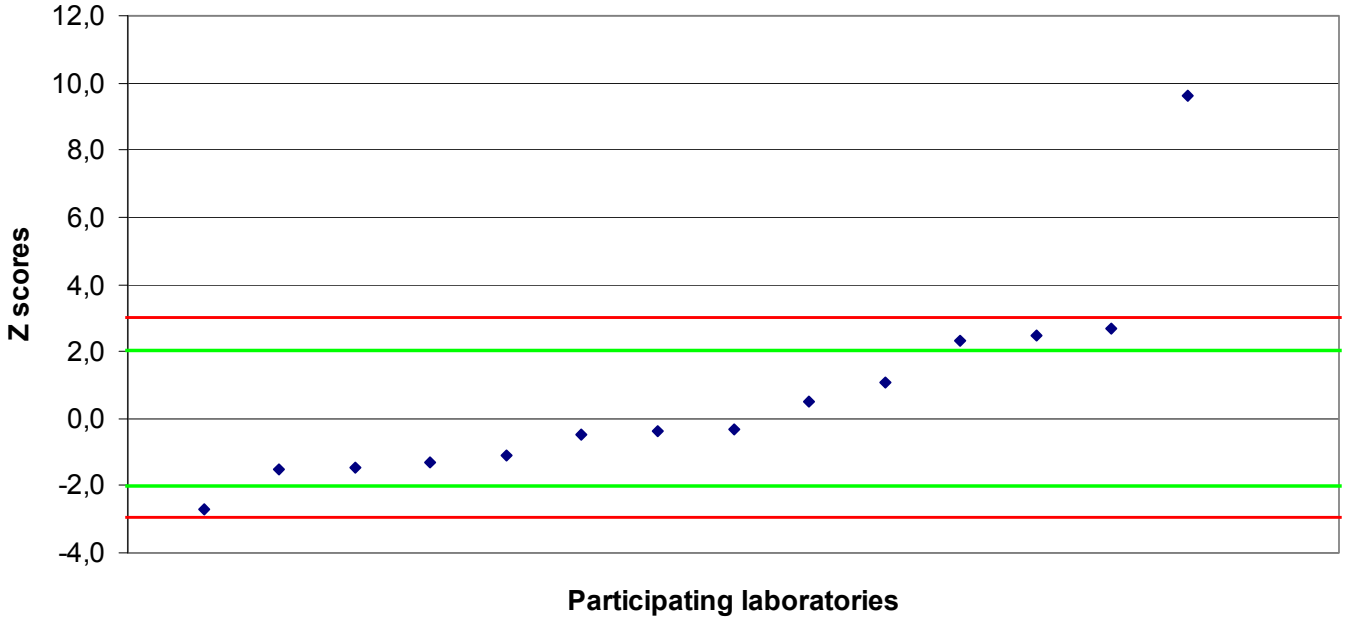
Graph 20': Z scores of the participating laboratories for endosulfan I in sample #2



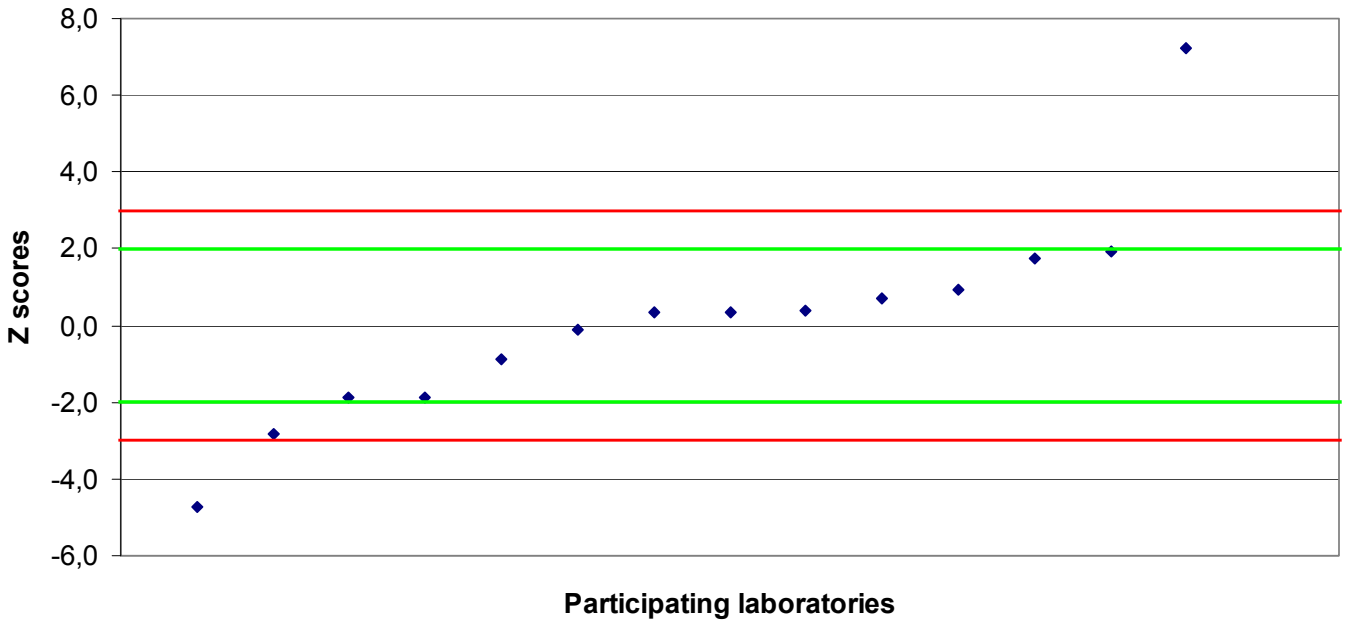
Graph 21': Z scores of the participating laboratories for endosulfan I in sample #3



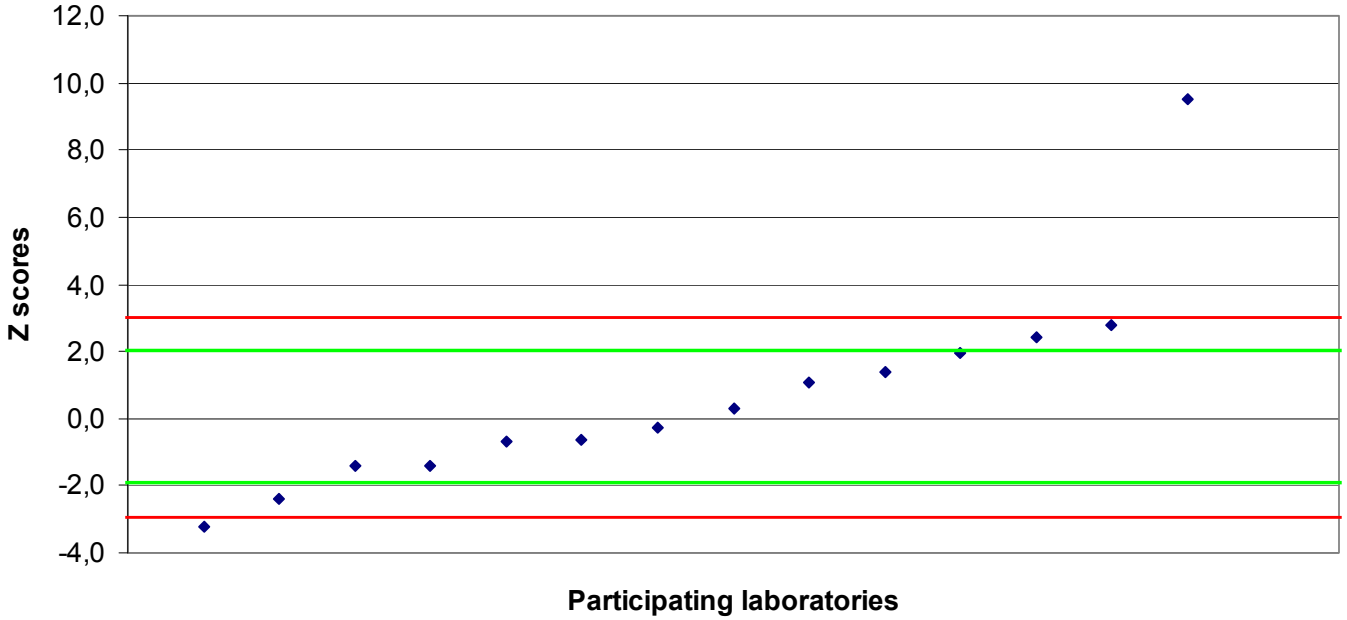
Graph 22': Z scores of the participating laboratories for endosulfan II in sample #1



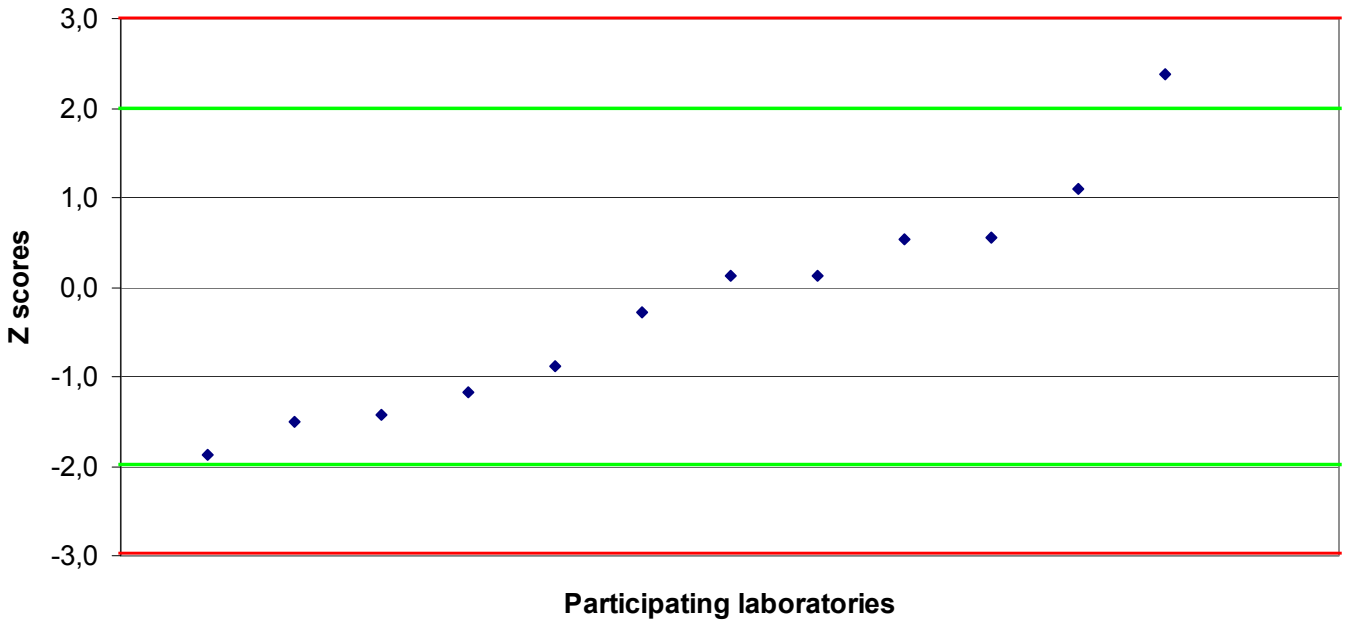
Graph 23': Z scores of the participating laboratories for endosulfan II in sample #2

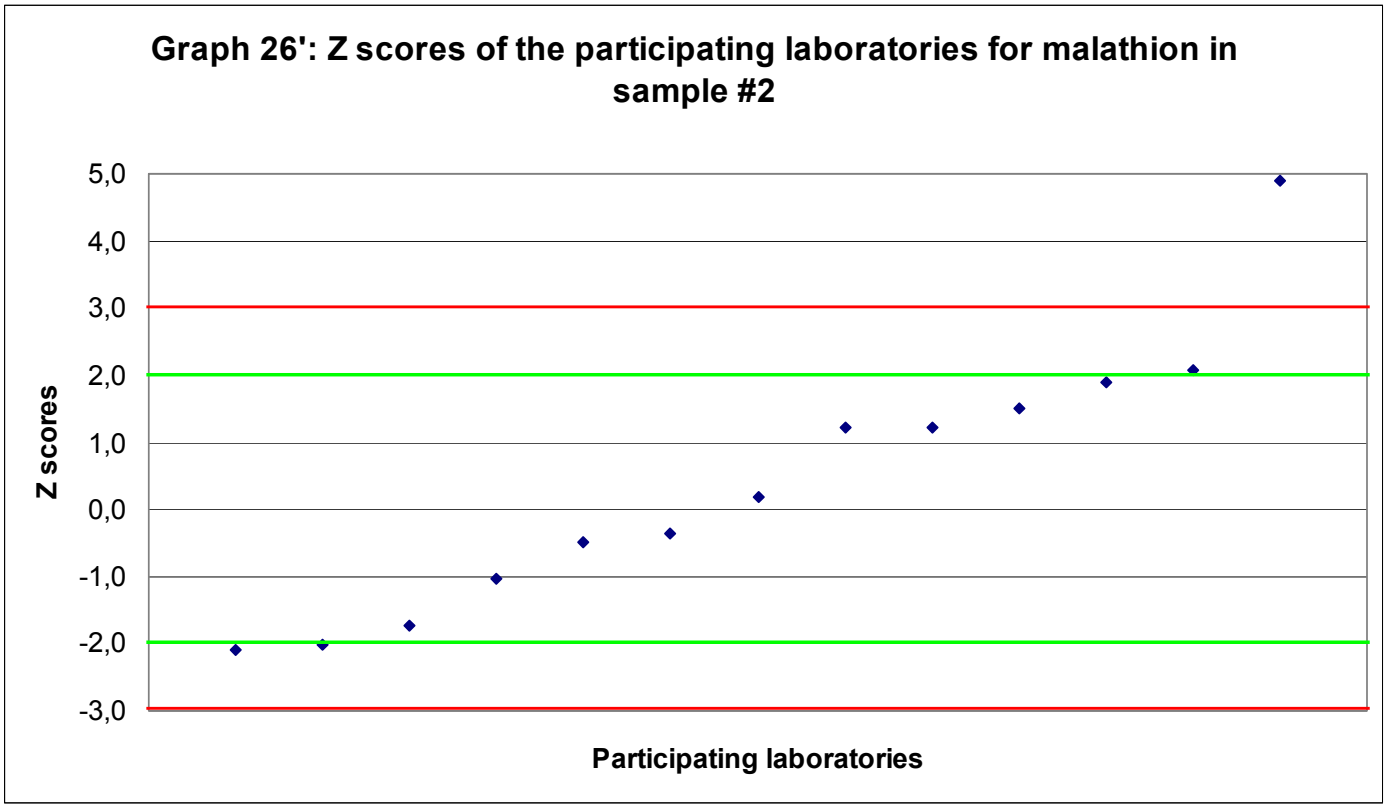


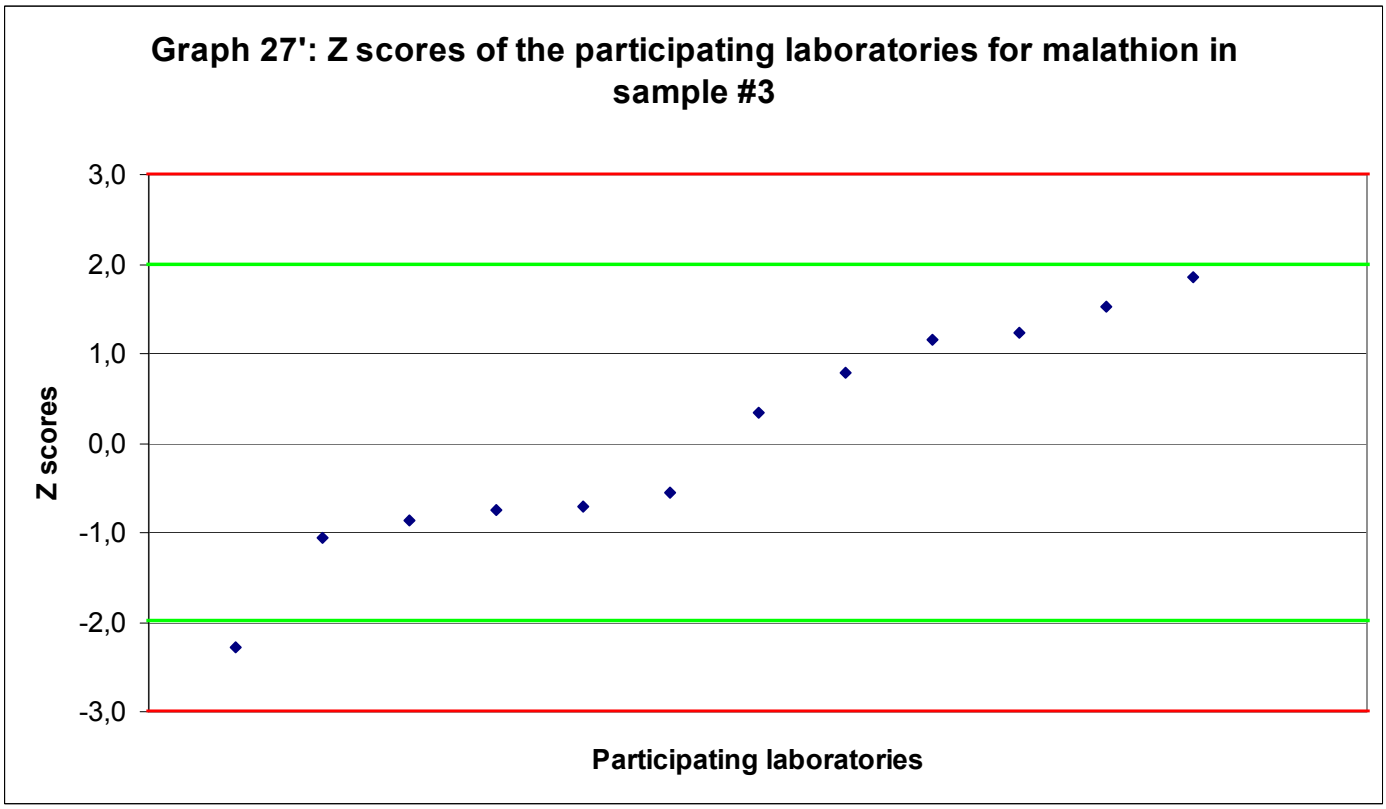
Graph 24': Z scores of the participating laboratories for endosulfan II in sample #3



Graph 25': Z scores of the participating laboratories for malathion in sample #1




Graph 26': Z scores of the participating laboratories for malathion in sample #2
5,0
4,0
3,0
2,0
1,0
0,0
-1,0
-2,0
-3,0
Z scores
Participating laboratories


Graph 27': Z scores of the participating laboratories for malathion in sample #3
3,0
2,0
1,0
0,0
-1,0
-2,0
-3,0
Z scores
Participating laboratories

Annex D: Electronic files sent to the laboratories

Annex D.1: Instruction letter for the laboratories

Standards Council of Canada
Conseil canadien des normes

IAAC

Centre d'expertise en analyse environnementale Québec

12th December 2012

Dear Participating Laboratory,

Re: Pesticides in Tomatoes Proficiency Testing Program

Instructions to Participating Laboratories

This **IAAC T 009 Pesticides in Tomatoes Proficiency Testing Program** is coordinated by Standards Council of Canada in partnership with our collaborator, the Le *Centre d'expertise en analyse environnementale du Québec (CEAEQ).* This IAAC T 009 2012 PT program is specifically designed to evaluate the performance of participating laboratories for some of the commonly used pesticides in the world.

To ensure that results from this program can be analysed properly, participating laboratories are asked to adhere carefully to the following instructions.

1. SAMPLES

a) Your accreditation body (AB) has forwarded these PT samples and instruction information (hard copy) from our collaborator, the Le *Centre d'expertise en analyse environnementale du Québec (CEAEQ).* The sample package you received contains individually labelled samples for your laboratory. This package consists of three samples for pesticides in tomatoes with no preservative in 15 ml amber glass bottles.

Each set of three bottles were sealed in a leak-proof plastic sleeve and placed in a standard packing carton, an absorbent paper and Styrofoam. The matrix is composed of lyophilized dry tomatoes to which parameters required have been added. The 3 samples for each set have concentrations that are unique, randomly spanning the concentration ranges for each parameter within the low to high concentrations identified in the following table.

Parameter	Concentration range
All pesticides	From 0.1 to 30 mg/kg

b) Your confidential lab code number is identified on the hard copy of "*Lab number.xls*" enclosed with your laboratory's samples.

c) Your AB should have also forwarded to you electronic copies of the files: 1) "*IAAC T 009 2012 instruction letter for laboratory.doc*", 2) "*IAAC T 009 2012 receipt of samples acknowledgement form (for laboratories).doc*", 3) "*Labcode_IAAC T 009 2012-Results.xls*" and 4) "*IAAC T 009 2012 - Information-Analysis Conditions.xls"*.

d) Upon receipt of your package, you should check the package and carefully inspect the samples for any physical damages.

e) You shall promptly acknowledge the receipt of the samples to the SCC Coordinator (with a cc to your AB) by emailing the completed document "*IAAC T 009 2012 receipt of samples acknowledgement form (for laboratories).doc*" to SBoisvenue@scc.ca. New samples will be re-sent by SCC/CEAEQ for any damaged samples.

f) The samples shall be stored in a secure environment at room temperature (around 20°C) before use. **Do not open the bottles until the analysis**. The analysis should be done **within a week** after the opening.

2. SAMPLE ANALYSIS

a) Participating laboratories are required to determine the concentration of Carbaryl, Carbofuran, Cypermethrin, Diazinon, Dimethoate, Endosulfan I, Endosulfan II, Malathion, p,p'-DDT (mg/kg) in the samples.

b) Participating laboratories should use their accredited test methods (or if not accredited their normal test methods) which are normally used to test their customer samples. Please record the exact method used on the results sheet *"Lab number.xls*".

- Analysis must be done on the **3 grams** container provided.
- You must combine each sample with 12 grams of water.
- It is very important to shake well the samples to insure its homogeneity.
- You must avoid introducing too much air in the sample.
- We suggest that you run the analysis in duplicate.

3. RESULTS and DOCUMENTS TO BE SUBMITTED

a) Report all the results for the appropriate parameter of the electronic spreadsheet *"Labcode_IAAC T 009 2012-Results.xls"* **It is very important to keep the exact file name. Do not change it.** It will make unusable the file for data compilation.

b) Estimate and report the expanded uncertainty (± mg/kg as appropriate) for individual analyte.

c) Fill in the information whether this is an accredited test method in the section method of the form.

d) Fill in the information of your performed analytical method for each parameter of the "*IAAC T 009 2012 - Information-Analysis Conditions.xls"*.

e) Submit your results electronically via **this completed electronic form to your AB** on or before **January 31st 2013**.

Notes: 1. Unless there are very special circumstances, all results submitted after the deadline shall be rejected by the organizers.
2. To avoid poor transmission quality, results by fax are not accepted.

Annex D.2: Receipt of samples acknowledgement form for the laboratories

E-mail to: Sylvie Boisvenue
E-mail: SBoisvenue@scc.ca
Phone: 1 613 238 3222 ext 449

Standards Council of Canada
Conseil canadien des normes

Centre d'expertise en analyse environnementale Québec

IAAC T 009 2012 Pesticides in Tomatoes Proficiency Testing Program

Receipt of Samples Acknowledgement Form for Participating Laboratories

In order to monitor the progress of this IAAC T 009 2012 Proficiency Testing Program, we kindly ask you, once you have received the package containing the samples for your registered laboratories and confirmed the status of this package and the samples, to please complete this Receipt of Samples Acknowledgement Form and email this form to the contact above **by no later than 2012-12-26.**

Thank you in advance for your cooperation.

Nominated Laboratory:

Date of receipt of samples:

Accreditation Body Name:

Lab Name:

Lab Contact Person:

Confidential Lab Code No.:

Shipping Address:

Country:

Phone No.:

E-mail address of contact:

We acknowledge the receipt of the box containing the samples for our registered laboratory for the IAAC T 009 2012 Proficiency Testing Program.

The sample package and samples were found to be * __ damaged / __ intact and should be __ suitable / ___ not suitable for laboratory testing.

Remarks:

* - Check (√) as appropriate

4. GENERAL ENQUIRIES

Thank you in advance for your cooperation. We look forward to receiving the results from your laboratory from your AB. If you have any queries or suggestions, please do not hesitate to contact me (with a cc to your AB contact).

Yours Sincerely,

Sylvie Boisvenue
SBoisvenue@scc.ca

Information on material and analysis conditions

IAAC T 009 2012 (Pesticides in tomatoes)

Laboratory Name:			
Sample Reception Date:		Analysis Date:	

If you perform a pretreatment, please describe it:							
extraction technique	☐ ASE	☐ Soxhlet	☐ SFE	☐ microwave	☐ other	Please specify:	
cleanup	☐ silica	☐ alumina	☐ carbon	☐ other		Please specify:	
GC column type	☐ DB5	☐ DB5-MS	☐ RTx-Dioxin	☐ other		Please specify:	
GC column length	☐ 60 m	☐ 30 m	☐ < 30 m	☐ > 30 m			
GC column diameter	☐ 0.25 mm	☐ 0.20 mm	☐ > 0.25 mm	☐ < 0.20 mm			
GC column phase thickness	☐ 0.15 um	☐ 0.20 um	☐ 0.25 um	☐ < 0.15 um	☐ > 0.25 um		
injector type	☐ split/splitless	☐ on-column	☐ PTV or equivalent	☐ other (please specify:)			
injector temperature (at +- 15oC)	☐ 250oC	☐ 275oC	☐ 300oC	☐ oven tracking	☐ programmed	☐ > 300oC	☐ <200oC
confirmation column used	☐ DB-225	☐ Rtx-Dioxin	☐ other (please specify:)				
MS system	☐ Waters/Micromass/VG		☐ Thermo/Finnigan-MAT		☐ Jeol	☐ other (please specify:)	
If you use another system for a confirmation, please describe it:							
method (please print)							
comments (please print)							

Supervisor name: _____

Signature: _____ **Report Date:** _____

Annex D.3: Information – Analysis Conditions form for the laboratories

Annex D.4: Results spreadsheet for the laboratories

Centre d'expertise en analyse environnementale Québec

Laboratory Name
Location

N° lab. : **N° confid. :**

IAAC T009 -

Domain	Parameter	Units	#1	#2	#3	Method
10040	Cypermethrin	mg/kg				
10040	p.p' DDT	mg/kg				
10040	Dimethoate	mg/kg				
10040	Carbaryl	mg/kg				
10040	Carbofuran	mg/kg				
10040	Diazinon	mg/kg				
10040	Endosulfane I	mg/kg				
10040	Endosulfane II	mg/kg				
10040	Malathion	mg/kg				

Comments: _____

_____

_____

Supervisor name (Please print) _____

Supervisor signature _____

Report date _____

Annex E: Email communication during the study

Annex E.1: Email for clarification on the results reporting

2013-01-08

Hello,

Concerning the report of the results for the **PT IAAC T009 2012 - Pesticides in tomatoes** here is an important message. The results need to be reported in mg/kg on a dry weight basis. Even if we ask to combine the material with water, you must report the results in milligrams of pesticide by kilograms of dry tomatoes.

Thank you,

Guillaume Bourque, Chimiste
Division des matériaux de référence
Direction de l'accréditation et des relations externes
Centre d'expertise en analyse environnementale du Québec
Ministère du Développement durable, de l'Environnement, de la Faune et des Parcs

2700, rue Einstein, bureau B.2.245
Québec (Québec) G1P 3W8
Téléphone : 418 643-1301, poste 352
Télécopieur : 418 646-7612
guillaume.bourque@mddefp.gouv.qc.ca
http://www.ceaeq.gouv.qc.ca
Commande matériaux de référence et essai d'aptitude :
materiaux.reference@mddefp.gouv.qc.ca

Annex E.2: Email for results deadline extension

2013-01-21

Dear IAAC T009 2012 participants,

Some of the participating laboratories encountered difficulties with the delivery of the PT samples. To make it fair for everyone, we decided to extend the period allowed before sending your results. The new deadline is now :**February 14th 2013** .

Regards,

Guillaume Bourque, Chimiste
Division des matériaux de référence
Direction de l'accréditation et des relations externes
Centre d'expertise en analyse environnementale du Québec
Ministère du Développement durable, de l'Environnement, de la Faune et des Parcs

2700, rue Einstein, bureau B.2.245
Québec (Québec) G1P 3W8
Téléphone : 418 643-1301, poste 352
Télécopieur : 418 646-7612
guillaume.bourque@mddefp.gouv.qc.ca
http://www.ceaeq.gouv.qc.ca
Commande matériaux de référence et essai d'aptitude :
materiaux.reference@mddefp.gouv.qc.ca

Annex E.3: Email for results confirmation

2013-03-22

Dear IAAC T009 2012 participant,

Please find enclosed an interim report of the proficiency testing study. You are requested to check the correctness of the results given for your laboratory in this report. If there is any problem detected with these results, you must contact us as soon as possible.

Your confidential number is:

Regards,

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Annex F: Homogeneity and stability testing

Table F1: Homogeneity testing of sample #1

Pesticides	Carbaryl	Carbofuran	Cypermethrin	Diazinon	Dimethoate	Endosulfan I	Endosulfan II	Malathion	p,p'-DDT
Units	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Analytical results	0,83 0,94 0,96 1,01 0,97 0,95 0,95 0,94 0,96	1,00 1,09 1,07 1,14 1,08 1,10 1,06 1,06 1,08	2,8 2,69 2,75 2,94 2,72 2,85 2,77 2,85 2,78	0,31 0,36 0,34 0,36 0,35 0,35 0,34 0,32 0,32	1,47 1,49 1,49 1,61 1,55 1,55 1,54 1,59 1,59	0,39 0,45 0,45 0,47 0,45 0,46 0,43 0,39 0,39	0,85 0,98 0,98 1,03 0,97 0,99 0,96 0,88 0,88	0,92 1,02 1,01 1,08 1,04 1,06 1,02 0,95 0,97	0,67 0,73 0,75 0,80 0,74 0,74 0,74 0,69 0,68
Mean (**X**)	0,95	1,08	2,79	0,34	1,54	0,43	0,95	1,01	0,73
Sample's standard deviation (S_s)	0,048	0,037	0,076	0,018	0,050	0,033	0,061	0,052	0,041
Sample's standard deviation in %	5%	3%	3%	5%	3%	8%	6%	5%	6%
Proficiency testing's standard deviation (σ_{pt})	0,232	0,284	1,790	0,044	0,052	0,199	0,270	0,186	0,409
$0,3(\sigma_{pt})$	0,070	0,085	0,537	0,013	0,016	0,060	0,081	0,056	0,123
$S_s \leq 0,3(\sigma_{pt})$	Yes	Yes	Yes	No	No	Yes	Yes	Yes	Yes

Table F2: Homogeneity testing of sample #2

Pesticides	Carbaryl	Carbofuran	Cypermethrin	Diazinon	Dimethoate	Endosulfan I	Endosulfan II	Malathion	p,p'-DDT
Units	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Analytical results	0,90 1,02 0,97 1,14 1,00 1,13 1,17 1,13 1,01 0,94	0,89 0,98 0,94 1,02 0,97 1,00 1,02 0,97 0,96 0,96	4,02 4,25 3,92 4,42 3,92 3,92 4,22 3,93 4,38 3,68	0,26 0,28 0,26 0,27 0,28 0,27 0,27 0,25 0,26 0,28	2,16 2,28 2,14 2,40 2,18 2,22 2,31 2,27 2,26 2,11	0,31 0,31 0,31 0,32 0,3 0,3 0,31 0,29 0,29 0,31	0,79 0,82 0,78 0,84 0,79 0,78 0,79 0,77 0,78 0,78	1,06 1,12 1,06 1,14 1,09 1,10 1,12 1,07 1,08 1,09	1,02 1,06 1,01 1,11 1,00 0,97 1,02 0,97 1,04 0,96
Mean (**X**)	1,04	0,97	4,07	0,27	2,23	0,31	0,79	1,09	1,02
Sample's standard deviation (S_s)	0,095	0,039	0,239	0,010	0,088	0,010	0,021	0,027	0,046
Sample's standard deviation in %	9%	4%	6%	4%	4%	3%	3%	2%	5%
Proficiency testing's standard deviation (σ_{pt})	0,531	0,288	3,013	0,073	0,113	0,173	0,304	0,223	0,576
$0,3(\sigma_{pt})$	0,159	0,086	0,904	0,022	0,034	0,052	0,091	0,067	0,173
$S_s \leq 0,3(\sigma_{pt})$	Yes	Yes	Yes	Yes	No	Yes	Yes	Yes	Yes

Table F3: Homogeneity testing of sample #3

Pesticides	Carbaryl	Carbofuran	Cypermethrin	Diazinon	Dimethoate	Endosulfan I	Endosulfan II	Malathion	p,p'-DDT
Units	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Analytical results	0,90	1,15	2,57	0,46	1,56	0,66	1,23	1,07	0,81
	0,86	1,12	2,47	0,47	1,51	0,64	1,15	1,04	0,73
	0,97	1,20	3,01	0,48	1,77	0,66	1,25	1,12	0,91
	0,86	1,13	2,5	0,47	1,55	0,63	1,14	1,04	0,74
	0,94	1,18	2,54	0,47	1,62	0,63	1,16	1,09	0,77
	0,82	1,08	2,41	0,47	1,42	0,63	1,13	1,01	0,67
	0,89	1,16	2,86	0,48	1,68	0,65	1,22	1,12	0,78
	0,93	1,17	2,84	0,48	1,70	0,67	1,25	1,12	0,83
	1,00	1,22	2,64	0,48	1,65	0,66	1,22	1,13	0,83
	0,91	1,17	2,58	0,49	1,55	0,69	1,25	1,13	0,77
Mean ($\bar{X}$)	0,91	1,16	2,64	0,48	1,60	0,65	1,20	1,09	0,78
Sample's standard deviation (S_s)	0,054	0,040	0,196	0,008	0,103	0,020	0,049	0,044	0,066
Sample's standard deviation in %	6%	3%	7%	2%	6%	3%	4%	4%	8%
Proficiency testing's standard deviation (σ_{pt})	0,305	0,410	1,847	0,080	0,055	0,338	0,509	0,177	0,416
$0,3(\sigma_{pt})$	0,092	0,123	0,554	0,024	0,017	0,102	0,153	0,053	0,125
$S_s \leq 0,3(\sigma_{pt})$	↓ Yes	↓ Yes	↓ Yes	↓ Yes	↓ No	↓ Yes	↓ Yes	↓ Yes	↓ Yes

Table F4: Stability testing of sample #1

Pesticides	Carbaryl	Carbofuran	Cypermethrin	Diazinon	Dimethoate	Endosulfan I	Endosulfan II	Malathion	p,p'-DDT
Units	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Stability results (**Y**)	0,93	0,93	2,17	0,17	0,16	0,30	0,76	0,49	0,55
Homogeneity mean (**X**)	0,95	1,08	2,79	0,34	1,54	0,43	0,95	1,01	0,73
| X - Y |	0,01	0,15	0,62	0,17	1,38	0,13	0,19	0,52	0,18
$0,3(\sigma_{pt})$	0,070	0,085	0,537	0,013	0,016	0,060	0,081	0,056	0,123
| X - Y | ≤ $0,3(\sigma_{pt})$	Yes	No	No	No	No	No	No	No	No

Table F5: Stability testing of sample #2

Pesticides	Carbaryl	Carbofuran	Cypermethrin	Diazinon	Dimethoate	Endosulfan I	Endosulfan II	Malathion	p,p'-DDT
Units	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Stability results (**Y**)	1,02	0,85	3,38	0,13	0,37	0,19	0,60	0,56	0,73
Homogeneity mean (**X**)	1,04	0,97	4,07	0,27	2,23	0,31	0,79	1,09	1,02
| X - Y |	0,02	0,12	0,69	0,13	1,87	0,11	0,19	0,54	0,28
$0,3(\sigma_{pt})$	0,159	0,086	0,904	0,022	0,034	0,052	0,091	0,067	0,173
| X - Y | ≤ $0,3(\sigma_{pt})$	Yes	No	Yes	No	No	No	No	No	No

Table F6: Stability testing of sample #3

Pesticides	Carbaryl	Carbofuran	Cypermethrin	Diazinon	Dimethoate	Endosulfan I	Endosulfan II	Malathion	p,p'-DDT
Units	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Stability results (**Y**)	1,00	1,15	2,10	0,24	0,20	0,43	0,98	0,60	0,54
Homogeneity mean (**X**)	0,91	1,16	2,64	0,48	1,60	0,65	1,20	1,09	0,78
| X - Y |	0,10	0,00	0,54	0,24	1,40	0,22	0,22	0,49	0,24
$0,3(\sigma_{pt})$	0,092	0,123	0,554	0,024	0,017	0,102	0,153	0,053	0,125
| X - Y | $\leq 0,3(\sigma_{pt})$	No	Yes	Yes	No	No	No	No	No	No