Results of Proficiency Test Pesticides in Textile December 2014

Organised by: Institute for Interlaboratory Studies
Spijkenisse, the Netherlands

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1 INTRODUCTION

Since the 1990's, many countries have adopted environmental standards and requirements restricting the use of harmful chemicals in the production of textiles and clothing. Laws and regulations impose some of these standards and requirements. In addition to mandatory environmental standards and requirements for textiles, there are some Ecolabelling schemes imposing environmental requirements for textile products on a voluntary basis. Well-known programs are Milieukeur (the Netherlands) and Öko-Tex Standard 100 (Germany).
The Institute for Interlaboratory Studies organizes since 2004 a scheme of proficiency test for Pesticides in textile. As part of the annual proficiency test program 2014/2015, the institute decided to continue this proficiency test on Pesticides in Textile.
In this 2014 interlaboratory study 25 laboratories in 12 different countries participated. See appendix 4 for the number of participants per country.
In this report, the results of the 2014 proficiency test are presented and discussed. This report is also electronically available through the iis internet site www.iisnl.com.

2 SET UP

The Institute for Interlaboratory Studies in Spijkenisse was the organiser of this proficiency test. Sample preparation and analyses of fit for use and homogeneity were subcontracted to an ISO17025 accredited laboratory. It was decided to use two different textile samples in this PT, both positive on a number of pesticides. The participants were requested to report rounded and unrounded results. The unrounded results were preferably used for statistical evaluation.

2.1 QUALITY SYSTEM

The Institute for Interlaboratory Studies in Spijkenisse, the Netherlands, is accredited in accordance with ISO/IEC 17043:2010, (R007), since January 2000, by the Dutch Accreditation Council (Raad voor Accreditatie, see also www.RVA.nl). This ensures strict adherence to protocols for sample preparation and statistical evaluation and 100% confidentially of participant's data. Feedback from the participants on the reported data is encouraged and customer's satisfaction is measured on regular basis by sending out questionnaires.

2.2 PROTOCOL

The protocol followed in the organisation was the one as described for proficiency testing in the report 'iis Interlaboratory Studies: Protocol for the Organisation, Statistics and Evaluation' of April 2014 (iis-protocol, version 3.3). This protocol can be downloaded from the iis website www.iisnl.com.

2.3 CONFIDENTIALITY STATEMENT

All data presented in this report must be regarded as confidential and for use by the participating companies only. Disclosure of the information in this report is only allowed by means of the entire report. Use of the contents of this report for third parties is only allowed by written permission of the Institute for Interlaboratory Studies. Disclosure of the identity of one or more of the participating companies will be done only after receipt of a written agreement of the companies involved.

2.4 SAMPLES

Two different textile samples, both positive on pesticides, were prepared by a third party. Sample #14250 was a cotton fabric fortified with 4,4'-DDD and Methoxychlor. Sample #14251 was a cotton fabric positive on Dimethoate. The two samples were each cut into pieces, well mixed and divided over 40 subsamples of 5 grams each. The samples were tested for homogeneity by determination of a pesticide in accordance with an in house test method on 5 stratified randomly selected samples. See the following tables for the test results:

	Methoxychlor in mg/kg
Sample #14250-1	13.8
Sample #14250-2	14.2
Sample #14250-3	14.5
Sample #14250-4	14.6
Sample #14250-5	14.8

Table 1: homogeneity test results of sub samples #14250

	Dimethoate in mg/kg
Sample #14251-1	1.80
Sample #14251-2	1.83
Sample #14251-3	1.69
Sample #14251-4	1.74
Sample #14251-5	1.89

Table 2: homogeneity test results of sub samples #14251

From the above results of the homogeneity test, the repeatabilities were calculated and compared with 0.3 times the corresponding reproducibility of the reference method in agreement with the procedure of ISO 13528, Annex B2 in the next table:

	Methoxychlor in mg/kg	Dimethoate in mg/kg
r (samples #14250)	1.10	--
r (samples #14251)	--	0.22
Reference method	Horwitz	Horwitz
0.3 x R (reference method)	1.29	0.22

Table 3: repeatabilities of subsamples #14250 and #14251.

For the determination of the pesticides content an In-house extraction method was used. Both calculated repeatabilities of the homogeneity test results are in agreement with the usual repeatability of the laboratory that performed the homogeneity tests. Therefore, homogeneity of subsamples #14250 and #14251 was assumed.

In total approx. 5 grams of each of the samples #14250 and #14251 were sent to the participating laboratories on November 19, 2014.

2.5 ANALYSES

The participants were asked to determine the concentrations of a limited number of prescribed pesticides, applying the analytical procedure that is routinely used in the laboratory.
To get comparable results a detailed report form, was sent together with the set of samples. On the report forms the requested pesticides, including the units and questions about the analytical details, were pre-printed. In addition, a letter of instructions was sent along.

3 RESULTS

During four weeks after sample despatch, the results of the individual laboratories were received. The original data are tabulated per sample in the appendix 1 of this report.
The laboratories are represented by the code numbers.
Directly after the deadline, a reminder fax was sent to those laboratories that did not report results at that moment.
Shortly after the deadline, the available results were screened for suspect data. A result was called suspect in case the Huber Elimination Rule (a robust outlier test) found it to be an outlier. The laboratories that produced these suspect data were asked to check the results. Additional or corrected results are used for the data analysis and the original results are placed under 'Remarks' in the result tables in appendix 1.

3.1 STATISTICS

The statistical calculations were performed as described in the procedures in the report ‘iis Interlaboratory Studies, Protocol for the Organisation, Statistics and Evaluation’ of April 2014 (iis-protocol, version 3.3).

First, the normality of the distribution of the various data sets per determination was checked by means of the Lilliefors-test a variant of the Kolmogorov-Smirnov test and by the calculation of skewness and kurtosis. Evaluation of the three normality indicators in combination with the visual evaluation of the graphic Kernel density plot, lead to judgement of the normality being either ‘unknown’, ‘OK’, ‘suspect’ or ‘not OK’.
After removal of outliers, this check was repeated. Not all data sets proved to have a normal distribution, in which cases the statistical evaluation of the results should be used with due care.

In accordance to ISO 5725 (1986 and 1994) the original results per determination were submitted subsequently to Dixon, Grubbs and or Rosner General ESD outlier tests. Outliers are marked by D(0.01) for the Dixon test, by G(0.01) or DG(0.01) for the Grubbs test and by R(0.01) for the Rosner General ESD test. Stragglers are marked by D(0.05) for the Dixon test, by G(0.05) or DG(0.05) for the Grubbs test and by R(0.05) for the Rosner General ESD test (ref. 17). Both outliers and stragglers were not included in the calculations of averages and standard deviations.
Finally, the reproducibilities were calculated from the standard deviations by multiplying them with a factor of 2.8.

For each assigned value the uncertainty was determined in accordance with ISO13528. Subsequently the calculated uncertainty was evaluated against the respective requirement based on the target reproducibility in accordance with ISO13528. When the uncertainty passed the evaluation no remarks are made in the report. However, when the uncertainty failed the evaluation it is mentioned in the report and it will have significant consequences for the evaluation of the test results.

3.2 GRAPHICS

In order to visualise the data against the reproducibilities from literature, Gauss plots were made, using the sorted data for one determination (see appendix 1). On the Y-axis the reported analysis results are plotted. The corresponding laboratory numbers are under the X-axis.
The straight horizontal line presents the consensus value (a trimmed mean). The four striped lines, parallel to the consensus value line, are the +3s, +2s, -2s and -3s target reproducibility limits of the selected standard. Outliers and other data, which were excluded from the calculations, are represented as a cross. Accepted data are represented as a triangle. Furthermore, Kernel Density Graphs were made. This is a method for producing a smooth density approximation to a set of data that avoids some problems associated with histograms (see appendix 5; nr.14 and 15). Also a normal Gauss curve was projected over the Kernel Density Graph for reference.

3.3 Z-SCORES

To evaluate the performance of the participating laboratories the z-scores were calculated. As it was decided to evaluate the performance of the participants in this proficiency test (PT) against the literature requirements, e.g. ISO reproducibilities, the z-scores were calculated using a target standard deviation. This results in an evaluation independent of the spread of this Interlaboratory Study.
The target standard deviation was calculated from the literature reproducibility by division with 2.8.

The standard uncertainly (u_x) was calculated from the (target) standard deviation in accordance with ISO13528, paragraph 5.6:

$$u_x = 1.25 * (\text{st.dev}(n)) / \sqrt{n}$$

In ISO13528 is stated that if $u_x \geq 0.3$ * standard deviation for proficiency testing, the uncertainly of the assigned value is not negligible and need to be included in the interpretation of the results of the proficiency test. Therefore in this PT report z'-scores were calculated instead of the usual z-scores. The z'(target)-scores were calculated in accordance with ISO13528 paragraph 7.6:

$$z'(\text{target}) = (\text{result} - \text{mean of PT}) / \sqrt{((\text{target standard deviation})^2 + (u_x)^2)}$$

The z'(target) scores are listed in the result tables in appendix 1.
Absolute values for z<2 are very common and absolute values for z>3 are very rare.
Therefore the usual interpretation of z-scores is as follows:

$|z| < 1$ good
$1 < |z| < 2$ satisfactory
$2 < |z| < 3$ questionable
$3 < |z|$ unsatisfactory

4 EVALUATION

During the execution of this proficiency test no serious problems occurred.
Four participants did not report any test results. Two other participants reported the test results after the final reporting date. The 21 participants reported 53 numerical test results. Observed were 3 statistical outlying results, which is 5.7% of the numerical results. In proficiency studies, outlier percentages of 3 % - 7.5 % are quite normal.

All original data sets proved to have a normal distribution.

Due to the lack of relevant standard test methods for the determination of pesticides with precision data, the calculated reproducibilities were compared with the reproducibilities calculated using Horwitz, see also paragraph 5.

4.1 EVALUATION PER SAMPLE AND PESTICIDE

All statistical results reported on the textile samples are summarised in appendix 1 and relevant method information is summarized in appendix 3 and all other positively reported pesticide test results are listed in appendix 2.

4,4'-DDD: The determination of this pesticide may be problematic at the level of 5.1 mg/kg. Two statistical outliers were observed. The calculated reproducibility after rejection of the statistical outliers is not in agreement with the estimated target reproducibility (Horwitz').

Methoxychlor: The determination of this pesticide may be problematic at the level of 10.4 mg/kg. One statistical outlier was observed. The calculated reproducibility after rejection of the statistical outlier is not in agreement with the estimated target reproducibility (Horwitz').

Dimethoate: The determination of this pesticide may be problematic at an average level of 0.8 mg/kg. No statistical outliers were observed. However, the calculated reproducibility is not in agreement with the estimated target reproducibility (Horwitz').
It is noticed that the results seem bimodal divided. When both groups were evaluated separately, the spread of each group is in agreement with the estimated target reproducibility calculated using the Horwitz equation.

4.2 PERFORMANCE EVALUATION FOR THE GROUP OF LABORATORIES

A comparison has been made between the strict reproducibilities as estimated by the Horwitz equation and the reproducibilities as found for the group of participating laboratories.
The number of significant results, the average results, the calculated reproducibilities (standard deviation*2.8) and the target reproducibilities (estimated via the Horwitz equation), are compared in the next 2 tables.

Parameter	*Unit*	*n*	*Average*	*2.8 * sd*	*R(target)*
4,4'-DDD	mg/kg	19	5.1	4.1	2.1
Metoxychlor	mg/kg	20	10.4	10.0	4.3

Table 4: reproducibilities of pesticides in sample #14250

Parameter	*Unit*	*n*	*Average*	*2.8 * sd*	*R(target)*
Dimethoate	mg/kg	11	0.78	1.17	0.57

Table 5: reproducibilities of pesticides in sample #14251

Without further statistical calculations it can be concluded that for all determined pesticides the group of participating laboratories has difficulties with the analysis. See also the discussion in paragraphs 4.1 and 5.

5 COMPARISON WITH PREVIOUS INTERLABORATORY STUDIES

The precision that was found for the pesticide 4,4'-DDD during the present proficiency test did improve, while the precision for the other two pesticides was worse than before.
The relative low number of participating laboratories may (partly) explain for the relatively large spreads.

	Nov 2014	*Nov 2013*	*Nov 2012*	*Nov 2011*	*Nov 2010*	*Feb 2010*	*Feb 2009*	*Feb 2008*
Carbaryl	--	--	--	--	52	--	--	--
Cyhalothrin-lambda	--	--	45	--	41	--	--	35
Cypermethrin (=Σ)	--	26	28	--	--	15	--	--
4,4'-DDD	29	--	--	--	38	--	--	--
Deltamethrin	--	16	--	12	--	--	--	31
Dimethoate	54	--	--	--	--	--	35	--
α/β-Endosulfan	--	--	--	27-33	--	15-20	21	--
Fenvalerate	--	--	13-28	--	11	--	24-37	32
Esfenvalerate	--	--	22-41	--	42	--	--	--
Methoxychlor	35	--	--	22	28	--	--	14
Monocrotophos	--	--	38	--	--	--	--	--
Parathion	--	--	--	--	73	--	--	--
Quinalfos	--	--	--	24-39	--	24	--	--

Table 6: Comparison of uncertainties (in %) in iis proficiency tests on pesticides in textile

6 DISCUSSION

When the results of this interlaboratory study were compared to the Ecolabelling Standards and Requirements for Textiles in EU (see table 5), it could be noticed that a number of the reporting laboratories would make a different decision about the acceptability of the textiles for the determined parameters.

Ecolabel	Baby	Direct skin contact	With no direct skin contact	Decoration material
Pesticides, total mg/kg	0.5	1.0	1.0	1.0

Table 7: Ecolabelling Standards and Requirements for Textiles in EU

General

In this proficiency test for the determination of pesticides in textile, all the participants identified all spiked pesticides correctly. However, the quantification was more problematic. The spreads of the group regretfully could not be compared with the precision of a Standard Test Method because of the lack of a suitable test method with precision data.

Surprisingly, the results of the homogeneity data are higher than the consensus values that were determined during the PT. The reason is unknown. It may be caused by an incidental error (e.g. a weighing or dilution error) of the laboratory that performed the homogeneity analyses prior to use.

The majority of the participants used in house methods (see appendix 3). This may be an explanation for the relative large spreads found. As the details of the test methods are not known, it is difficult to give a significant conclusion.

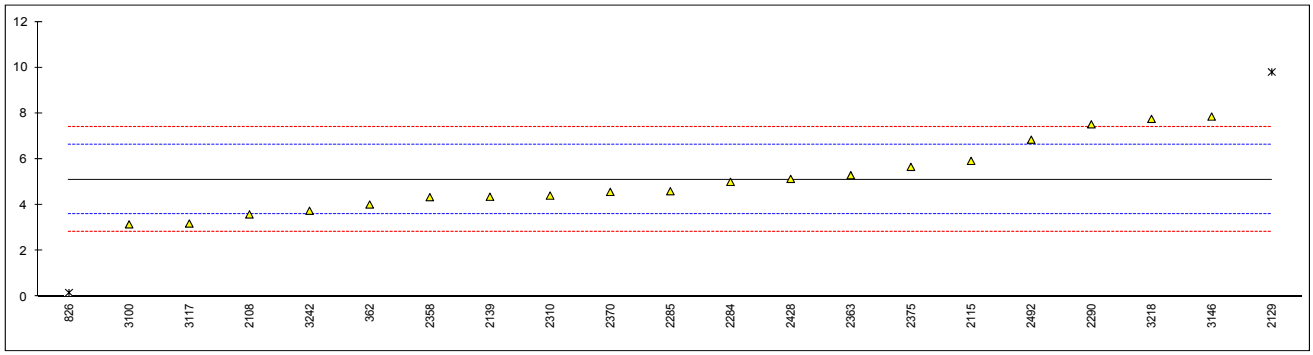
Finally, each laboratory has to evaluate its performance in this study and make decisions about necessary corrective actions. Therefore, participation on a regular basis in this scheme could be helpful to improve the performance and thus improve of the quality of the analytical results.

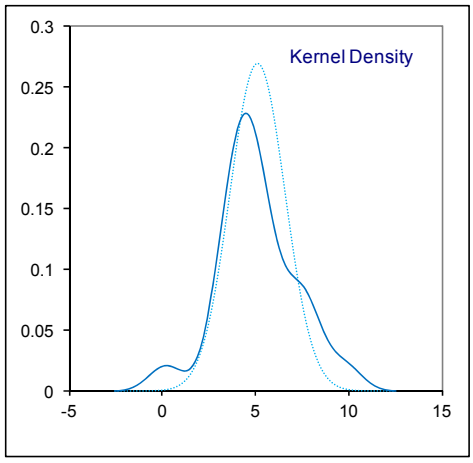
APPENDIX 1

Determination of 4,4'-DDD on sample #14250; results in mg/kg

lab	method	value	mark	z'(targ)	Remarks
362	INH-120	4.021		-1.42	
826	EPA8081B	0.174	DG(0.05)	-6.46	
2108	in house	3.59		-1.99	
2115	OekoTex Std 100	5.925		1.07	
2129	INH-400	9.804	DG(0.05)	6.15	
2139	OekoTex	4.36		-0.98	
2284	in house	5.01		-0.13	
2285	GB/T18412.1	4.602		-0.66	
2290	in house	7.521		3.16	
2310	EPA8081B	4.41		-0.91	
2358	in house	4.344		-1.00	
2363	in house	5.3		0.25	
2370	EPA8081B	4.57		-0.70	
2375	EPA8081B	5.663		0.73	
2390		-----		-----	
2413		-----		-----	
2428	GB/T18412.1	5.14		0.04	
2492	in house	6.851		2.28	
2612		-----		-----	
3100	GB/T18412.1	3.156		-2.55	
3117	OekoTek Std 200	3.1915		-2.51	
3146	in house	7.86		3.61	
3172		-----		-----	
3218	in house	7.76		3.47	
3242	in house	3.75		-1.78	

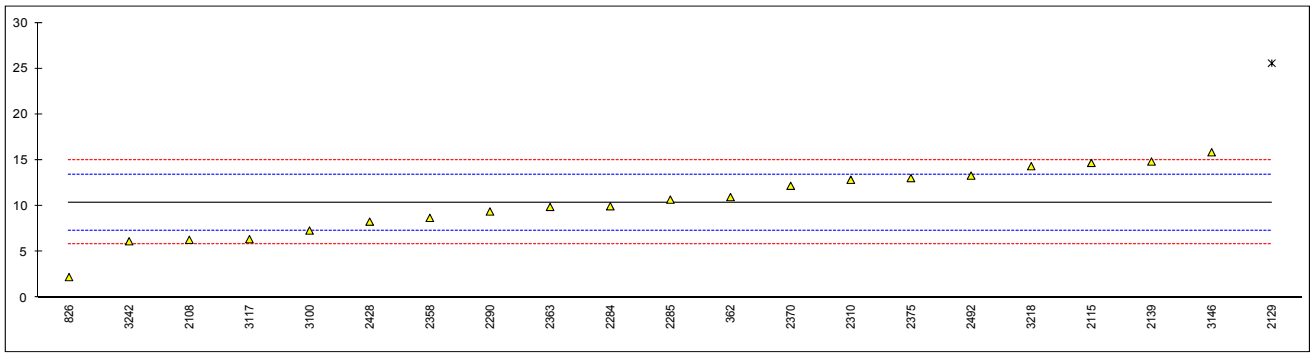
normality	OK
n	19
outliers	2
mean (n)	5.107
st.dev. (n)	1.4810
R(calc.)	4.147
R(Horwitz')	2.138

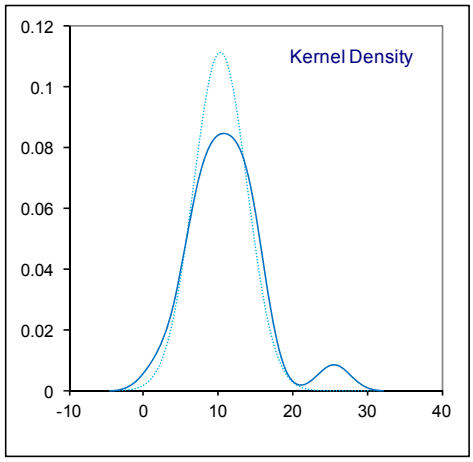




Determination of Methoxychlor on sample #14250; results in mg/kg

lab	method	value	mark	z'(targ)	remarks
362	INH-120	10.97		0.39	
826	EPA8081B	2.241		-5.32	
2108	in house	6.31		-2.66	
2115	OekoTex Std 100	14.700		2.83	
2129	INH-400	25.584	G(0.05)	9.95	
2139	OekoTex	14.85		2.93	
2284	in house	9.97		-0.27	
2285	GB/T18412.1	10.695		0.21	
2290	in house	9.4	C	-0.64	First reported 25.321
2310	EPA8081B	12.86		1.63	
2358	in house	8.704		-1.09	
2363	in house	9.9		-0.31	
2370	EPA8081B	12.2		1.19	
2375	EPA8081B	13.041		1.74	
2390		-----		-----	
2413		-----		-----	
2428	GB/T18412.1	8.29		-1.36	
2492	in house	13.315		1.92	
2612		-----		-----	
3100	GB/T18412.1	7.321		-2.00	
3117	OekoTek Std 200	6.3840		-2.61	
3146	in house	15.86		3.59	
3172		-----		-----	
3218	in house	14.34		2.59	
3242	in house	6.15		-2.76	
	normality	OK			
	n	20			
	outliers	1			
	mean (n)	10.375			
	st.dev. (n)	3.5874			
	R(calc.)	10.045			
	R(Horwitz')	4.280			

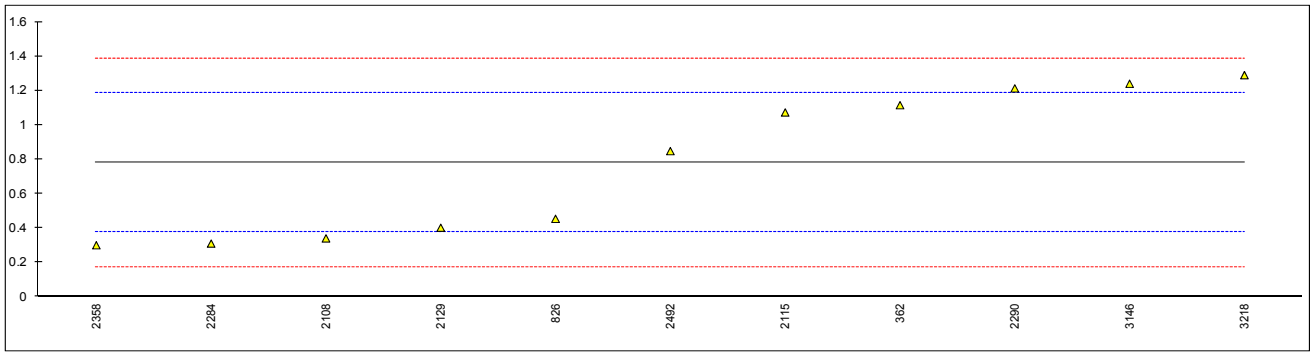


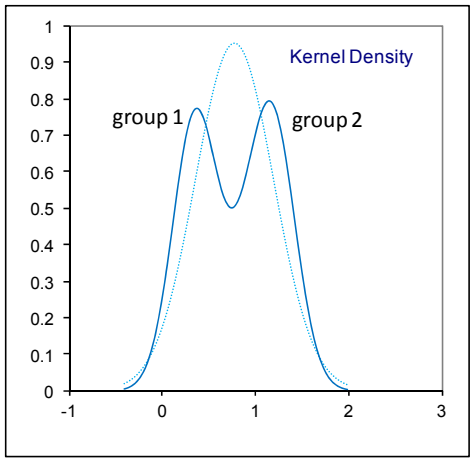


Determination of Dimethoate on sample #14251; results in mg/kg

lab	method	value	mark	z'(targ)	remarks
362	INH-120	1.115		1.65	
826	EPA8081B	0.454		-1.61	
2108	in house	0.34		-2.18	
2115	OekoTex Std 100	1.073		1.45	
2129	INH-400	0.402		-1.87	
2139		-----		-----	
2284	in house	0.31		-2.32	
2285	GB/T18412.1	n.d.		-----	
2290	in house	1.213		2.14	
2310	EPA8081B	n.d.		-----	
2358	in house	0.3001		-2.37	
2363	in house	n.d.		-----	
2370	EPA8081B	n.d.		-----	
2375	EPA8081B	n.d.		-----	
2390		-----		-----	
2413		-----		-----	
2428	GB/T18412.1	n.d.		-----	
2492	in house	0.848		0.33	
2612		-----		-----	
3100	GB/T18412.1	n.d.		-----	
3117		-----		-----	
3146	in house	1.24		2.27	
3172		-----		-----	
3218	in house	1.29		2.52	
3242	in house	n.d.		-----	

			Group 1	Group 2
	normality	OK	OK	suspect
	n	11	5	6
	outliers	0	0	0
	mean (n)	0.7805	0.3612	1.1298
	st.dev. (n)	0.41903	0.06535	0.15974
	R(calc.)	1.1733	0.1830	0.4473
	R(Horwitz')	0.5666	0.1886	0.4969





APPENDIX 2

Summary of all other reported pesticides; results in mg/kg

	#14250	
lab	2,4-DDD	Parathion
362		
826	5.565	
2108		
2115		
2129	0.040	0.032
2139		
2284		
2285		
2290		
2310		
2358		
2363		
2370		
2375		
2390		
2413		
2428		
2492		
2612		
3100		
3117		
3146		
3172		
3218		
3242		

	#14251				
lab	4,4-DDD	2,4-DDD	Parathion	Endosulfan1	Endosulfan2
362	0.1158				
826		0.339	0.211		
2108				0.72	0.36
2115					
2129					
2139					
2284					
2285					
2290					
2310	0.35				
2358	0.5237				
2363					
2370					
2375	0.069				
2390					
2413					
2428					
2492					
2612					
3100					
3117					
3146					
3172					
3218					
3242					

APPENDIX 3

Details of the methods used by the participants:

Lab	Release/ extraction	time	Extraction solution	calibration	Chromatographic analysis
362	Liquid extraction	12h	Hexane;Acetone	External standard	GC/MSD
826	--	90 min	Hexane;Acetone	--	ECD & GC/MSD
2108	--	--	--	--	GC/MS/MS
2115	ASE	20 min	Acetone	Internal standard	GC/MS – GC/MS-MS
2129	ASE	5 min	Acetone; 0.1%HAc	External standard	MSD-NCI & MSD-EI
2139	Ultrasonic	60 min	Hexane;Acetone	--	GC/MS
2284	Ultrasonic	30 min	Dichloromethane; Acetone	Internal standard	GC/MS
2285	Ultrasonic	25 min	Hexane;Ethylacetate	External standard	GC/MS
2290	Ultrasonic	60 min	Methanol; MeOH/Acetone	External standard	GC-MS & LC/MS-MS
2310	Ultrasonic	60 min	Hexane;Acetone	External standard	GC/MSD & GC/ECD
2358	Ultrasonic	60 min	Hexane;Acetone	Internal standard	GC/MS & GC/ECD
2363	Ultrasonic	60 min	Hexane;Acetone; ACN	External standard	GC/MS & LC/MS
2370	Ultrasonic	60 min	Hexane;Acetone	Internal standard	MS
2375	Ultrasonic	60 min	Hexane;acetone	Standard addition	MS
2390	--	--	--	--	--
2413	--	--	--	--	--
2428	Ultrasonic	20 min	Hexane;Acetone	External standard	GC/MS
2492	--	3 hr	Acetone	Standard addition	MS
2612	--	--	--	--	--
3100	Ultrasonic	60 min	Hexane;Acetone	External standard	GC/MS
3117	Ultrasonic	25 min	Hexane; Ethylacetate	External Standard	GC/MSD
3146	ASE	30 min	Hexane;Aceetone	Internalstandard	MS
3172	--	--	--	--	--
3218	Ultrasonic	60 min	Hexane;Acetone; MeOH	External standard	MS
3242	Shaking	60 min	Dichloromethane;Acetone	External standard	GC/ECD & GC/MS

APPENDIX 4

Number of participants per country

1 lab in	BULGARIA
4 labs in	GERMANY
2 labs in	HONG KONG
2 labs in	INDIA
2 labs in	ITALY
2 labs in	KOREA
7 labs in	P.R. of CHINA
1 lab in	PAKISTAN
1 lab in	TAIWAN R.O.C.
1 lab in	TURKEY
1 lab in	UNITED STATES OF AMERICA
1 lab in	VIETNAM

APPENDIX 5

Abbreviations:

C	= final result after checking of first reported suspect result
D(0.01)	= outlier in Dixon's outlier test
D(0.05)	= straggler in Dixon's outlier test
G(0.01)	= outlier in Grubbs' outlier test
G(0.05)	= straggler in Grubbs' outlier test
DG(0.01)	= outlier in Double Grubbs' outlier test
DG(0.05)	= straggler in Double Grubbs' outlier test
R(0.01)	= outlier in Rosner outlier test
R(0.05)	= straggler in Rosner outlier test
n.a.	= not applicable
n.d.	= not detected

Literature:

1 iis Interlaboratory Studies, Protocol for the Organisation, Statistics & Evaluation, April 2014
2 Öko-Tex Standard 100; January 2014
3 Thai Green label. TGL-16. July 2002
4 Impacts of Environmental Standards and requirements in EU Countries. Aug 99
5 Horwitz. Journal of AOAC International Vol. 79 No.3. 1996
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7 W.J. Conover. Practical; Nonparametric Statistics. J. Wiley&Sons. NY. p.302. (1971)
8 ISO 5725. (1986)
9 ISO 5725. parts 1-6. (1994)
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