

Results of Proficiency Test
Pesticides in Textile
November 2013

Organised by: Institute for Interlaboratory Studies
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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 2013/2014, the institute decided to continue this proficiency test on Pesticides in Textile.

In this 2013 interlaboratory study 26 laboratories in 12 different countries participated. See appendix 4 for the number of participants per country.

In this report, the results of the 2013 proficiency test are presented and discussed.

2 SET UP

The Institute for Interlaboratory Studies in Spijkenisse was the organiser of this proficiency test. Sample preparation and analyses were subcontracted to an 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, has implemented a quality system based on ISO/IEC 17043:2010. This ensures strict adherence to protocols for sample preparation and statistical evaluation and 100% confidentiality 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 of this proficiency test was the one as described for proficiency testing in the report 'iis Interlaboratory Studies: Protocol for the Organisation, Statistics and Evaluation' of January 2010 (iis-protocol, version 3.2).

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 #13232 was a cotton fabric fortified with Cypermethrin. Sample #13233 was a cotton fabric fortified with Deltamethrin. The two samples were each cut into pieces, well mixed and divided over 35 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 4 stratified randomly selected samples. See the following tables for the test results:

	Cypermethrin in mg/kg
Sample #13232-1	2.3
Sample #13232-2	2.0
Sample #13232-3	2.8
Sample #13232-4	2.9

Table 1: homogeneity test results of sub samples #13232

	Deltamethrin in mg/kg
Sample #13233-1	13.8
Sample #13233-2	15.0
Sample #13233-3	14.5
Sample #13233-4	14.6

Table 2: homogeneity test results of sub samples #13233

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 #13232 and #13233 was assumed.

In total approx. 5 grams of each of the samples #13232 and #13233 were sent to the participating laboratories on November 6, 2013.

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 gathered. The original data are tabulated per determination in appendix 1 of this report. The laboratories are presented by their code numbers.

Directly after the deadline, a reminder fax was sent to the laboratories that had not reported 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 data analysis and original results are placed under 'Remarks' in the result tables in appendix 1.

3.1 STATISTICS

For the statistical evaluation the *unrounded* (when available) figures were used instead of the rounded results. Results reported as '<... ' or '>... ' were not used in the statistical evaluation.

First, the normality of the distribution of the various data sets per determination was checked by means of the Lilliefors-test. 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 and Grubbs 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. Stragglers are marked by D(0.05) for the Dixon test, by G(0.05) or DG(0.05) for the Grubbs test. Both outliers and stragglers were not included in the calculations of averages and standard deviations.

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 consequences for the evaluation of the test results.

Finally the reproducibilities were calculated from the standard deviations by multiplying them with a factor of 2.8.

Statistical calculations were performed as described in the report 'iis Interlaboratory Studies: Protocol for the Organisation, Statistics and Evaluation' of January 2010 (iis-protocol, version 3.2).

3.2 GRAPHICS

In order to visualize 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, nos.15-16).

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 z-scores were calculated in accordance with:

$$Z_{(\text{target})} = (\text{result} - \text{average of PT}) / \text{target standard deviation}$$

When a laboratory did use a test method with a reproducibility that is significantly different from the reproducibility of the reference test method used in this report, it is strongly advised to recalculate the z-score, while using the reproducibility of the actual test method used, this in order to evaluate the fit-for-useness of the reported test result.

Absolute values for $z < 2$ are very common and absolute values for $z > 3$ are very rare. 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. Five other participants reported the test results after the final reporting date. The 22 participants reported 56 numerical test results. Observed were 6 statistical outlying results, which is 10.7% of the numerical results. In proficiency studies, outlier percentages of 3 % - 7.5 % are quite normal.

Not all original data sets proved to have a normal distribution. A not normal distribution was found for Deltamethrin in sample #13233. For this determination the result of the statistical evaluation should be used with due care.

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.

Cypermethrin: The determination of this pesticide may be problematic at the level of 5.3 mg/kg. Three statistical outliers were observed. The calculated reproducibility after rejection of the statistical outliers is not in agreement with the estimated target reproducibility (Horwitz).

Deltamethrin: The determination of this pesticide may be problematic at the level of 9.9 mg/kg. Three statistical outliers were observed. The calculated reproducibility after rejection of the statistical outliers is not in agreement with the estimated target reproducibility (Horwitz).

Quinalfos: Both samples (#13232 and #13233) did contain very little of this component (both below <0.5 mg/kg), which is near or below the detection limit. Therefore no significant conclusions were drawn.

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.

<i>Parameter</i>	<i>Unit</i>	<i>n</i>	<i>Average</i>	<i>2.8 * sd</i>	<i>R(target)</i>
Cypermethrin	mg/kg	18	5.30	3.89	1.85
Quinalfos	mg/kg	7	<0.5	n.a.	n.a.

Table 3: reproducibilities of pesticides in sample #13232

<i>Parameter</i>	<i>Unit</i>	<i>n</i>	<i>Average</i>	<i>2.8 * sd</i>	<i>R(target)</i>
Deltamethrin	mg/kg	18	9.89	4.49	3.14
Quinalfos	mg/kg	12	<0.5	n.a.	n.a.

Table 4: reproducibilities of pesticides in sample #13233

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 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 all of the reporting laboratories would make the same decision about the acceptability of the textiles for the determined parameters. All participants would reject the textiles.

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

Table 5: 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. The spreads of the group regrettably could not be compared with the precision of a Standard Test Method because of the lack of a suitable test method with precision data.

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.

The precisions that were found for the pesticides Cypermethrin and Deltamethrin during the present proficiency test did not improve.

The relative low number of participating laboratories may (partly) explain for the relatively large spreads.

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

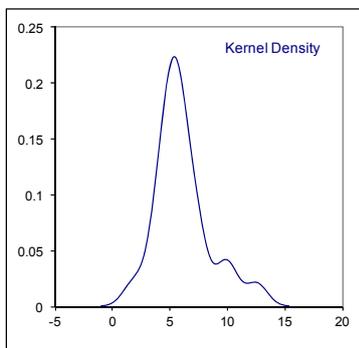
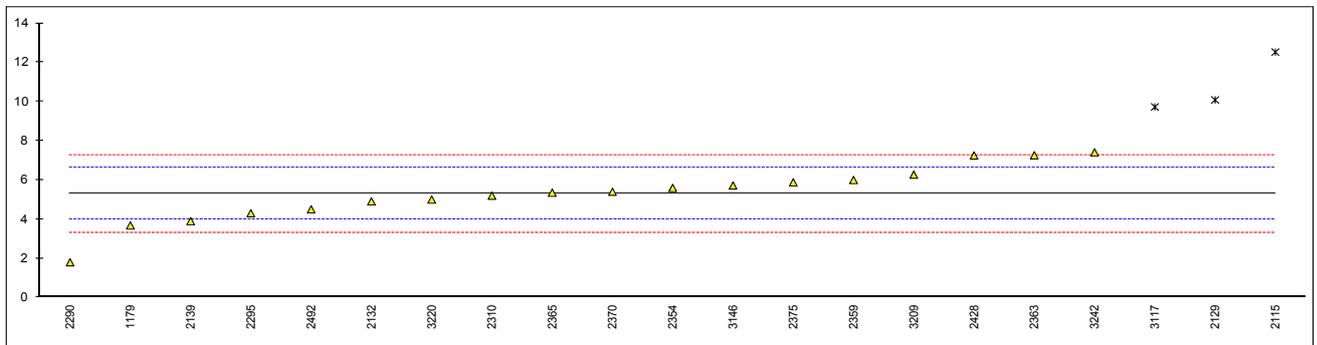
Table 6: Comparison of uncertainties (in %) in iis proficiency tests on pesticides in textile

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 Cypermethrin on sample #13232; results in mg/kg

lab	method	value	mark	z(targ)	remarks
1179		3.680		-2.46	
2115		12.53	G(0.05)	10.95	
2129		10.090	DG(0.05)	7.26	
2132	in house	4.91		-0.59	
2139	in house	3.90		-2.12	
2290	in house	1.8	C	-5.31	First reported 10.124
2295	in house	4.3	C	-1.52	First reported 10.2
2310	in house	5.2		-0.15	
2354	in house	5.595		0.44	
2359	USEPA8081/8141/8270	6.0		1.06	
2363	in house	7.262		2.97	
2365	GB/T18412	5.35		0.07	
2370	USEPA8081	5.40		0.15	
2375	USEPA8081/8141/8270/8321	5.8804		0.88	
2428	EPA8081	7.25	C	2.95	First reported 9.26
2483		----		----	
2492	in house	4.50		-1.21	
2508		----		----	
2561		----		----	
2588		----		----	
3117	Oeko-Tex Std 200	9.73	C,DG(0.05)	6.71	First reported 12.04
3146		5.72		0.63	
3172		----		----	
3209	GB/T18412	6.274		1.47	
3220	in house	5.0		-0.46	
3242	in house	7.41		3.19	
	normality	OK			
	n	18			
	outliers	3			
	mean (n)	5.302			
	st.dev. (n)	1.3908			
	R(calc.)	3.894			
	R(Horwitz)	1.848			

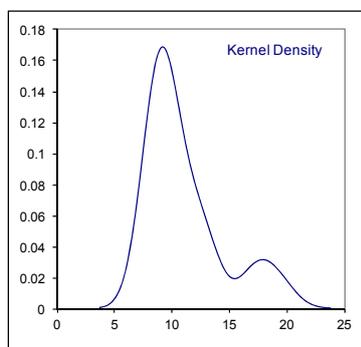
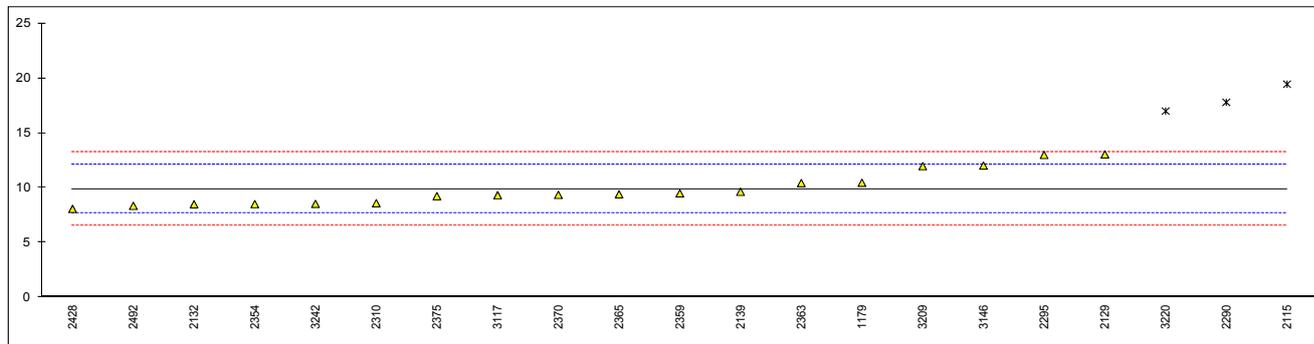


Determination of Quinalfos on sample #13232; results in mg/kg

lab	method	value	mark	z(targ)	remarks
1179		0.055		----	
2115		----		----	
2129		<0.05		----	
2132	in house	0.02		----	
2139		----		----	
2290	in house	<0.5		----	
2295	in house	n.d.		----	
2310	in house	0.05		----	
2354	in house	n.d.		----	
2359	USEPA8081/8141/8270	n.d.		----	
2363	in house	<0.2		----	
2365	GB/T18412	n.d.		----	
2370	USEPA8081	n.d.		----	
2375	USEPA8081/8141/8270/8321	0.0616		----	
2428	EPA8081	n.d.		----	
2483		----		----	
2492		----		----	
2508		----		----	
2561		----		----	
2588		----		----	
3117		----		----	
3146		<0.8		----	
3172		----		----	
3209	GB/T18412	n.d.		----	
3220	in house	n.d.		----	
3242	in house	n.d.		----	
	normality	n.a.			
	n	7			
	outliers	0			
	mean (n)	<0.5			
	st.dev. (n)	n.a.			
	R(calc.)	n.a.			
	R(lit)	n.a.			

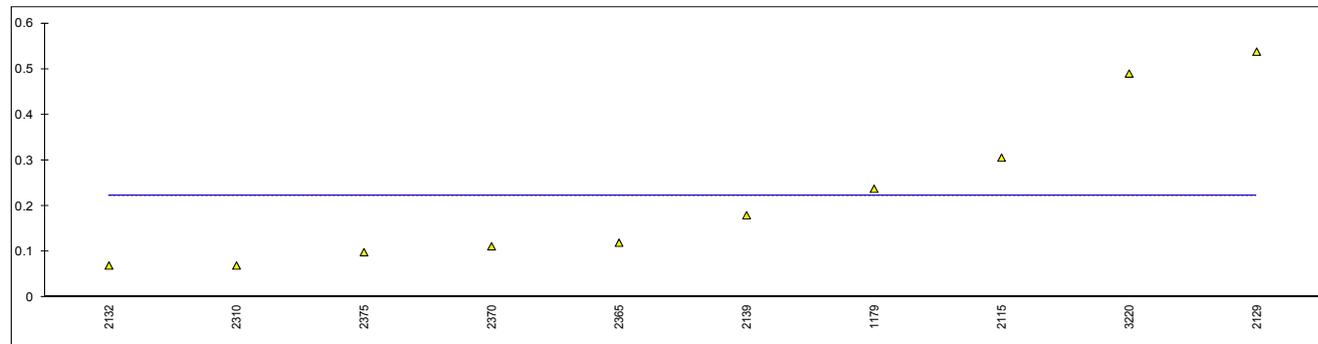
Determination of Deltamethrin on sample #13233; results in mg/kg

lab	method	value	mark	z(targ)	remarks
1179		10.46		0.51	
2115		19.45	DG(0.05)	8.53	
2129		13.050		2.82	
2132	in house	8.5		-1.24	
2139	in house	9.64		-0.22	
2290	in house	17.8	DG(0.05)	7.06	
2295	in house	13	C	2.77	First reported 16.8
2310	in house	8.6		-1.15	
2354	in house	8.515		-1.23	
2359	USEPA8081/8141/8270	9.5		-0.35	
2363	in house	10.435		0.49	
2365	GB/T18412	9.41		-0.43	
2370	USEPA8081	9.36		-0.47	
2375	USEPA8081/8141/8270/8321	9.2415		-0.58	
2428	EPA8081	8.08		-1.62	
2483		----		----	
2492	in house	8.36		-1.37	
2508		----		----	
2561		----		----	
2588	in house	<0.5		<-8.38	False negative?
3117	Oeko-Tex Std 200	9.33		-0.50	
3146		12.03		1.91	
3172		----		----	
3209	GB/T18412	11.98		1.86	
3220	in house	17	C,G(0.01)	6.34	First reported 15.0
3242	in house	8.54		-1.21	
normality		not OK			
n		18			
outliers		3			
mean (n)		9.891			
st.dev. (n)		1.6017			
R(calc.)		4.485			
R(Horwitz)		3.138			



Determination of Quinalfos on sample #13233; results in mg/kg

lab	method	value	mark	z(targ)	remarks
1179		0.238		----	
2115		0.306		----	
2129		0.538		----	False positive?
2132	in house	0.07		----	
2139	in house	0.18		----	
2290	in house	<0.5		----	
2295	in house	n.d.		----	
2310	in house	0.07		----	
2354	in house	n.d.		----	
2359	USEPA8081/8141/8270	n.d.		----	
2363	in house	<0.2		----	
2365	GB/T18412	0.12		----	
2370	USEPA8081	0.112		----	
2375	USEPA8081/8141/8270/8321	0.0992		----	
2428	EPA8081	n.d.		----	
2483		----		----	
2492		----		----	
2508		----		----	
2561		----		----	
2588		----		----	
3117		----		----	
3146		<0.8		----	
3172		----		----	
3209	GB/T18412	n.d.		----	
3220	in house	0.49	C	----	First reported 49
3242	in house	n.d.		----	
	normality	OK			
	n	12			
	outliers	0			
	mean (n)	<0.5			
	st.dev. (n)	n.a.			
	R(calc.)	n.a.			
	R(lit)	n.a.			



APPENDIX 2

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

#13232						
lab	Deltamethrin	Esfenvalerate	Fenvalerate	Cyhalothrin	Lambda-cyh.	Remarks
1179		0.037	0.029			
2115			0.137			
2129		0.022	0.035			
2132						
2139						
2290						
2295		0.86				
2310						
2354						
2359						
2363						
2365						
2370						
2375						
2428						
2483						
2492						
2508						
2561						
2588						
3117						
3146						
3172						
3209						
3220				12.5		False positive result?
3242						

#13233						
lab	Cypermethrin	Esfenvalerate	Fenvalerate	Cyhalothrin	Lambda-cyh.	remarks
1179		0.014	0.009			
2115						
2129	0.055	0.009	0.014	0.004	0.004	
2132						
2139						
2290						
2295						
2310						
2354						
2359						
2363						
2365						
2370						
2375						
2428						
2483						
2492						
2508						
2561						
2588						
3117						
3146						
3172						
3209						
3220		50.0				False positive result?
3242						

APPENDIX 3

Details of the methods used by the participants:

Lab	component	Brand name	composition	Batch
1179	--			
2115	--			
2129	Cypermethrin	Inst.of org. Ind. Chem	Mixture of isomers	
	Deltamethrin	Dr. Ehrenstorfer	Mixture of isomers	
	Fenvalerate	Dr. Ehrenstorfer	single	
	Esfenvalerate	Dr. Ehrenstorfer	single	
	Parathion-ethyl	Fluka	single	
	Monocrotophos	Dr. Ehrenstorfer	single	
	Λ -Cyhalothrin	Dr. Ehrenstorfer	single	
	Quinalfos	Dr. Ehrenstorfer	single	
2132	--	Chem service		
2139	Cypermethrin	Accustd	single	Lot 213111289
	Deltamethrin	Accustd	single	Lot 213081351
	Quinalphos	Accustd	single	Lot 211041478-01
2290	Cypermethrin	Chem service	single	N-11545
	Deltamethrin	Chem service	single	N-11579
2295	Cypermethrin	Dr. Ehrenstorfer	single	C11890000
	Deltamethrin	Fluka	single	S2B8279XV
	Esfenvalerate	Fluka	single	S2B8234XV
2310	Cypermethrin	Accustd	single	15908
	Deltamethrin	Accustd	single	13805
	Quinalphos	Dr. Ehrenstorfer	single	10818
2354	Cypermethrin	Chem service	single	1983200
	Deltamethrin	Chem service	single	2023700
2359	Cypermethrin	Chem service	single	1216600
	Deltamethrin	Chem service	single	1046300
2363	Cypermethrin	Dr. Ehrenstorfer	single	90313
	Deltamethrin	Dr. Ehrenstorfer	single	80917
	Fenvalerate	Dr. Ehrenstorfer	single	00308
	Esfenvalerate	Chem service	single	421-32B
	Parathion	Dr. Ehrenstorfer	single	00115
	Monocrotophos	Dr. Ehrenstorfer	single	01203
	Λ -Cyhalothrin	Chem service	single	446-94A
	Quinalfos	Dr. Ehrenstorfer	single	10818
2365	Cypermethrin	Sigma-Aldrich	single	Sze7197x
	Deltamethrin	Dr. Ehrenstorfer	single	89017
	Quinalphos	Dr. Ehrenstorfer	single	01208
2370	Cypermethrin	Chem service	mixture	352-150B
	Deltamethrin	Chem service	mixture	364-25B
	Quinalphos	Fluka	mixture	Szba249xv
2375	--			
2428	Cypermethrin	Dr. Ehrenstorfer	single	20326CY
	Deltamethrin	Dr. Ehrenstorfer	single	20326CY
2483	--			
2492	--	LGC		
2508	--			
2561	--			
2588	Deltamethrin	Pestanal	single	Szbc059xv
3117	Cypermethrin	Dr. Ehrenstorfer	single	C11890000
	Deltamethrin	Dr. Ehrenstorfer	single	XA1212000CY
3146	Cypermethrin	Suplco		1538500V
	Deltamethrin	Fluka		Bcbf2789v
3172	--			
3209	Cypermethrin	Chem service	mixture	1852600
	Deltamethrin	Accu standard	single	213081351
3220	--	CPI international	mixture	
3242	Cypermethrin	Fluka	mixture	Szb7197xv
	Deltamethrin	Fluka	mixture	Sze8297x

APPENDIX 4

Number of participants per country

3 labs in GERMANY
3 labs in HONG KONG
3 labs in INDIA
2 labs in ITALY
1 lab in KOREA
6 labs in P.R. of CHINA
1 lab in PAKISTAN
1 lab in TAIWAN R.O.C.
2 labs in THAILAND
1 lab in THE NETHERLANDS
2 labs in TURKEY
1 lab in UNITED KINGDOM
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
n.a.	= not applicable
n.d.	= not detected
W	= withdrawn on request of the participant
fr.	= first reported

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