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Distribution list:
- Twenty-nine participating laboratories

Contents

Summary

In November 2016 a proficiency test for pesticides in the feed matrices soy acid oil and soybean meal was organised by RIKILT, Wageningen University & Research in accordance with ISO 17043. RIKILT Wageningen University & Research is accredited for the organisation of proficiency tests in the field of contaminants, mycotoxins, plant toxins and veterinary drugs in feed and feed ingredients according to ISO/IEC 17043 (R013). However, the specific matrix-compound used in this proficiency test is not part of the accreditation. The primary goal of this proficiency test was to give participants the opportunity to evaluate or demonstrate their competence for the analysis of pesticides in the feed matrices soy acid oil and soybean meal.

Two materials were prepared and dispatched with cool packs to the participants. The consensus values of the pesticides in each material are given in Table 1 (mg/kg):

Table 1 *Consensus values of the pesticides in the proficiency materials.*

Material A: soy acid oil		Material B: soybean meal	
Compound	**Consensus value mg/kg**	**Compound**	**Consensus value mg/kg**
Anthraquinone	0.072	Azoxystrobin	0.379
Biphenyl	0.144	Boscalid	0.999
Cis-chlordane	0.030	Chlorpyrifos	0.039
Chlorpyrifos	0.239	Cypermethrin	0.070
p,p'-DDE	0.048	Cyproconazole	0.070
Cis-deltamethrin	0.089	Ortho-phenylphenol	0.144
Alpha-endosulfan	0.076	Pirimiphos-methyl	0.224
Endosulfan sulfate	0.134	Tebuconazole	0.168
Pirimiphos-methyl	0.178		

Material A was prepared by spiking a sample of soy acid oil with a solution of pesticides to the required target concentrations, followed by homogenization. Material B was prepared by spiking a sample of slurried soybean meal followed by extensive mixing, freeze-drying and milling of the samples.

Homogeneity assessment showed that both materials were sufficiently homogeneous for proficiency testing. The stability test demonstrated no statistically significant loss of the pesticides in soybean meal during the timescale of the proficiency test. For all the pesticides in soy acid oil, there was an apparent increase in concentration of the samples stored in the refrigerator, except for cis-chlordane. This increase was not accounted for in the calculation of the z-scores. The stability test showed a consequential loss for cis-chlordane in soy acid oil during the storage in the refrigerator. This instability was taken into account in the calculation of the z-scores. The apparent increase and decrease are not likely to be caused by instability given the fact that a similar trend was observed for multiple pesticides, and because of the known persistence of most pesticides. This was further supported by the robust standard deviations obtained from the data of the participant, which was generally good.

Thirty-one participants subscribed for the participation in this proficiency test, of which 29 reported results. One participant submitted the results 13 days after the closing date for reporting, but the results were still taken into account. Two participants were unable to report results.

For calculating of the accuracy z-scores in this test a target standard deviation of 25% was taken as an acceptable deviation for reproducibility conditions. However, the quantification of alpha-endosulfan in material A resulted in a high uncertainty of the consensus value and, therefore, the results of this pesticide were not statistically evaluated.

The results of the proficiency test on pesticides in soy acid oil and soybean meal are summarized in Table 2. Seven participants showed optimal performance by detecting the pesticides with a correct quantification/qualification within the participants' scope and the absence of false positive and false negative results. Ten participants did not analyse the pesticides in material A, of which one laboratory indicated that soy acid oils are not in their scope. Five participants did not report results for the pesticides in material B due to the absence of the compounds from their scope.
For material A 38 false negative results were reported for 8 of the 9 pesticides and 2 false positive results and for material B 4 false negative results were reported for 4 of the 8 pesticides by 1 participant each and 2 participants reported a false positive result.

Table 2 *Summarized performance of laboratories reporting results in the proficiency test on pesticides in the feed matrices soy acid oil and soybean meal.*

Compound	# of participants	FN[1)]	FP[1)]	Used z-score	Correct results (%)
Material A (soy acid oil)					
Anthraquinone	8			z'_a	100
Biphenyl	14	2		z_a	71
Cis-chlordane	18	8		z_{ai}	50
Chlorpyrifos	16	1		z_a	81
p,p'-DDE	18	5		z_a	67
Cis-deltamethrin	15	3		z'_a	67
Alpha-endosulfan	20	6		No stat. evaluation	
Endosulfan sulfate	19	9		z'_a	47
Pirimiphos-methyl	17	4		z_a	76
Imizalil			2		
Material B (soybean meal)					
Azoxystrobin	23			z_a	91
Boscalid	22			z_a	95
Chlorpyrifos	23			z_a	91
Cypermethrin	22	1		z'_a	68
Cyproconazole	22	1		z_a	82
Ortho-phenylphenol	21	1		z'_a	86
Pirimiphos-methyl	24	1		z_a	83
Tebuconazole	23			z_a	96
Cyfluthrin			1		
Carbendazim1			1		

1) FN = false negatives; FP= false positives.

Based on the results of this test it can be concluded that the variation in results for soy acid oil is larger than the variation in the results of soybean meal and that there is a need for improvement of the quantification of pesticides in soy acid oil. The larger variation might be related to the nature of the material. Soy acid oil consists of fat and fatty acids which makes this matrix challenging for pesticide residue analysis.

1 Introduction

Proficiency testing is conducted to provide participants with a powerful tool to evaluate and demonstrate the reliability of the data that are produced by the laboratory. Proficiency testing is an important requirement of the EU Additional Measures Directive 93/99/EEC [1] and is demanded by ISO/IEC 17025:2005 [2].

The preparation of the materials, including the homogeneity and stability testing of the materials, and the evaluation of the quantitative results were carried out under accreditation according to ISO/IEC 17043:2010 [3] accreditation by the Dutch Accreditation Board (R013). However, the specific matrix-compound used in this proficiency test is not part of the accreditation.

There is no harmonised legislation in the EU for pesticides in the matrices soy acid oil and soybean meal. However, maximum levels (ML) for pesticides in soy are regulated in Regulation (EC) No 396/2005 [10] and amendments thereof.

The aim of this proficiency test was to give participants the opportunity to evaluate or demonstrate their competence for the analysis of pesticides in the feed matrices soy acid oil and soybean meal.

2 Material and methods

2.1 Scope of the PT

This proficiency test focused on the pesticides anthraquinone, biphenyl, cis-chlordane, chlorpyrifos, p,p'-DDE, cis-deltamethrin, alpha-endosulfan, endosulfan-sulfate and pirimiphos-methyl in soy acid oil and azoxystrobin, boscalid, chlorpyrifos, cypermethrin, cyproconazole, ortho-phenylphenol, pirimiphos-methyl and tebuconazole in soybean meal. The target concentrations for this test are presented in Table 4. Two matrices were under investigation. Soy acid oil is a vegetable oil extracted from the seeds of soybeans. The second matrix was soybean meal, which is a by-product released during the extraction of soybean oil.

2.2 Participants

Thirty-one participants registered for the participation in the proficiency test and 29 participants reported their results. All of these participants are situated in Europe. Two participants were unable to report results. In case the results were delivered after the deadline, the results were evaluated but no optimal performance was granted. Each participant was asked *a priori*, to indicate which compounds were included in the scope of their method. The participants were asked to report the results through a web application designed for proficiency tests.

2.3 Material preparation

Two spiked materials, material A and material B, were prepared for the proficiency test. Material A was prepared by adding a solution of a pesticide mix in ethyl acetate to 1700 grams of soy acid oil aiming at the levels presented in Table 3. The oil was heated to 37 °C and shaken during the entire process to allow better distribution of the pesticides. For material B, 2 kilograms of soybean meal was first fortified by adding a solution of pesticide mix in methanol aiming at the levels as presented in Table 3. The soybean meal was mixed with six litres of water and homogenized using a concrete mixer according to in-house standard operating procedures [4]. The fortified slurry was immediately freeze-dried, homogenized and stored in the refrigerator until use.

Table 3 *Target concentrations of pesticides in the proficiency materials.*

Material A		Material B	
Compound	**Target concentration (mg/kg)**	**Compound**	**Target concentration (mg/kg)**
anthraquinone	0.10	azoxystrobin	0.35
biphenyl	0.08	boscalid	1
cis-chlordane	0.05	chlorpyrifos	0.05
chlorpyrifos	0.25	cypermethrin	0.1
p,p'-DDE	0.05	cyproconazole	0.07
cis-deltamethrin	0.10	ortho-phenylphenol	0.15
alpha-Endosulfan	0.10	pirimiphos-methyl	0.25
endosulfan-sulfate	0.15	tebuconazole	0.15
pirimiphos-methyl	0.12		

2.4 Material distribution and instructions

Each of the participating participants received a randomly assigned laboratory code, generated by the web application. The sample sets with the corresponding number, consisting of two coded samples (Annex 1) were sent to the participating participants on January 16th 2017. The sample sets were packed in a insulation box with cool packs and were dispatched to the participants immediately by courier. The samples were accompanied by a letter describing the requested analysis (Annex 2) and an acknowledgement of receipt form. By e-mail the participants received instructions on how to use the web application to report the results.

The participants were asked to store the samples in the refrigerator and to analyse the samples according to their routine method. A single analysis result for the pesticides in each sample was requested. The deadline for submitting the quantitative results was March 10th 2017, allowing the participants eight weeks for the analysis.

Results should be reported for pesticides as mg/kg product. Participants were asked to provide information on their analytical method (extraction solvent, clean-up procedure, internal standards used, detection technique, limit of detection, limit of quantification).

2.5 Sample identification

For material A, 25 grams of soy acid oil was weighed into airtight closed polypropylene centrifuge tubes of 50 ml. After freeze-drying and homogenization, material B was divided into sub-portions of 30 gram and stored in polypropylene, airtight closed containers. After preparation of materials A and B the tubes and containers were stored in the refrigerator until use.
The samples for the participants were randomly selected and coded using a web application designed for proficiency tests. The code used was Pesticides/2017/feed/000, in which the three digit number at the end of the code was automatically generated by the RIKILT Laboratory Quality Services web application. One sample set was prepared for each laboratory consisting of one random selected sample of each material A and B. The codes of the samples for each sample set are presented in Annex 1. For homogeneity and stability testing, 44 randomly selected tubes of material A and 44 containers of material B were assigned.

2.6 Homogeneity study

For testing the homogeneity of material A ten containers of material A were analysed in duplicate for the pesticides chlorpyrifos, cis-deltamethrin and pirimiphos-methyl. The homogeneity of the other compounds in material A were not tested, since the homogeneity test of chlorpyrifos, cis-deltamethrin and pirimiphos-methyl was considered adequate to prove sufficient homogeneity of the material since the pesticides added were dissolved in one solution before spiking the matrix, and because the matrix was a liquid during homogenisation. Also ten containers of material B were analysed in duplicate for all the spiked pesticides to determine the homogeneity of the material.

The homogeneity of the materials was tested according to The International Harmonized Protocol for Proficiency Testing of Analytical Laboratories [7] and ISO 13528:2015 [5]. For homogeneity a target standard deviation for proficiency assessment (σ_P) of 25% was used as a fit-for-purpose standard deviation in the feed matrices soy acid oil and soybean meal which is in line with the target RSD used in proficiency tests on pesticides as organised by the EURL. With this procedure the between-sample standard deviation (s_s) and the within-sample standard deviation (s_w) were compared with the standard deviation for proficiency assessment. The method applied for homogeneity testing is considered suitable if $s_w < 0.5*\sigma_P$ and a material is considered adequately homogeneous if $s_s < 0.3*\sigma_P$. The results of the homogeneity study, the grand mean with the corresponding RSD are presented in Table 4 and the statistical evaluation of material A and material B are presented in Annex 3.

The pesticides measured in Material A for the homogeneity study fulfilled the criteria. Concentrations in this specific run were determined against standards in solvent, as opposed to standard in the matrix soy acid oil as used for all other measurements. This resulted in lower concentrations of chlorpyrifos (7 times) and cis-deltamethrin (5 times) than anticipated due to absence of matrix effects. For pirimiphos-methyl the concentration was comparable with the target concentration.

Cypermethrin in material B was the only analyte for which the criteria did not comply. This originated from a high variation in the ten results in duplicate, causing s_s (0.007 mg/kg) exceeding the critical value $0.3\sigma_P$ (0.003 mg/kg) and s_w (0.007 mg/kg) exceeding $0.5\sigma_P$ (0.004 mg/kg). During the measurements of cypermethrin a poor sensitivity of the LC-MS/MS equipment was observed. Despite the deviation of the pesticide cypermethrin, the material B was considered to be homogeneous, since the other seven pesticides fulfilled the homogeneity requirements and were spiked in the same solution.

The pesticides in material A and material B demonstrated to be sufficiently homogeneous for use in the proficiency test.

Table 4 *Concentration of pesticides in material A and material B obtained during homogeneity testing.*

Material code	Material A		Material B		
	Conc. mg/kg	RSD %		Conc. mg/kg	RSD %
chlorpyrifos	0.0367	2.2	azoxystrobin	0.377	6.9
cis-deltamethrin	0.019	5.4	boscalid	0.969	5.1
pirimiphos-methyl	0.101	1.8	chlorpyrifos	0.042	4.9
			cypermethrin	0.034	29.1
			cyproconazole	0.068	3.0
			ortho-phenylphenol	0.128	10.8
			pirimipfos-methyl	0.235	5.0
			tebuconazole	0.157	3.1

2.7 Stability of the materials

On January 18th 2016, the day the materials were distributed to the participants, three randomly selected samples of material A and six randomly selected samples of material B were stored at <-18°C. It is assumed that the pesticides are stable at these storage conditions. Also, three samples of material A and six samples of material B were stored in the refrigerator.

On March 13th 2017, 56 days after distribution of the samples, three samples of materials A and six samples of material B that were stored at <-18°C and in the refrigerator were analysed for pesticides. For each set of test samples, the average of the results and the standard deviation were calculated.

First it is determined whether a consequential instability of the analytes occur [5, 7]. A consequential instability is observed when the average value of an analyte in the samples stored in the refrigerator is more than $0.3\sigma_P$ below the average value of the analyte in the samples stored at <-18°C. If so, the instability has a significant influence on the calculated z-scores. A possible statistically significant instability is determined using a Students t-test [5].

For anthraquinone, biphenyl, chlorpyrifos, p,p'-DDE, cis-deltamethrin, alpha-endosulfan, endosulfan-sulfate and pirimiphos-methyl in material A there was a consequential difference between the samples stored in the refrigerator and the samples stored at <-18°C. The average concentration in the refrigerator was higher than the average concentration of the samples stored at <-18°C. The concentration showed an increase of resp. 20, 53, 17, 20, 50, 9, 20 and 12 %. This increase in

concentration was not incorporated in the calculation of the z-scores. The results of the stability of material A is presented in Annex 4.
For cis-chlordane in material A there was also a consequential difference between the samples stored in the refrigerator and the samples stored at <-18°C. The average concentration in the refrigerator was lower than the average concentration of the samples stored at <-18°C. The concentration showed a decrease of 14 %.
The apparent increase and decrease are not likely to be caused by instability given the fact that a similar trend was observed for multiple pesticides, and because of the known persistence of most pesticides.
For the pesticides in materials B, no consequential nor statistical significant difference were observed among the samples stored at <-18°C and the samples stored in the refrigerator. The compounds in the materials are, therefore, considered stable for the duration of the study. The results of the stability of material B is presented in Annex 4.

2.8 Interpretation of the results

A result was assigned as false negative result if a compound was not detected, taken into account the reported scope of the participant, the consensus value and the reported LOQ of the participant.

*For example: the consensus value of compound A is 0.07 mg/kg and a participants' LOQ= 0.02 mg/kg. Taken into account the 25% standard deviation in this test, the -2z threshold would be at 0.035 mg/kg (0.07-(2*25% of 0.07)). Since the LOQ of this participant is lower than the -2z value this participant should be able to detect the presence. If the LOQ would have been 0.04 mg/kg no false negative result would be assigned.*

Also, when no LOQ values were reported and the compound was reported as not detected (nd), or the compound was not reported but was within the participants' scope, a false negative (FN) result was assigned.

For false positive results it was decided to apply a cut-off level of 0.04 mg/kg for the materials and concentrations below 0.04 mg/kg were not assigned as false positive results.

3 Statistical evaluation

The statistical evaluation was carried out according to the International Harmonized Protocol for the Proficiency Testing of Analytical Laboratories [7], elaborated by ISO, IUPAC and AOAC and ISO 13528:2015 [5] in combination with the insights published by the Analytical Methods Committee [8, 9] regarding robust statistics.

For the evaluation of the quantitative results, the consensus value, the uncertainty of the consensus value, the standard deviation for proficiency assessment and z-scores were calculated.

3.1 Calculation of the consensus value

The consensus value (X) was determined using robust statistics [5, 8, 9]. The advantage of robust statistics is that all values are taken into account: outlying observations are retained, but given less weight. Furthermore, it is not expected to receive normally distributed data in a proficiency test. When using robust statistics, the data do not have to be normally distributed in contrast to conventional outlier elimination methods.

The robust mean of the reported results of all participants, calculated from an iterative process that starts at the median of the reported results using a cut-off value depending on the number of results, was used as the consensus value [5, 8].

3.2 Calculation of the uncertainty of the consensus value

The uncertainty of the consensus value is calculated to determine the influence of this uncertainty on the evaluation of the participants. A high uncertainty of the consensus value will lead to a high uncertainty of the calculated participants z_a-scores. If the uncertainty of the consensus value and thus the uncertainty of the z_a-score is high, the evaluation could indicate unsatisfactory method performance without any cause within the laboratory. In other words, illegitimate conclusions could be drawn regarding the performance of the participating participants from the calculated z_a-scores if the uncertainty of the consensus value is not taken into account.

The uncertainty of the consensus value (the robust mean) is calculated from the estimation of the standard deviation of the consensus value and the number of values used for the calculation of the consensus value [5]:

$$u = 1.25 * \frac{\hat{\sigma}}{\sqrt{n}}$$

where:
u = Uncertainty of the consensus value;
n = Number of values used to calculate the consensus value;
$\hat{\sigma}$ = The estimate of the standard deviation of the consensus value resulting from robust statistics.

According to ISO 13528:2015 [5] the uncertainty of the consensus value (u) is negligible and therefore does not have to be included in the statistical evaluation if:

$u \leq 0.3\sigma_P$

where:
u = The uncertainty of the consensus value;
σ_P = Standard deviation for proficiency assessment (§3.3).

In case the uncertainty of the consensus value does not comply with this criterion, the uncertainty of the consensus value should be taken into account when evaluating the performance of the participants regarding the accuracy (§3.4). In case the uncertainty is > $0.7\sigma_P$ the calculated z-scores should not be used for evaluation of participants performance and are presented for information only.

3.3 Calculation of the standard deviation for proficiency assessment (σ_P)

A target standard deviation for proficiency assessment (σ_P) of 25% was used as a fit-for-purpose standard deviation which is in line with the target RSD used in proficiency tests on pesticides as organised by the EURL.

$\sigma_P = 0.25c$

where:
σ_P = Expected standard deviation in proficiency tests for animal feed;
c = Concentration of the analyte (mg/kg).

3.4 Performance characteristics with regard to the accuracy

For illustrating the performance of the participating participants with regard to the accuracy a z_a-score is calculated. For the evaluation of the performance of the participants, ISO 13528:2015 [5] is applied. According to these guidelines z_a-scores are classified as presented in Table 5.

Table 5 *Classification of z_a-scores.*

$\|z_a\| \leq 2$	Satisfactory
$2 < \|z_a\| < 3$	Questionable
$\|z_a\| \geq 3$	Unsatisfactory

If the calculated uncertainty of the consensus value complies with the criterion mentioned in §3.2, the uncertainty is negligible. In this case the accuracy z-score is calculated from:

$$z_a = \frac{\overline{x} - X}{\sigma_P}$$ Equation I

where:
z_a = Accuracy z-score;
$\overline{x}$ = The average result of the laboratory;
X = Consensus value;
σ_P = Standard deviation for proficiency assessment.

However, if the uncertainty of the consensus value does not comply with the criterion mentioned in §3.2, it could influence the evaluation of the participants. Although, according to ISO 13528 in this case no z-scores can be calculated, we feel that evaluation of the participating participants is of main importance justifying the participating participants' effort. Therefore in this case, the uncertainty is taken into account by calculating the accuracy z-score [5]:

$$z'_a = \frac{\bar{x} - X}{\sqrt{\sigma_P^2 + u^2}}$$ Equation II

where:
z'_a = Accuracy z-score taking into account the uncertainty of the consensus value;
$\bar{x}$ = The average result of the laboratory;
X = Consensus value;
σ_P = Standard deviation for proficiency assessment;
u = Uncertainty of the consensus value.

A consequential instability of the proficiency materials can influence the evaluation of the laboratory performance. Therefore, in that case the consequential instability is taken into account when calculating z-scores. Because instability only regards one side of the confidence interval (a decrease of the concentration) this correction only applies to the lower 2s limit and results in an asymmetrical confidence interval.

In the case of a consequential instability the accuracy z-score for the participants that reported an amount below the consensus value is corrected for this instability by:

$$z_{ai} = \frac{\bar{x} - X}{\sqrt{\sigma_P^2 + \Delta^2}}$$ Equation III

where:
z_{ai} = Accuracy z-score taking into account the instability of the consensus value;
$\bar{x}$ = The average result of the laboratory;
X = Consensus value;
σ_P = Standard deviation for proficiency assessment;
Δ = Difference between average concentration of compound stored at <-18 °C, < 4 °C and average concentration at room temperature.

In some cases the uncertainty of the consensus value does not comply with the criterion in §3.2 and a consequential instability is observed. In this case the z'_a-score for the participants that reported an amount below the consensus value is corrected for this instability by:

$$z'_{ai} = \frac{\bar{x} - X}{\sqrt{\sigma_P^2 + \Delta^2 + u^2}}$$ Equation IV

where:
z'_{ai} = Accuracy z-score taking into account the uncertainty and instability of the consensus value;
$\bar{x}$ = The average result of the laboratory;
X = Consensus value;
σ_P = Standard deviation for proficiency assessment;
Δ = Difference between average concentration of compound stored at <-18 °C, < 4 °C and average concentration at room temperature;
u = Uncertainty of the consensus value.

4 Methods and Results

4.1 Participants

Thirty-one participants registered for the proficiency test. All samples were received in good order and twenty-eight participants submitted the results in time, one participant reported too late and two participants were unable to report results. Participant PT498 was the only laboratory which indicated not to perform oil analysis. The performance of individual participants is summarized in Annex 9. Laboratory PT484 reported an unsatisfactory result (z'_a-score 47.95) for cis-deltamethrin in material A and laboratory PT500 reported an unsatisfactory result (z_a-score 11.36) for cyproconazole in material B. Possibly a reporting error was made respectively for cis-deltamethrin (reporting 1.25 mg/kg instead of 0.125 mg/kg and cyproconazole (reporting 0.27 mg/kg instead of 0.027 mg/kg).

4.2 Methods of analysis applied by participants

An overview of the information provided by the participants regarding the methods applied in this proficiency test is presented in Annex 5. The samples were analysed using various extraction methods, purification steps and detection techniques.
Reported limits of detection (LODs) and limits of quantification (LOQs) for the pesticides are presented in Table 6.

Table 6 *Overview of reported LOD and LOQ reported by the participants.*

Material A			Material B		
Compound	**LOD (mg/kg)**	**LOQ (mg/kg)**	**Compound**	**LOD (mg/kg)**	**LOQ (mg/kg)**
Anthraquinone	0.0018 – 0.01	0.01 – 0.05	Azoxystrobin	0.0007 – 0.01	0.00737 – 0.05
Biphenyl	0.003 – 0.01	0.01 -0.02	Boscalid	0.0009 – 0.01	0.00661 – 0.05
Cis-chlordane	0.0001 – 0.01	0.005 – 0.05	Chlorpyrifos	0.0009 – 0.01	0.004 – 0.02
Chlorpyrifos	0.0009 – 0.01	0.004 – 0.02	Cypermethrin	0.0015 – 0.01	0.005 – 0.02
p,p'-DDE	0.0001 – 0.01	0.00427 – 0.02	Cyproconazole	0.00193 – 0.03	0.0064 – 0.03
Deltamethrin	0.0025 – 0.01	0.00834 – 0.02	Phenylphenol, ortho	0.003 – 0.02	0.01 – 0.02
Alpha-endosulfan	0.0001 – 0.01	0.00457 – 0.05	Pirimiphos-methyl	0.0007 – 0.01	0.004 – 0.05
Endosulfan sulfate	0.0001 – 0.01	0.005 – 0.05	Tebuconazole	0.0019 – 0.01	0.0063 – 0.05
Pirimiphos-methyl	0.0007 – 0.01	0.004 – 0.05			

4.3 Performance participants material A

Participants PT481, PT483, PT 485, PT487, PT489, PT490, PT498, PT499, PT506 and PT509 did not analyse material A. Participants PT484 and PT501 reported results above the cut-off level of 0.04 mg/kg, by reporting the presence of imazalil at 0.149 mg/kg and 0.184 mg/kg, which are considered false positive results. Results for material A are presented in Annex 6.

4.3.1 Anthraquinone

Eight participants reported quantitative results for anthraquinone. Twenty participants did not analyse anthraquinone of which 16 reported anthraquinone as not tested (although some of these participants reported the matrix-pesticide combination in their scope) and 4 participants (PT484, PT485, PT489, PT505) did not report quantitative results for anthraquinone due to the absence of the compound in their scope.

The lowest concentration reported was 0.04 mg/kg and the highest was 0.104 mg/kg. The consensus value was 0.072 mg/kg with a robust standard deviation of 0.017 mg/kg (resulting in an RSD_R of 24%) expressing the reproducibility within this proficiency test. The robust standard deviation of 0.017 mg/kg is comparable to the target standard deviation σ_P of 0.018 mg/kg (25% of the consensus value) suggested in §3.3 for feed material.

The uncertainty of the consensus value was 0.008 mg/kg. Since this value exceeds $0.3\sigma_P$ (0.005 mg/kg, §3.2), the uncertainty is taken into account in the evaluation, and therefore z'_a-scores using equation II, were calculated. With respect to the accuracy all results were satisfactory.

4.3.2 Biphenyl

Twelve participants reported quantitative results for biphenyl in material A. Participants PT484 and PT489 did not report quantitative results for biphenyl, even though they included biphenyl in their scope and therefore a FN result was assigned. Fourteen participants did not analyse biphenyl of which 12 reported biphenyl as not tested (although some of these participants reported the matrix - pesticide combination in their scope) and 2 participants (PT485, PT505) did not report quantitative results for biphenyl due to the absence of the compound in their scope.

The lowest concentration reported was 0.06 mg/kg and the highest was 0.325 mg/kg. The consensus value was 0.144 mg/kg with a robust standard deviation of 0.019 mg/kg (resulting in an RSD_R of 13.5%) expressing the reproducibility within this proficiency test. The robust standard deviation of 0.019 mg/kg is almost 2 times lower than the target standard deviation σ_P of 0.036 mg/kg.

The uncertainty of the consensus value was 0.007 mg/kg. Since this value does not exceed $0.3\sigma_P$ (0.011 mg/kg, §3.2), the uncertainty is not taken into account in the evaluation, and therefore z_a-scores using equation I (§3.4), were calculated. With respect to the accuracy, laboratory PT508 reported a questionable result and laboratory PT491 produced an unsatisfactory result.

4.3.3 Cis-chlordane

Nine participants reported quantitative results for cis-chlordane in material A. Participants PT485 and PT489 did not report quantitative results for cis-chlordane, even though they included cis-chlordane in their scope and therefore a FN result was assigned. PT494, PT501, PT503, PT504, PT508 and PT511 failed to detect the presence of cis-chlordane and reported also a false negative result.
PT491 did not report a quantitative result due to the absence of this compound in their scope. The laboratory reported not detected instead of not tested. Laboratory PT505 reported a correct qualitative result (<0.050 mg/kg) because the consensus value was 0.030 mg/kg and this value was higher than the -2z value of 0.015 mg/kg. Nine participants did not analyse cis-chlordane of which 8 reported cis-chlordane as not tested (although some of these participants reported the matrix - pesticide combination in their scope) and PT484 did not report an quantitative result due to the absence of the compound in their scope.

The lowest concentration reported was 0.024 mg/kg and the highest was 0.053 mg/kg. The consensus value was 0.030 mg/kg with a robust standard deviation of 0.003 mg/kg (resulting in an RSD_R of 11.5%) expressing the reproducibility within this proficiency test. The robust standard deviation of 0.003 mg/kg is almost 2 times lower than the target standard deviation σ_P of 0.007 mg/kg.

The uncertainty of the consensus value was 0.001 mg/kg. Since this value does not exceed $0.3\sigma_P$ (0.002 mg/kg, §3.2), the uncertainty is not taken into account in the evaluation.

A consequential instability during storage in the refrigerator was observed (14% decrease) and thus the instability was taken into account by calculating z_{ai}-score (§3.2, equation III) for labs that reported a value below the consensus value. With respect to the accuracy one result was unsatisfactory (PT493). When no instability was observed this result would remain the same.

4.3.4 Chlorpyrifos

Fifteen participants reported quantitative results for chlorpyrifos in material A. Participant PT489 did not report a quantitative result for chlorpyrifos, even though they included chlorpyrifos in their scope and therefore a FN result was assigned. Twelve participants did not analyse chlorpyrifos of which 10 reported chlorpyrifos as not tested (although some of these participants reported the matrix - pesticide combination in their scope) and 2 participants (PT485 and PT505) did not report quantitative results due to the absence of the compound in their scope.

The lowest concentration reported was 0.035 mg/kg and the highest was 0.431 mg/kg. The consensus value was 0.239 mg/kg with a robust standard deviation of 0.030 mg/kg (resulting in an RSD_R of 12.4%) expressing the reproducibility within this proficiency test. The robust standard deviation of 0.030 mg/kg is 2 times lower than the target standard deviation σ_P of 0.060 mg/kg.

The uncertainty of the consensus value was 0.010 mg/kg. Since this value does not exceed $0.3\sigma_P$ (0.018 mg/kg, §3.2), the uncertainty is not taken into account in the evaluation, and therefore z_a-scores using equation I (§3.4), were calculated. With respect to the accuracy, laboratory PT484 and laboratory PT493 produced an unsatisfactory result.

4.3.5 p,p'-DDE

Twelve participants reported quantitative results for p,p'-DDE in material A. Laboratory PT505 reported a correct qualitative result (<0.050 mg/kg) because the consensus value was 0.048 mg/kg and this value was higher than the -2z value of 0.024 mg/kg. Participants PT485 and PT489 did not report a quantitative result for p,p'-DDE, even though they included p,p'-DDE in their scope and therefore a FN result was assigned. Participants PT494, PT501 and PT508 failed to detect the presence of p,p'-DDE and reported also a false negative result. PT491 did not report a quantitative result due to the absence of this compound in their scope. The laboratory reported not detected instead of not tested. Nine participants did not analyse p,p'-DDE of which 8 reported p,p'-DDE as not tested (although some of these participants reported the matrix - pesticide combination in their scope) and PT484 did not report a quantitative result due to the absence of the compound in their scope.

The lowest concentration reported was 0.011 mg/kg and the highest was 0.060 mg/kg. The consensus value was 0.048 mg/kg with a robust standard deviation of 0.010 mg/kg (resulting in an RSD_R of 20.4%) expressing the reproducibility within this proficiency test. The robust standard deviation of 0.010 mg/kg is comparable to the target standard deviation σ_P of 0.012 mg/kg.

The uncertainty of the consensus value was 0.0036 mg/kg. Since this value does not exceed $0.3\sigma_P$ (0.004 mg/kg, §3.2), the uncertainty is not taken into account in the evaluation, and therefore z_a-scores using equation I (§3.4), were calculated. With respect to the accuracy, laboratory PT500 reported an unsatisfactory result.

4.3.6 Cis-deltamethrin

Twelve participants reported quantitative results for cis-deltamethrin in material A. Participant PT489 did not report a quantitative result for deltamethrin, even though they included cis-deltamethrin in their scope and therefore a FN result was assigned. Participants PT501 and PT504 failed to detect the presence of cis-deltamethrin and reported a false negative result. Thirteen participants did not analyse cis-deltamethrin of which 11 reported cis-deltamethrin as not tested (although some of these participants reported the matrix - pesticide combination in their scope) and 2 participants (PT485 and PT505) did not report quantitative results due to the absence of the compound in their scope.

The lowest concentration reported was 0.022 mg/kg and the highest was 1.25 mg/kg. The consensus value was 0.089 mg/kg with a robust standard deviation of 0.026 mg/kg (resulting in an RSD_R of 29.3%) expressing the reproducibility within this proficiency test. The robust standard deviation of 0.026 mg/kg is 1.2 times higher than the target standard deviation σ_P of 0.022 mg/kg.

The uncertainty of the consensus value was 0.009 mg/kg. Since this value exceeds $0.3\sigma_P$ (0.007 mg/kg, §3.2), the uncertainty is taken into account in the evaluation, and therefore z'_a-scores using equation II (§3.4), were calculated. With respect to the accuracy, laboratory PT484 and PT500 reported an unsatisfactory result.

4.3.7 Alpha-endosulfan

Thirteen participants reported quantitative results for alpha-endosulfan in material A. Participants PT484, PT485 and PT489 did not report a quantitative result for alpha-endosulfan, even though they included alpha-endosulfan in their scope and therefore a FN result was assigned. Participants PT494, PT501 and PT504 failed to detect the presence of alpha-endosulfan and reported also a false negative result. Participant PT486 reported a correct qualitative result (nd) because the consensus value was 0.076 mg/kg and the reported LOQ 0.05 mg/kg was higher than the -2z value of 0.028 mg/kg. Eight participants reported alpha-endosulfan as not tested (although some of these participants reported the matrix - pesticide combination in their scope).

The lowest concentration reported was 0.02 mg/kg and the highest was 0.123 mg/kg. The consensus value was 0.076 mg/kg with a robust standard deviation of 0.041 mg/kg (resulting in an RSD_R of 54.6%) expressing the reproducibility within this proficiency test. The robust standard deviation of 0.041 mg/kg is 2 times higher than the target standard deviation σ_P of 0.019 mg/kg.

The uncertainty of the consensus value was 0.014 mg/kg. Since this value exceeds $0.7\sigma_P$ (0.013 mg/kg, §3.2), no statistical evaluation is appropriate.

4.3.8 Endosulfan sulfate

Ten participants reported quantitative results for endosulfan sulfate in material A. Participants PT484, PT485, PT489 and PT510 did not report a quantitative result for endosulfan sulfate, even though they included endosulfan-sulfate in their scope and therefore a FN result was assigned. Participants PT479, PT480, PT486, PT488 and PT501 failed to detect the presence of endosulfan sulfate and reported also a false negative result. PT491 did not report a quantitative result due to the absence of this compound in their scope. The participant reported not detected instead of not tested. Eight participants did not analysed endosulfan-sulfate of which 7 participants reported endosulfan sulfate as not tested (although some of these participants reported the matrix - pesticide combination in their scope) and participant PT505 did not report an quantitative result due to the absence of the compound in their scope.

The lowest concentration reported was 0.101 mg/kg and the highest was 0.264 mg/kg. The consensus value was 0.134 mg/kg with a robust standard deviation of 0.028 mg/kg (resulting in an RSD_R of 21.1%) expressing the reproducibility within this proficiency test. The robust standard deviation of 0.028 mg/kg is 1.2 times lower than the target standard deviation σ_P of 0.034 mg/kg.

The uncertainty of the consensus value was 0.011 mg/kg. Since this value exceeds $0.3\sigma_P$ (0.010 mg/kg, §3.2), the uncertainty is taken into account in the evaluation, and therefore z'_a-scores using equation II (§3.4), were calculated. With respect to the accuracy, laboratory PT511 reported an unsatisfactory result.

4.3.9 Pirimiphos-methyl

Thirteen participants reported quantitative results for pirimiphos-methyl in material A. Participants PT484 and PT489 did not report a quantitative result for pirimiphos-methyl, even though they included alpha-endosulfan in their scope and therefore a FN result was assigned. Participants PT479 and PT486 failed to detect the presence of pirimiphos-methyl and reported also a false negative result. Eleven participants did not analyse pirimiphos of which 9 participants reported pirimiphos-methyl as not tested (although some of these participants reported the matrix - pesticide combination in their scope) and 2 participants (PT485 and 505) did not report quantitative results due to the absence of the compound in their scope.

The lowest concentration reported was 0.108 mg/kg and the highest was 0.226 mg/kg. The consensus value was 0.178 mg/kg with a robust standard deviation of 0.038 mg/kg (resulting in an RSD_R of 21%) expressing the reproducibility within this proficiency test. The robust standard deviation of 0.038 mg/kg is 1.2 times lower than the target standard deviation σ_p of 0.045 mg/kg.

The uncertainty of the consensus value was 0.013 mg/kg. Since this value does not exceed $0.3\sigma_p$ (0.0134 mg/kg, §3.2), the uncertainty is not taken into account in the evaluation, and therefore z_a-scores using equation I (§3.4), were calculated. With respect to the accuracy all quantitative results were satisfactory.

4.4 Performance participants material B

Laboratory PT485, PT490, PT492, PT497 and PT505 did not report quantitative results for the pesticides due to the absence of the added pesticides from their scope. Two FP results were reported in material B. Laboratory PT481 reported the presence of cyfluthrin as 0.0839 mg/kg and laboratory PT500 reported the presence of carbendazim as 0.087 mg/kg. Results for material B are presented in Annex 7.

4.4.1 Azoxystrobin

Twenty-three participants reported quantitative results for azoxystrobin in material B. Seven participants did not analyse azoxystrobin of which 6 participants reported azoxystrobin as not tested (although some of these participants reported the matrix - pesticide combination in their scope) and laboratory PT505 did not report an quantitative result due to the absence of the compound in their scope.

The lowest concentration reported was 0.026 mg/kg and the highest was 0.489 mg/kg. The consensus value was 0.379 mg/kg with a robust standard deviation of 0.065 mg/kg (resulting in an RSD_R of 17.1%) expressing the reproducibility within this proficiency test. The robust standard deviation of 0.065 mg/kg is 1.5 times lower than the target standard deviation σ_P of 0.095 mg/kg.

The uncertainty of the consensus value was 0.017 mg/kg. Since this value does not exceed $0.3\sigma_P$ (0.028 mg/kg, §3.2), the uncertainty is not taken into account in the evaluation.

No consequential instability was observed for azoxystrobin during the storage period of 56 days. Therefore, z_a-scores using equation I (§3.4), were calculated. With respect to the accuracy, laboratory PT487 reported a questionable result and laboratory PT508 an unsatisfactory result.

4.4.2 Boscalid

Twenty-two participants reported quantitative results for boscalid in material B. Seven participants did not analyse boscalid of which 6 participants reported boscalid as not tested (although some of these participants reported the matrix - pesticide combination in their scope) and participant PT505 did not report quantitative results for boscalid due to the absence of the compound in their scope.

The lowest concentration reported was 0.136 mg/kg and the highest was 1.38 mg/kg. The consensus value was 0.999 mg/kg with a robust standard deviation of 0.262 mg/kg (resulting in an RSD_R of 26.2%) expressing the reproducibility within this proficiency test. The robust standard deviation of 0.262 mg/kg is comparable to the target standard deviation σ_P of 0.250 mg/kg.

The uncertainty of the consensus value was 0.070 mg/kg. Since this value does not exceed $0.3\sigma_P$ (0.075 mg/kg, §3.2), the uncertainty is not taken into account in the evaluation.

No consequential instability was observed for boscalid during the storage period of 56 days. Therefore, z_a-scores using equation I (§3.4), were calculated. With respect to the accuracy, laboratory PT508 reported an unsatisfactory result.

4.4.3 Chlorpyrifos

Twenty-two participants reported quantitative results for chlorpyriphos in material B. Laboratory PT506 reported a correct qualitative result (nd) because the consensus value was 0.039 mg/kg and their LOQ of 0.02 mg/kg was the same as the -2z line of 0.020 mg/kg. Six participants did not analyse chlorpyrifos of which 5 participants reported chlorpyrifos as not tested (although some of these participants reported the matrix - pesticide combination in their scope) and participant PT505 did not report quantitative results due to the absence of the compound in their scope.

The lowest concentration reported was 0.012 mg/kg and the highest was 0.054 mg/kg. The consensus value was 0.039 mg/kg with a robust standard deviation of 0.010 mg/kg (resulting in an RSD_R of 26.4%) expressing the reproducibility within this proficiency test. The robust standard deviation of 0.010 mg/kg is the same as the target standard deviation σ_P of 0.01 mg/kg.

The uncertainty of the consensus value was 0.0028 mg/kg. Since this value does not exceed $0.3\sigma_P$ (0.0029 mg/kg, §3.2), the uncertainty is not taken into account in the evaluation.

No consequential instability was observed for chlorpyriphos during the storage period of 56 days. Therefore, z_a-scores using equation I (§3.4), were calculated. With respect to the accuracy, laboratory PT504 and PT508 reported a questionable result.

4.4.4 Cypermethrin

Twenty-one participants reported quantitative results for cypermethrin in material B. Laboratory PT498 failed to detect the presence of cypermethrin and reported a FN result. Seven participants did not analyse cypermethrin of which 6 participants reported cypermethrin as not tested (although some of these participants reported the matrix - pesticide combination in their scope) and participant PT505 did not report quantitative results due to the absence of the compound in their scope.

The lowest concentration reported was 0.012 mg/kg and the highest was 0.135 mg/kg. The consensus value was 0.070 mg/kg with a robust standard deviation of 0.030 mg/kg (resulting in an RSD_R of 42.6%) expressing the reproducibility within this proficiency test. The robust standard deviation of 0.030 mg/kg is almost 2 times higher than the target standard deviation σ_P of 0.017 mg/kg.

The uncertainty of the consensus value was 0.008 mg/kg. Since this value exceeds $0.3\sigma_P$ (0.005 mg/kg, §3.2), the uncertainty is taken into account in the evaluation.

No consequential instability was observed for cypermethrin during the storage period of 56 days. Therefore, z'_a-scores using equation VI (§3.4), were calculated. With respect to the accuracy, three results were questionable (PT 481, PT484, PT487) and three results were unsatisfactory (PT491, PT493, PT508).

4.4.5 Cyproconazole

Twenty-one participants reported quantitative results for cyproconaole in material B. Laboratory PT508 failed to detect the presence of cyproconazole and reported a FN result. Seven participants did not analyse cyproconazole of which 6 participants reported cyproconazole as not tested (although some of these participants reported the matrix - pesticide combination in their scope) and participant PT505 did not report quantitative results due to the absence of the compound in their scope.

The lowest concentration reported was 0.022 mg/kg and the highest was 0.27 mg/kg. The consensus value was 0.070 mg/kg with a robust standard deviation of 0.013 mg/kg (resulting in an RSD_R of 18.5%) expressing the reproducibility within this proficiency test. The robust standard deviation of 0.013 mg/kg is comparable to the target standard deviation σ_P of 0.018 mg/kg.

The uncertainty of the consensus value was 0.004 mg/kg. Since this value does not exceed $0.3\sigma_p$ (0.005 mg/kg, §3.2), the uncertainty is not taken into account in the evaluation.

No consequential instability was observed for cyproconazole during the storage period of 56 days. Therefore, z_a-scores using equation I (§3.4), were calculated. With respect to the accuracy, laboratory PT487 and PT506 reported a questionable result and laboratory PT500 reported an unsatisfactory result.

4.4.6 Ortho-phenylphenol

Twenty participants reported quantitative results for ortho-phenylphenol in material B. Laboratory PT504 failed to detect the presence of ortho-phenylphenol and reported a FN result. Seven participants reported ortho-phenylphenol as not tested and participant PT505 did not report an quantitative result due to the absence of the compound in their scope.

The lowest concentration reported was 0.017 mg/kg and the highest was 0.255 mg/kg. The consensus value was 0.144 mg/kg with a robust standard deviation of 0.043 mg/kg (resulting in an RSD_R of 29.8%) expressing the reproducibility within this proficiency test. The robust standard deviation of 0.043 mg/kg is 1.2 times higher than the target standard deviation σ_P of 0.036 mg/kg.

The uncertainty of the consensus value was 0.012 mg/kg. Since this value exceeds $0.3\sigma_P$ (0.011 mg/kg, §3.2), the uncertainty is taken into account in the evaluation.

No consequential instability was observed for ortho-phenylphenol during the storage period of 56 days. Therefore, z'_a-scores using equation II (§3.4), were calculated. With respect to the accuracy one result was questionable (PT484) and one result was unsatisfactory (PT508).

4.4.7 Pirimiphos-methyl

Twenty-three participants reported quantitative results for pirimiphos-methyl in material B. Participant PT484 did not report a quantitative result for pirimiphos-methyl, but this compound was within the participants' scope, therefore a FN result was assigned. Four participants reported pirimiphos-methyl as not tested (although some of these participants reported the matrix - pesticide combination in their scope) and participant PT505 did not report an quantitative result due to the absence of the compound in their scope.

The lowest concentration reported was 0.047 mg/kg and the highest was 0.349 mg/kg. The consensus value was 0.224 mg/kg with a robust standard deviation of 0.061 mg/kg (resulting in an RSD_R of 27%) expressing the reproducibility within this proficiency test. The robust standard deviation of 0.061 mg/kg is comparable to the target standard deviation σ_P of 0.056 mg/kg.

The uncertainty of the consensus value was 0.016 mg/kg. Since this value does not exceed $0.3\sigma_P$ (0.017 mg/kg, §3.2), the uncertainty is not taken into account in the evaluation.

No consequential instability was observed for pirimiphos-methyl during the storage period of 56 days. Therefore, z_a-scores using equation I (§3.4), were calculated. With respect to the accuracy one result was questionable (PT481) and two result were unsatisfactory (PT504, PT508).

4.4.8 Tebuconazole

Twenty-three participants reported quantitative results for tebuconazole in material B. Six participants reported tebuconazole as not tested and participant PT505 did not report an quantitative result due to the absence of the compound in their scope.

The lowest concentration reported was 0.021 mg/kg and the highest was 0.23 mg/kg. The consensus value was 0.168 mg/kg with a robust standard deviation of 0.038 mg/kg (resulting in an RSD_R of 22.4%) expressing the reproducibility within this proficiency test. The robust standard deviation of 0.038 mg/kg is comparable to the target standard deviation σ_P of 0.042 mg/kg.

The uncertainty of the consensus value was 0.010 mg/kg. Since this value does not exceed $0.3\sigma_p$ (0.013 mg/kg, §3.2), the uncertainty is not taken into account in the evaluation.

No consequential instability was observed for tebuconazole during the storage period of 56 days. Therefore, z_a-scores using equation I (§3.4), were calculated. With respect to the accuracy one result was unsatisfactory (PT508).

4.5 False positive and false negative results

In this PT, 4 FP and 42 FN results were reported. An overview of the FP and FN results is shown in Annex 8 and Table 7.

In material A (traces of) 2,4D, bromuconazole, cyproconazole, beta-endosulfan, haloxyfop, imazalil, metalaxyl, permethrin, ortho-phenylphenol, tebuconazole, tetraconazole and thiophanate-methyl (0.011 mg/kg to 0.82 mg/kg were detected by several participants. In material B (traces of) 2,4D, acetamiprid, biphenyl, carbendazim, cyfluthrin, p,p-DDD, alpha-endosulfan, fluazifop, haloxyfop, heptachlor, imidacloprid and tricyclazole (0.005 mg/kg to 0.13 mg/kg) were detected.

Table 7 *False positive and false negative results.*

Compound	Material A	Compound	Material B
biphenyl	2 FN	cypermethrin	1 FN
cis-chordane	8 FN	cyproconazole	1 FN
chlorpyrifos	1 FN	ortho-phenylphenol	1 FN
p,p'-DDE	5 FN	pirimiphos-methyl	1 FN
cis-deltamethrin	3 FN		
alpha-endosulfan	6 FN		
endosulfan-sulfate	9 FN		
pirimiphos-methyl	4 FN		
Imizalil	2 FP		
Cyfluthrin			1 FP
Carbendazim			1 FP

FN = false negatives; FP= false positives

5 Discussion and conclusions

Thirty-one participants subscribed for the proficiency test on pesticides in the feed matrices soy acid oil and soybean and twenty-nine reported results. Twenty-eight participants submitted the results in time, PT485 reported too late but the results were still taken into account and PT482 and PT507 were unable to report results. Each participant was asked to indicate *a priori* which compounds were included in their scope. This allowed the evaluation of the results which regard to the participants' scope.

Two materials were sent to the participants. The pesticides were homogeneously distributed in the materials. An overview of each participant's performance is shown in Annex 9 and a summary of the results is presented in Table 8.

Table 8 *Summarized performance of participants reporting results.*

Compound	# of participants.	quant. result	qual. result	FN[1)]	q z-score	u z-score	used z-score	correct results (%)
			Material A					
anthraquinone	8	8					z'_a	100
biphenyl	14	12		2	1	1	z_a	71
cis-chlordane	18	9	1	8		1	z_{ai}	50
chlorpyrifos	16	15		1		2	z_a	81
p,p'-DDE	18	12	1	5		1	z_a	67
cis-deltamethrin	15	12		3	1	1	z'_a	67
alpha-endosulfan	20	13	1	6			No stat. eval.	
endosulfan sulfate	19	10		9		1	z'_a	47
Pirimiphos-methyl	17	13		4			z_a	76
			Material B					
Azoxystrobin	23	23			1	1	z_a	91
Boscalid	22	22				1	z_a	95
Chlorpyrifos	23	22	1		2		z_a	91
Cypermethrin	22	21		1	3	3	z'_a	68
Cyproconazole	22	21		1	2	1	z_a	82
Ortho-phenylphenol	21	20		1	1	1	z'_a	86
Pirimiphos-methyl	24	23		1	1	2	z_a	83
Tebuconazole	23	23				1	z_a	96

FN false negatives
q questionable z-score
u unsatisfactory z-score
quant. quantitative result
qual. qualitative result

Seven participants showed optimal performance by detecting the pesticides with a correct quantification/qualification within the participants' scope, the absence of false positive and false negative results and reporting within the deadline. Twenty-two participants reported FN, FP, questionable or unsatisfactory z-scores. A total of 4 FP and 42 FN results were reported. Ten participants did not analyse the pesticides in material A and five participants did not report quantitative or qualitative results for the pesticides in material B due to the absence of the compounds from their scope.

Based on the results of this proficiency test it was concluded that:

- The results show that the variation in results for soy acid oil is larger than the variation in the results of soybean meal. The larger variation might be related to the nature of the material. Soy acid oil consists of fat and fatty acids which makes this matrix challenging for pesticide residue analysis.
- There is a need for improvement of quantification of pesticides in soy acid oil especially for cis-chlordane, alpha-endosulfan and endosulfan sulfate. For cis-chlordane and endosulfan sulfate resp. 50 and 47% of the results were satisfactory. The results of alpha-endosulfan showed a large variation (high uncertainty, RSD_R. of 54.6%), no statistical evaluation could be applied.
- The quantification of cypermethrin in soybean meal needs additional attention, since the variation of the results was large. The relative standard deviation of the reproducibility of cypermethrin was 43%.

References

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8 Analytical Methods Committee. 1989. Robust statistics - How not to reject outliers Part 1. Basic concepts. Analyst 114:1693-1697.

9 Analytical Methods Committee. 1989. Robust statistics - How not to reject outliers Part 2. Inter-laboratory trials. Analyst. 114:1699-1702.

10 Regulation (EC) No 396/2005 of 23 February 2005 on maximum residue levels of pesticides in or on food and feed of plant and animal origin and amending Council 91/414/EEC.

Annex 1 Codification of the samples

Participants code	Material A*	Material B*
PT479	130	359
PT480	843	165
PT481	622	518
PT483	110	636
PT484	303	169
PT485	337	344
PT486	690	515
PT487	929	224
PT488	561	313
PT489	205	177
PT490	733	916
PT491	641	973
PT492	137	352
PT493	962	713
PT494	708	479
PT497	892	426
PT498		468
PT499	552	959
PT500	837	902
PT501	269	724
PT502	939	104
PT503	745	148
PT504	583	987
PT505	703	321
PT506	906	716
PT508	281	514
PT509	192	761
PT510	143	431
PT511	739	271

* All sample codes start with Pesticides/2017/feed/

Annex 2 Instruction letter

WAGENINGEN
UNIVERSITY & RESEARCH

P.O. Box 230 | 6700 AE WAGENINGEN | The Netherlands

RIKILT

DATE
January 12, 2017

SUBJECT
Invitation proficiency test pesticides in acid oil and soyabean meal

OUR REFERENCE
1701719/RIK

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Dear participant,

Thank you very much for your interest in the proficiency study for the analysis of pesticides in the feed matrices acid oil and soyabean meal. Hereby I send you a parcel containing two randomly coded samples. Each sample consists of approximately 25 grams of test material. The samples may contain one or more of the analytes indicated below (in alphabetical order):

pesticides included in the scope of the laboratory (*)			
2,4-D	DDT- o,p'	Fludioxonil	Pirimicarb
Acetamiprid	DDT- p,p'	Fluopyram	Pirimicarb-desmethyl
Aldrin	Deltamethrin-cis	Fluquinconazole	Pirimiphos-methyl
Anthraquinone	Diazinon	Fluroxypyr	Prochloraz
Azinphos-methyl	Dichlorvos	Fluxapyroxad	Procymidone
Azoxystrobin	Dieldrin	Haloxyfop	Profenofos
Bifenthrin	Difenoconazole	HCB	Propamocarb
Biphenyl	Dimethoate	HCH alpha	Propiconazole
Boscalid	Dimoxystrobin	HCH beta	Prothioconazole-desthio
Bromuconazole	Diniconazole	Heptachlor	Pyraclostrobin
Carbendazim	Diphenylamine	Imazalil	Pyrimethanil
Carbofuran	Endosulfan-alpha	Imidacloprid	Spinosad
Carbofuran, 3-hydroxy	Endosulfan-beta	Iprodione	Tebuconazole
Chlorantraniliprole	Endosulfan-sulfate	Isoprothiolane	Tefluthrin
Chlordane, cis-	Endrin	Lambda-cyhalothrin	Tetraconazole
Chlordane, trans-	Endrin ketone	Lindane	Tetramethrin
Chlorothalonil	Epoxiconazole	Malaoxon	Thiabendazole
Chlorpropham	Famoxadone	Malathion	Thiacloprid
Chlorpyrifos	Fenbuconazole	Mandipropamid	Thiophanate-methyl
Chlorpyrifos-methyl	Fenhexamid	Mecoprop	Triadimefon
Cyfluthrin (sum of isomers)	Fenitrothion	Metalaxyl	Triadimenol
Cypermethrin (sum of isomers)	Fenpropidin	Metconazole	Tricyclazole
Cyproconazole	Fenpropimorph	Omethoate	Trifloxystrobin
Cyprodinil	Fenvalerate (sum of isomers)	Parathion	Triticonazole
DDD- p,p'	Fipronil	Permethrin (sum of isomers)	Vinclozolin
DDE- p,p'	Fluazifop	Phenylphenol-ortho	

Instructions:

- After arrival the samples should be stored at +4 °C.
- Before analysis, homogenize the samples according to your laboratory procedure.
- Carry out a **single analysis** for each sample and treat the test material as if it was a sample for routine analysis and make use of your own reference standards
- Please upload your results via the web application (https://crlwebshop.wur.nl/apex/f?p=307:LOGIN) before **March 10th 2017**.
- Report all the results in mg/kg sample as received. For the analytes found and reported, please provide the recovery (%) if available. Mention under the button "Method" in the column "Remark", whether or not the result has been corrected for recovery.

- Your username is:
- Your password is:
- Your lab code to enter this proficiency test is:

- Please inform us about your applied method and detection technique (preferably via the web application).

Please contact me if you have any questions or need any assistance.

With kind regards,

D. Pereboom

Diana Pereboom
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Annex 3 Statistical evaluation of homogeneity data

	chlorpyrifos in A (mg/kg)	
Sample No.	Replicate 1	Replicate 2
Hom/A001	0.036	0.038
Hom/A002	0.038	0.037
Hom/A003	0.038	0.037
Hom/A004	0.038	0.037
Hom/A005	0.036	0.038
Hom/A006	0.035	0.037
Hom/A007	0.036	0.036
Hom/A008	0.037	0.036
Hom/A009	0.036	0.037
Hom/A010	0.036	0.036
Grand mean	0.037	
Cochran's test		
C	0.233	
Ccrit	0.602	
C < Ccrit?	NO OUTLIERS	
Target s = σ_P	0.009	
s_x	0.001	
s_w	0.001	
s_s	0.0	
Critical= 0.3 σ_P	0.003	
s_s < critical?	ACCEPTED	
s_w < 0.5 σ_P?	ACCEPTED	

s_x = Standard deviation of the sample averages.

s_w = Within-sample standard deviation.

s_s = Between-sample standard deviation.

Sample No.	cis-deltamethrin in A (mg/kg)	
	Replicate 1	Replicate 2
Hom/A001	0.020	0.020
Hom/A002	0.019	0.019
Hom/A003	0.018	0.018
Hom/A004	0.019	0.018
Hom/A005	0.020	0.020
Hom/A006	0.021	0.021
Hom/A007	0.020	0.020
Hom/A008	0.019	0.020
Hom/A009	0.019	0.018
Hom/A010	0.020	0.019
Grand mean	0.019	
Cochran's test		
C	0.393	
Ccrit	0.602	
C < Ccrit?	NO OUTLIERS	
Target s = σ_P	0.005	
s_x	0.001	
s_w	0.001	
s_s	0.001	
Critical= 0.3 σ_P	0.001	
s_s < critical?	ACCEPTED	
s_w < 0.5 σ_P?	ACCEPTED	

s_x = Standard deviation of the sample averages.

s_w = Within-sample standard deviation.

s_s = Between-sample standard deviation.

Sample No.	pirimiphos-methyl in A (mg/kg)	
	Replicate 1	Replicate 2
Hom/A001	0.101	0.102
Hom/A002	0.104	0.101
Hom/A003	0.105	0.099
Hom/A004	0.098	0.101
Hom/A005	0.102	0.098
Hom/A006	0.100	0.101
Hom/A007	0.100	0.099
Hom/A008	0.102	0.099
Hom/A009	0.100	0.100
Hom/A010	0.100	0.101
Grand mean	0.101	
Cochran's test		
C	0.352	
Ccrit	0.602	
C < Ccrit?	NO OUTLIERS	
Target s = σ_P	0.025	
s_x	0.001	
s_w	0.002	
s_s	0.0	
Critical= 0.3 σ_P	0.008	
s_s < critical?	ACCEPTED	
s_w < 0.5 σ_P?	ACCEPTED	

s_x = Standard deviation of the sample averages.

s_w = Within-sample standard deviation.

s_s = Between-sample standard deviation.

Sample No.	azoxystrobin in B (mg/kg)	
	Replicate 1	Replicate 2
Hom/A001	0.435	0.378
Hom/A002	0.410	0.371
Hom/A003	0.397	0.392
Hom/A004	0.401	0.395
Hom/A005	0.383	0.371
Hom/A006	0.383	0.326
Hom/A007	0.341	0.347
Hom/A008	0.392	0.358
Hom/A009	0.345	0.369
Hom/A010	0.382	0.362
Grand mean	0.377	
Cochran's test		
C	0.313	
Ccrit	0.602	
C < Ccrit?	NO OUTLIERS	
Target s = σ_P	0.094	
s_x	0.021	
s_w	0.023	
s_s	0.013	
Critical= 0.3 σ_P	0.028	
s_s < critical?	ACCEPTED	
s_w < 0.5 σ_P?	ACCEPTED	

s_x = Standard deviation of the sample averages.

s_w = Within-sample standard deviation.

s_s = Between-sample standard deviation.

Sample No.	boscalid in B (mg/kg)	
	Replicate 1	Replicate 2
Hom/A001	1.027	0.962
Hom/A002	0.984	0.971
Hom/A003	1.003	1.028
Hom/A004	1.076	1.006
Hom/A005	0.946	0.933
Hom/A006	0.957	0.878
Hom/A007	0.927	0.921
Hom/A008	1.009	1.010
Hom/A009	0.904	0.951
Hom/A010	0.970	0.914
Grand mean	0.969	
Cochran's test		
C	0.291	
Ccrit	0.602	
C < Ccrit?	NO OUTLIERS	
Target s = σ_P	0.242	
s_x	0.044	
s_w	0.033	
s_s	0.038	
Critical= 0.3 σ_P	0.073	
s_s < critical?	ACCEPTED	
s_w < 0.5 σ_P?	ACCEPTED	

s_x = Standard deviation of the sample averages.

s_w = Within-sample standard deviation.

s_s = Between-sample standard deviation.

Sample No.	chorpyrifos in B (mg/kg) Replicate 1	Replicate 2
Hom/A001	0.044	0.043
Hom/A002	0.041	0.038
Hom/A003	0.041	0.039
Hom/A004	0.045	0.043
Hom/A005	0.042	0.043
Hom/A006	0.041	0.044
Hom/A007	0.041	0.044
Hom/A008	0.044	0.042
Hom/A009	0.038	0.042
Hom/A010	0.039	0.042
Grand mean	0.042	
Cochran's test		
C	0.292	
Ccrit	0.602	
C < Ccrit?	NO OUTLIERS	
Target s = σ_P	0.010	
s_x	0.002	
s_w	0.002	
s_s	0.001	
Critical= 0.3 σ_P	0.003	
s_s < critical?	ACCEPTED	
s_w < 0.5 σ_P?	ACCEPTED	

s_x = Standard deviation of the sample averages.

s_w = Within-sample standard deviation.

s_s = Between-sample standard deviation.

Sample No.	cypermethrin in B (mg/kg) Replicate 1	Replicate 2
Hom/A001	0.050	0.028
Hom/A002	0.025	0.025
Hom/A003	0.033	0.050
Hom/A004	0.037	0.043
Hom/A005	0.033	0.024
Hom/A006	0.031	0.029
Hom/A007	0.023	0.027
Hom/A008	0.047	0.053
Hom/A009	0.022	0.035
Hom/A010	0.027	0.032
Grand mean	0.337	
Cochran's test		
C	0.441	
Ccrit	0.602	
C < Ccrit?	NO OUTLIERS	
Target s = σ_P	0.008	
s_x	0.008	
s_w	0.007	
s_s	0.007	
Critical= 0.3 σ_P	0.003	
s_s < critical?	NOT ACCEPTED	
s_w < 0.5 σ_P?	NOT ACCEPTED	

s_x = Standard deviation of the sample averages.

s_w = Within-sample standard deviation.

s_s = Between-sample standard deviation.

Sample No.	cyproconazole in B (mg/kg)	
	Replicate 1	Replicate 2
Hom/A001	0.067	0.073
Hom/A002	0.071	0.068
Hom/A003	0.069	0.069
Hom/A004	0.070	0.069
Hom/A005	0.068	0.069
Hom/A006	0.068	0.064
Hom/A007	0.066	0.070
Hom/A008	0.069	0.069
Hom/A009	0.065	0.067
Hom/A010	0.070	0.066
Grand mean	0.068	
Cochran's test		
C	0.363	
Ccrit	0.602	
C < Ccrit?	NO OUTLIERS	
Target s = σ_P	0.017	
s_x	0.001	
s_w	0.002	
s_s	0.0	
Critical= 0.3 σ_P	0.005	
s_s < critical?	ACCEPTED	
s_w < 0.5 σ_P?	ACCEPTED	

s_x = Standard deviation of the sample averages.

s_w = Within-sample standard deviation.

s_s = Between-sample standard deviation.

Sample No.	ortho-phenylphenol in B (mg/kg)	
	Replicate 1	Replicate 2
Hom/A001	0.126	0.116
Hom/A002	0.124	0.129
Hom/A003	0.159	0.157
Hom/A004	0.115	0.139
Hom/A005	0.151	0.116
Hom/A006	0.125	0.125
Hom/A007	0.122	0.117
Hom/A008	0.125	0.132
Hom/A009	0.107	0.125
Hom/A010	0.120	0.129
Grand mean	0.128	
Cochran's test		
C	0.513	
Ccrit	0.602	
C < Ccrit?	NO OUTLIERS	
Target s = σ_P	0.032	
s_x	0.012	
s_w	0.011	
s_s	0.009	
Critical= 0.3 σ_P	0.0096	
s_s < critical?	ACCEPTED	
s_w < 0.5 σ_P?	ACCEPTED	

s_x = Standard deviation of the sample averages.

s_w = Within-sample standard deviation.

s_s = Between-sample standard deviation.

Sample No.	pirimiphos-methyl in B (mg/kg)	
	Replicate 1	Replicate 2
Hom/A001	0.254	0.228
Hom/A002	0.248	0.215
Hom/A003	0.239	0.229
Hom/A004	0.238	0.243
Hom/A005	0.234	0.238
Hom/A006	0.223	0.240
Hom/A007	0.229	0.237
Hom/A008	0.245	0.234
Hom/A009	0.209	0.228
Hom/A010	0.234	0.255
Grand mean	0.235	
Cochran's test		
C	0.341	
Ccrit	0.602	
C < Ccrit?	NO OUTLIERS	
Target s = σ_P	0.059	
s_x	0.007	
s_w	0.013	
s_s	0.0	
Critical= 0.3 σ_P	0.018	
s_s < critical?	ACCEPTED	
s_w < 0.5 σ_P?	ACCEPTED	

s_x = Standard deviation of the sample averages.

s_w = Within-sample standard deviation.

s_s = Between-sample standard deviation.

Sample No.	tebuconazole in B (mg/kg)	
	Replicate 1	Replicate 2
Hom/A001	0.155	0.162
Hom/A002	0.156	0.161
Hom/A003	0.160	0.161
Hom/A004	0.165	0.151
Hom/A005	0.153	0.156
Hom/A006	0.157	0.150
Hom/A007	0.160	0.158
Hom/A008	0.158	0.165
Hom/A009	0.152	0.157
Hom/A010	0.159	0.147
Grand mean	0.157	
Cochran's test		
C	0.374	
Ccrit	0.602	
C < Ccrit?	NO OUTLIERS	
Target s = σ_P	0.039	
s_x	0.003	
s_w	0.005	
s_s	0.0	
Critical= 0.3 σ_P	0.012	
s_s < critical?	ACCEPTED	
s_w < 0.5 σ_P?	ACCEPTED	

s_x = Standard deviation of the sample averages.

s_w = Within-sample standard deviation.

s_s = Between-sample standard deviation.

Annex 4 Statistical evaluation of stability data

*Statistical evaluation for **antraquinone in material A.***

Storage temperature	-18 °C	4 °C
Time (days)	0	56
Calculated amounts (mg/kg)	0.081	0.097
	0.086	0.108
	0.098	0.115
Average amount (mg/kg)	0.089	0.106
n	3	3
st. dev (mg/kg)	0.009	0.009
Difference		-0.018
$0.3*\sigma_P$		0.007
Consequential difference? Diff < $0.3*\sigma_P$		YES

*Statistical evaluation for **biphenyl in material A.***

Storage temperature	-18 °C	4 °C
Time (days)	0	56
Calculated amounts (mg/kg)	0.110	0.171
	0.120	0.191
	*	0.168
Average amount (mg/kg)	0.115	0.177
n	2	3
st. dev (mg/kg)	0.007	0.012
Difference		-0.061
$0.3*\sigma_P$		0.009
Consequential difference? Diff < $0.3*\sigma_P$		YES

*outlier according to grubbs"test

*Statistical evaluation for **cis-chlordane in material A.***

Storage temperature	-18 °C	4 °C
Time (days)	0	56
Calculated amounts (mg/kg)	0.043	0.031
	0.056	0.049
	0.056	0.052
Average amount (mg/kg)	0.052	0.044
n	3	3
st. dev (mg/kg)	0.008	0.011
Difference		0.007
$0.3*\sigma_P$		0.004
Consequential difference? Diff < $0.3*\sigma_P$		YES

*Statistical evaluation for **chlorpyrifos in material A.***

Storage temperature	-18 °C	4 °C
Time (days)	0	56
Calculated amounts (mg/kg)	0.270	0.307
	0.256	0.328
	0.335	0.368
Average amount (mg/kg)	0.287	0.335
n	3	3
st. dev (mg/kg)	0.042	0.031
Difference		-0.047
$0.3*\sigma_P$		0.022
Consequential difference? Diff < $0.3*\sigma_P$		YES

*Statistical evaluation for **p,p'-DDE in material A.***

Storage temperature	-18 °C	4 °C
Time (days)	0	56
Calculated amounts (mg/kg)	0.041	0.044
	0.043	0.053
	0.041	0.053
Average amount (mg/kg)	0.042	0.050
n	3	3
st. dev (mg/kg)	0.001	0.005
Difference		-0.008
$0.3*\sigma_P$		0.003
Consequential difference? Diff < $0.3*\sigma_P$		YES

*Statistical evaluation for **cis-deltamethrin in material A.***

Storage temperature	-18 °C	4 °C
Time (days)	0	56
Calculated amounts (mg/kg)	0.086	0.109
	0.118	0.172
	0.083	0.148
Average amount (mg/kg)	0.096	0.143
n	3	3
st. dev (mg/kg)	0.020	0.032
Difference		-0.047
$0.3*\sigma_P$		0.007
Consequential difference? Diff < $0.3*\sigma_P$		YES

*Statistical evaluation for **alpha-endosulfan in material A.***

Storage temperature	-18 °C	4 °C
Time (days)	0	56
Calculated amounts (mg/kg)	0.108	0.094
	0.112	0.126
	0.111	0.141
Average amount (mg/kg)	0.110	0.120
n	3	3
st. dev (mg/kg)	0.002	0.024
Difference		-0.010
$0.3*\sigma_P$		0.008
Consequential difference? Diff < $0.3*\sigma_P$		YES

*Statistical evaluation for **endosulfan sulfate in material A.***

Storage temperature	-18 °C	4 °C
Time (days)	0	56
Calculated amounts (mg/kg)	0.132	0.147
	0.138	0.177
	0.159	0.190
Average amount (mg/kg)	0.143	0.171
n	3	3
st. dev (mg/kg)	0.014	0.022
Difference		-0.028
$0.3*\sigma_P$		0.011
Consequential difference? Diff < $0.3*\sigma_P$		YES

*Statistical evaluation for **pirimiphos-methyl in material A.***

Storage temperature	-18 °C	4 °C
Time (days)	0	56
Calculated amounts (mg/kg)	0.150	0.168
	0.161	0.208
	0.226	0.224
Average amount (mg/kg)	0.179	0.200
n	3	3
st. dev (mg/kg)	0.041	0.028
Difference		-0.021
$0.3*\sigma_P$		0.013
Consequential difference? Diff < $0.3*\sigma_P$		YES

*Statistical evaluation for **azostrobin in material B.***

Storage temperature	-18 °C	4 °C
Time (days)	0	56
Calculated amounts (mg/kg)	0.446	0.439
	0.451	0.402
	0.413	0.411
	0.355	0.437
	0.410	0.477
	0.463	0.439
Average amount (mg/kg)	0.423	0.434
n	6	6
st. dev (mg/kg)	0.039	0.026
Difference		-0.011
$0.3*\sigma_P$		0.032
Consequential difference? Diff < $0.3*\sigma_P$		NO

*Statistical evaluation for **boscalid in material B.***

Storage temperature	-18 °C	4 °C
Time (days)	0	56
Calculated amounts (mg/kg)	1.16	1.16
	1.19	1.12
	1.15	1.13
	*	1.16
	1.15	1.17
	1.13	1.15
Average amount (mg/kg)	1.16	1.15
n	5	6
st. dev (mg/kg)	0.020	0.020
Difference		0.010
$0.3*\sigma_P$		0.087
Consequential difference? Diff < $0.3*\sigma_P$		NO

*outlier according to Grubbs test

*Statistical evaluation for **chlorpyrifos in material B.***

Storage temperature	-18 °C	4 °C
Time (days)	0	56
Calculated amounts (mg/kg)	0.047	0.045
	0.044	0.044
	0.044	0.043
	0.048	0.043
	0.045	0.042
	0.043	0.043
Average amount (mg/kg)	0.045	0.043
n	6	6
st. dev (mg/kg)	0.002	0.001
Difference		0.002
$0.3*\sigma_P$		0.003
Consequential difference? Diff < $0.3*\sigma_P$		NO

*Statistical evaluation for **cypermethrin in material B.***

Storage temperature	-18 °C	4 °C
Time (days)	0	56
Calculated amounts (mg/kg)	0.070	0.058
	0.074	0.065
	0.067	0.066
	*	0.066
	0.056	0.062
	0.067	0.065
Average amount (mg/kg)	0.067	0.064
n	5	6
st. dev (mg/kg)	0.006	0.003
Difference		0.003
$0.3*\sigma_P$		0.005
Consequential difference? Diff < $0.3*\sigma_P$		NO

* Outlier according to Grubbs test

*Statistical evaluation for **cyproconazole in material B.***

Storage temperature	-18 °C	4 °C
Time (days)	0	56
Calculated amounts (mg/kg)	0.074	0.069
	0.073	0.070
	0.073	0.072
	0.078	0.071
	0.073	0.069
	0.068	0.071
Average amount (mg/kg)	0.073	0.071
n	6	6
st. dev (mg/kg)	0.003	0.001
Difference		0.003
$0.3*\sigma_P$		0.00549
Consequential difference? Diff < $0.3*\sigma_P$		NO

*Statistical evaluation for **ortho-phenylphenol in material B.***

Storage temperature	-18 °C	4 °C
Time (days)	0	56
Calculated amounts (mg/kg)	0.139	0.138
	0.145	0.140
	0.138	0.146
		0.137
	0.139	0.128
	0.133	0.134
Average amount (mg/kg)	0.139	0.137
n	5	6
st. dev (mg/kg)	0.004	0.006
Difference		0.002
$0.3*\sigma_P$		0.010
Consequential difference? Diff < $0.3*\sigma_P$		NO

*Statistical evaluation for **pirimiphos-methyl in material B.***

Storage temperature	-18 °C	4 °C
Time (days)	0	56
Calculated amounts (mg/kg)	0.246	0.241
	0.263	0.248
	0.252	0.244
	0.255	0.235
	0.248	0.236
	0.250	0.253
Average amount (mg/kg)	0.252	0.243
n	6	6
st. dev (mg/kg)	0.006	0.007
Difference		0.009
$0.3*\sigma_P$		0.019
Consequential difference? Diff < $0.3*\sigma_P$		NO

*Statistical evaluation for **tebuconazole in material B.***

Storage temperature	-18 °C	4 °C
Time (days)	0	56
Calculated amounts (mg/kg)	0.156	0.161
	0.168	0.161
	0.154	0.169
	0.176	0.166
	0.171	0.162
	0.161	0.163
Average amount (mg/kg)	0.164	0.164
n	6	6
st. dev (mg/kg)	0.009	0.003
Difference		0.001
$0.3*\sigma_P$		0.012
Consequential difference? Diff < $0.3*\sigma_P$		NO

Annex 5 Overview of the applied methods

Material A			
Lab	Sample purification	Internal standard	Detection technique
PT479	Yes, Quechers	yes	MS/MS
PT480	None	Sulfotep, PCB 31	"LC-MS/MS , GC-MS/MS"
PT484	Quechers		
PT486	Quechers	No	GC-MS
PT488	Thermal, Florisil, Solvent exchange, PSA, Thermal. In between centrifugation and in the end Filtration with RC.	LC = Triphenylphosphate, GC = PCD-153	LC-TQ and GC-TQ
PT491	Extraction with CalfloE and Celite, GPC	Triphenyl Phosphate and Chloropyriphosethyl_D10	GC-MS/MS and LC-MS/MS
PT492	Gel Permeation Chromatography	No	HRGC-ECD - double column/double detector system
PT493	dispersive PSA	no	LC-MS/MS and GC-MS/MS
PT494	2g of soy acid oil were mixed with 10 mL of ACN, shacked for 10 min and centrifuged. 8 mL of the supernatant was placed at -18°C for 2 hours and filtered into a tube containing 150 mg PSA / 900 mg MgSO4. Shacked for 10 min and centrifuged.	Tris-(1,3-dicloroisopropyl)-phosphat	GC-MS/MS triple quadrupole and for chlorpyrifos, cis-deltamethrin and pirimiphos-methyl LC-MS/Ms triple quadrupole was used
PT497	GPC, SPE Florisil	PCB 207	GC-ECD, two columns with different phases
PT500	d-SPE with Agilent EMR Lipid removal followed by a polish step with NaCl and MgSO4	Triphenylphosphate	GC-MS/MS, HPLC-MS/MS
PT501	Only Freeze	No Internal standard	GC-ECD, GC-NP, for chlorpyrifos and pirimiphos-methyl LC-MS/MS was used
PT502	dispersive SPE (PSA + C18)	Triphenylphosphate	GC-MS/MS and LC-MS/MS (MRM mode)
PT503			
PT504	GPC	Triphenylphosphate, Hexabroombenzeen	GC-MS/MS
PT505	extraction with hexane, clean up with Al2O3	Mirex	GC with ECD
PT508	liquid liquid extraction	yes	MS/MS
PT510	Thermal, Florisil, Solvent exchange, PSA, Thermal. In between centrifugation and in the end Filtration with RC	LC = Triphenylphosphate, GC = PCD-153	LC-TQ and GC-TQ

Material A			
Lab	Sample purification	Internal standard	Detection technique
PT511	Dispersive SPE and chemical filtration PSA	tetrabromobenzene, Dichlorvos D6, Terbutryn D5, Atrazine D5, Dimethoate D6, Cypermethrin C13, Chlordane C13, Alachlor D6, HCB C13, Antracene D12 and Chlorpyryfos-methyl D6	GC MS/MS and LC-MS/<S

Material B			
Lab	Sample purification	Internal standard	Detection technique
PT479	Quechers	yes	MS/MS
PT480	None	Sulfotep, PCB 31	"LC-MS/MS , GC-MS/MS"
PT481	Quechers extraction - Citrate buffered (EN 151662. Dispersive-SPE (Z-Sep)	Triphenylphosphate and no internal standard was used for azoxystrobin, cypermethrin, cyproconazole and tebuconazole.	LC-MS/MS, ESI in positive mode and for boscalid, chlorpirifos, ortho-phenylphenol and pirimiphos-methyl GC-MS/MS, Electron impact, positive was used
PT483	5 g soyabean meal, 10 ml water, 10 ml acetonitrile, extraction 15 min, freeze for 30 min, addition salts, mix, centrifuge, remove 8 ml ACN layer, freeze out fat over night, centrifuge, clean up with PSA/ C18 and EMR; another sample purification for the pesticides chlorpyrifos, cypermetrhin and pirimiphos-methyl (10 g, 100 ml water, 25 g NaCl, 200 ml acetone, 150 ml petrol ether, shake 90 min, wait for phase separation (overnight), filter, dry over sodium sulfate, evaporate, GPC, small silica gel column with different elution solvents)	D6 chlorpyriphosmethyl	LC-MS/MS and for chlorpyrifos, cypermethrin and pirimiphos-methyl GC-MS/MS was used
PT484			
PT485			
PT486	Quechers	NO	LC-MS/MS
PT487	dispersive SPE		GC-MS/MS
PT488	thermal, Florisil, Thermal. In between centrifugation and at the end Filtration over RC.	LC = TPP (Triphenylphosphate) GC = PCB-153	LC-TQ and GC-TQ
PT489	DSPE, freezing out	Pirimicarb D6, Chlorpyrifos D10, Nicarbazin	"LC-MS/MS , GC-MS/MS , GC-MS(NCI)"
PT490	d-SPE	PCB 209	GC-MS/MS
PT491	dispersive SPE	Triphenyl Phosphate and Chloropyriphosetyhl_D10	GC-MS/MS and LC-MS/MS
PT492	Quechers	No	GC/MSMS

Material B			
Lab	Sample purification	Internal standard	Detection technique
PT493	dispersive SPE PSA/C18	No	LC-MS/MS and GC-MS/MS
PT494	5 g of soyabean meal were procedured according to the method QuEChERS - Citrate buffered (EN 151662). Clean up was done by freezing out, not by using C18-sorbent.	Tris-(1,3-dicloroisopropyl)-phosphat	"LC-MS/MS triple quadrupole and for ortho-phenylphenol GC-MS/MS triple quadrupole was used
PT497	SPE Silica	PCB 207	GC-ECD, two columns with different polar phases
PT498	QUECHERS	TTP	QQQ
PT499	QUECHERS PSA+C18+GCB	dimethoate D6 used for all pesticides except for chlorpyrifos, cypermethrin, pirimiphos-methyl the internal standard triphenylphosphate was used.	LC-QQQ
PT500	No clean-up is needed. Only extraction with acidified ethyl acetate.	TPP (Triphenylphosphate)	GC-MS/MS, HPLC-MS/MS
PT501	Only freeze	No Internal Standard	LC-MS/MS,
PT502	dispersive SPE (PSA + C18)	Triphenylphosphate	GC-MS/MS and LC-MS/MS (MRM mode)
PT503			
PT504	Quechers and Gel Permeation Chromatography as sample purification for chlorpyrifos, cypermethrin, ortho-phenylphenol and pirimiphos-methyl	Triphenylphosphate, hexabroombenzeen was used for the pesticides chlorpyrifos, cypermethrin, ortho-phenylphenol and pirimiphos-methyl and none internal standard was used for the other pesticides.	LC-MS/MS and for chlorpyrifos, cypermethrin, ortho-phenylphenol and pirimiphos-methyl GC-MS/MS was used
PT505	extraction with hexane, clean up with Al2O3	Mirex	GC with ECD
PT506	Sample was clean-up with freezing and with dispersive solid phase extraction - PSA,MgSO4,C18	TRIS(2-chloro-1-(chloromethyl)ethyl)phosphate	GC-MS single quadrupole, with SIM mode from Agilent
PT508	liquid liquid extraction	yes	MS/MS
PT509			
PT510	Thermal, Florisil, Thermal. In between centrifugation and at the end Filtration over RC.	LC = TPP (Triphenylphosphate), GC = PCB-153	LC-TQ and GC-TQ
PT511	Dispersive SPE and chemical filtration PSA	tetrabromobenzene, Dichlorvos D6, Terbutryn D5, Atrazine D5, Dimethoate D6, Cypermethrin C13, Chlordane C13, Alachlor D6, HCB C13, Antracene D12 and Chlorpyryfos-methyl D6	GC MS/MS and LC-MS/S

Annex 6 Results material A

	anthraquinone CV: 0.072 mg/kg u: 0.008 mg/kg σ_p: 0.018 mg/kg robust σ: 0.017 mg/kg		biphenyl CV: 0.144 mg/kg u: 0.007 mg/kg σ_p: 0.036 mg/kg robust σ: 0.019 mg/kg		cis-chlordane CV: 0.030 mg/kg u: 0.001 mg/kg σ_p: 0.007 mg/kg robust σ: 0.003 mg/kg	
Lab code	Result (mg/kg)	z'_a-score	Result (mg/kg)	z_a-score	Result (mg/kg)	z_{ai}-score
PT479	0.08	0.40	0.154	0.29	0.025	-0.66
PT480	0.076	0.20	0.147	0.09	0.024	-0.80
PT481	nt		nt		nt	
PT483	nt		nt		nt	
PT484						
PT485						
PT486	nt		0.074	-1.94	nt	
PT487	nt		nt		nt	
PT488	0.04	-1.64	0.15	0.17	0.03	0.00
PT489						
PT490	nt		nt		nt	
PT491	nt		0.325	**5.04**	nd	
PT492	nt		nt		0.033	0.40
PT493	nt		nt		0.053	**3.07**
PT494	nt		0.14	-0.10	nd	
PT497	nt		nt		0.028	-0.26
PT498						
PT499	nt		nt		nt	
PT500	nt		0.2	1.57	0.031	0.14
PT501	nt		nt		nd	
PT502	0.085	0.66	0.131	-0.35	0.032	0.27
PT503	nt		nt		nd	
PT504	0.071	-0.06	0.144	0.01	nd	
PT505					<0.05	
PT506	nt		nt		nt	
PT508	0.065	-0.36	0.06	**-2.33**	nd	
PT509	nt		nt		nt	
PT510	0.042	-1.54	0.151	0.20	0.03	0.00
PT511	0.104	1.63	0.126	-0.49	nd	

CV = consensus value.

u = uncertainty of consensus value.

nt = not tested.

nd = not detected

	chlorpyrifos CV: 0.239 mg/kg u: 0.010 mg/kg σ_p: 0.060 mg/kg robust σ: 0.030 mg/kg		p,p'-DDE CV: 0.048 mg/kg u: 0.004 mg/kg σ_p: 0.012 mg/kg robust σ: 0.010 mg/kg		cis-deltamethrin CV: 0.089 mg/kg u: 0.009 mg/kg σ_p: 0.022 mg/kg robust σ: 0.026 mg/kg	
Lab code	Result (mg/kg)	z_a-score	Result (mg/kg)	z_a-score	Result (mg/kg)	z'_a-score
PT479	0.225	-0.23	0.06	0.95	0.08	-0.38
PT480	0.236	-0.05	0.056	0.62	0.075	-0.59
PT481	nt		nt		nt	
PT483	nt		nt		nt	
PT484	0.035	**-3.41**			1.25	**47.95**
PT485						
PT486	nt		nt		nt	
PT487	nt		nt		nt	
PT488	0.22	-0.31	0.051	0.21	0.07	-0.79
PT489						
PT490	nt		nt		nt	
PT491	0.253	0.24	nd		nt	
PT492	nt		0.032	-1.36	nt	
PT493	0.431	**3.22**	0.051	0.21	0.106	0.69
PT494	0.28	0.69	nd		0.1	0.45
PT497	nt		0.03	-1.53	nt	
PT498						
PT499	nt		nt		nt	
PT500	0.26	0.36	0.011	**-3.09**	0.022	**-2.78**
PT501	0.225	-0.23	nd		nd	
PT502	0.219	-0.33	0.047	-0.12	0.107	0.74
PT503	0.24	0.02	0.043	-0.45	0.119	1.23
PT504	0.265	0.44	0.059	0.87	nd	
PT505			<0.05			
PT506	nt		nt		nt	
PT508	0.17	-1.15	nd		0.095	0.24
PT509	nt		nt		nt	
PT510	0.222	-0.28	0.05	0.12	0.07	-0.79
PT511	0.316	1.29	0.055	0.54	0.072	-0.71

CV = consensus value.

u = uncertainty of consensus value.

Nt = not tested.

nd = not detected

	alpha-endosulfan CV: 0.077 mg/kg u: 0.014 mg/kg σ_p: 0.019 mg/kg robust σ: 0.041 mg/kg		endosulfan-sulfate CV: 0.134 mg/kg u: 0.011 mg/kg σ_p: 0.034 mg/kg robust σ: 0.028 mg/kg		pirimiphos-methyl CV: 0.178 mg/kg u: 0.013 mg/kg σ_p: 0.045 mg/kg robust σ: 0.038 mg/kg	
Lab code	Result (mg/kg)		Result (mg/kg)	z'_a-score	Result (mg/kg)	z_a-score
PT479	0.02	**No statistical evaluation**	nd		nd	
PT480	0.029		nd		0.13	-1.08
PT481	nt		nt		nt	
PT483	nt		nt		nt	
PT484						
PT485						
PT486	nd		nd		nd	
PT487	nt		nt		nt	
PT488	0.075		nd		0.162	-0.36
PT489						
PT490	nt		nt		nt	
PT491	nt		nd		0.161	-0.39
PT492	0.061		0.101	-0.94	nt	
PT493	0.104		0.15	0.45	0.186	0.17
PT494	nd		0.15	0.45	0.19	0.26
PT497	0.063		0.144	0.28	nt	
PT498						
PT499	nt		nt		nt	
PT500	0.11		0.11	-0.68	0.25	1.61
PT501	nd		nd		0.108	-1.58
PT502	0.102		0.109	-0.71	0.207	0.65
PT503	0.093		0.124	-0.29	0.193	0.33
PT504	nd		0.121	-0.37	0.188	0.22
PT505	0.114					
PT506	nt		nt		nt	
PT508	0.02		0.158	0.67	0.138	-0.90
PT509	nt		nt		nt	
PT510	0.07				0.164	-0.32
PT511	0.123		0.264	**3.67**	0.226	1.07

CV = consensus value.

u = uncertainty of consensus value.

nt = not tested.

nd = not detected

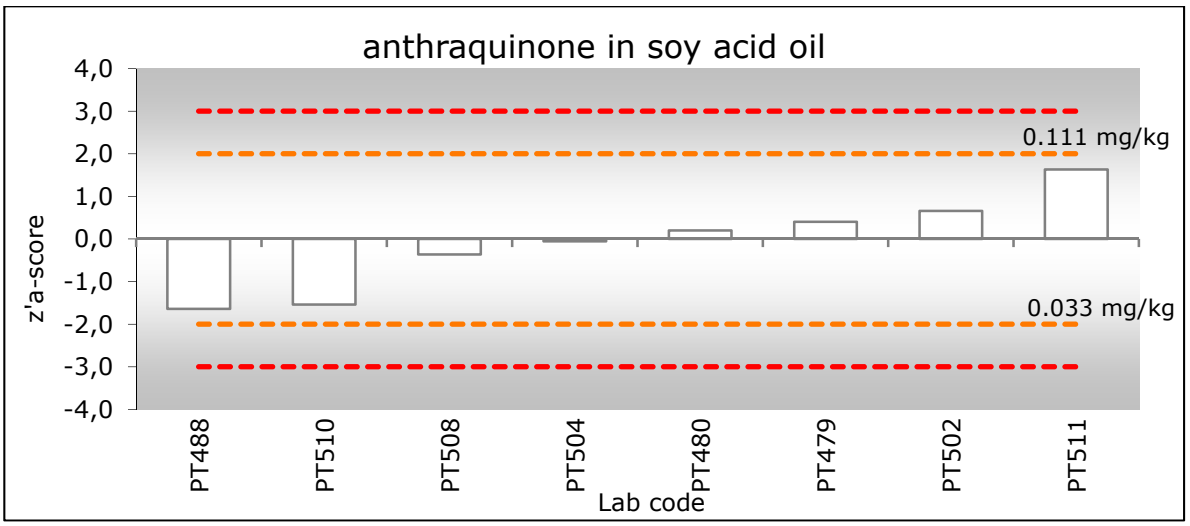

Figure a *Graphical representation of the z'_a-scores for anthraquinone. The X ± 2σ_P lines (dotted) are calculated according to equation II in §3.4.*

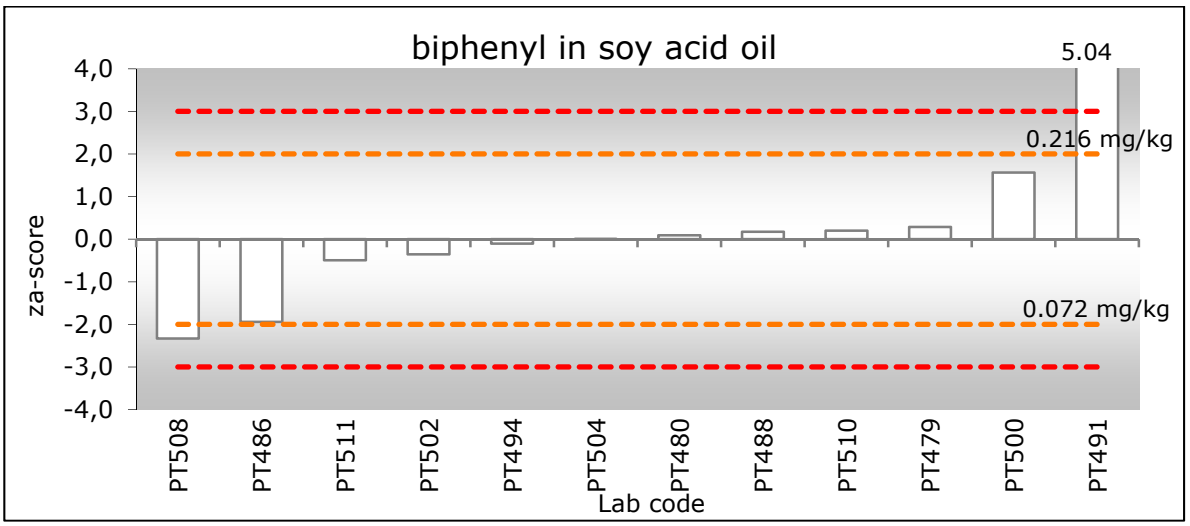

Figure b *Graphical representation of the z_a-scores for biphenyl. The X ± 2σ_P lines (dotted) are calculated according to equation I in §3.4.*

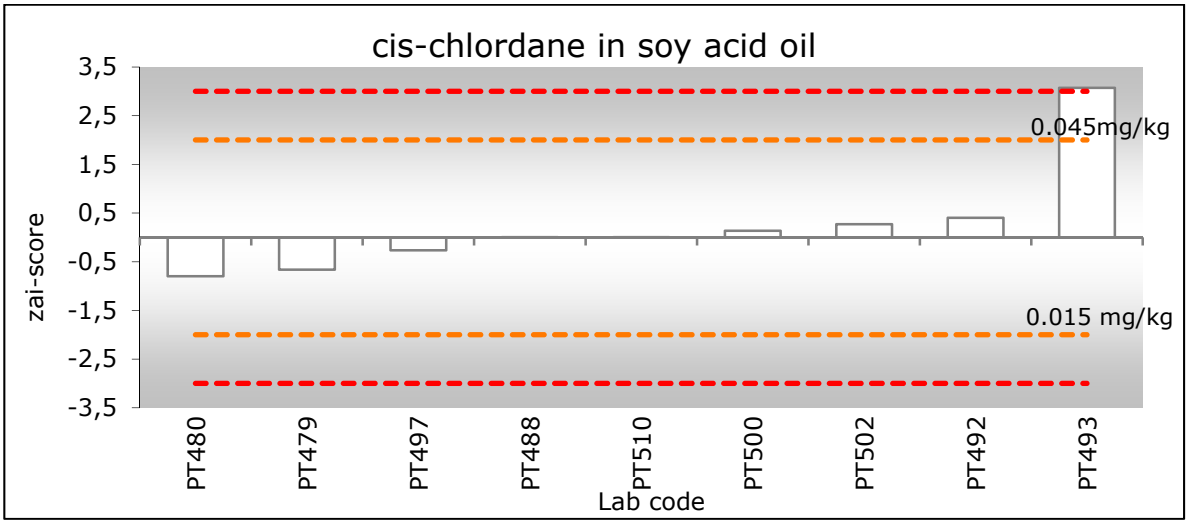

Figure c *Graphical representation of the z_{ai}-scores for cis-chlordane. The X ± 2σ_P lines (dotted) are calculated according to equation III in §3.4.*

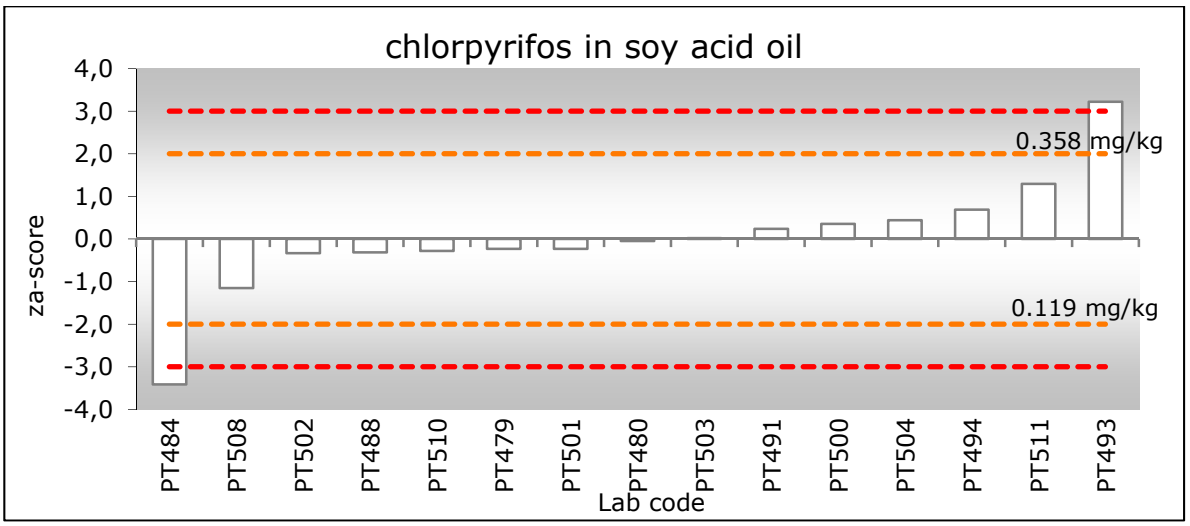

Figure d *Graphical representation of the z_a-scores for chlorpyrifos. The X ± 2σ_P lines (dotted) are calculated according to equation I in §3.4*

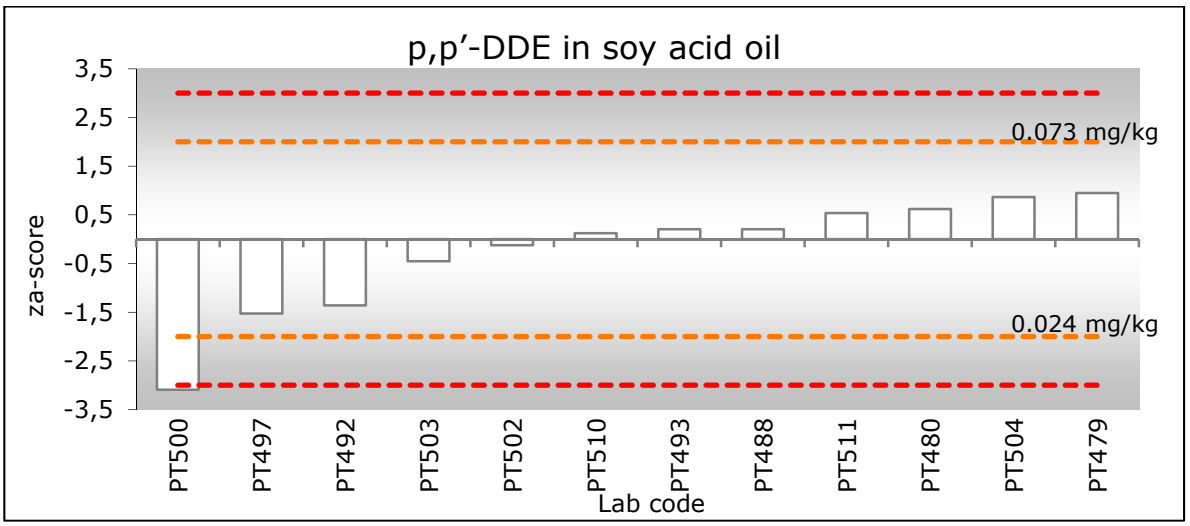

Figure e *Graphical representation of the z_a-scores for p,p'-DDE. The X ± 2σ_P lines (dotted) are calculated according to equation I in §3.4.*

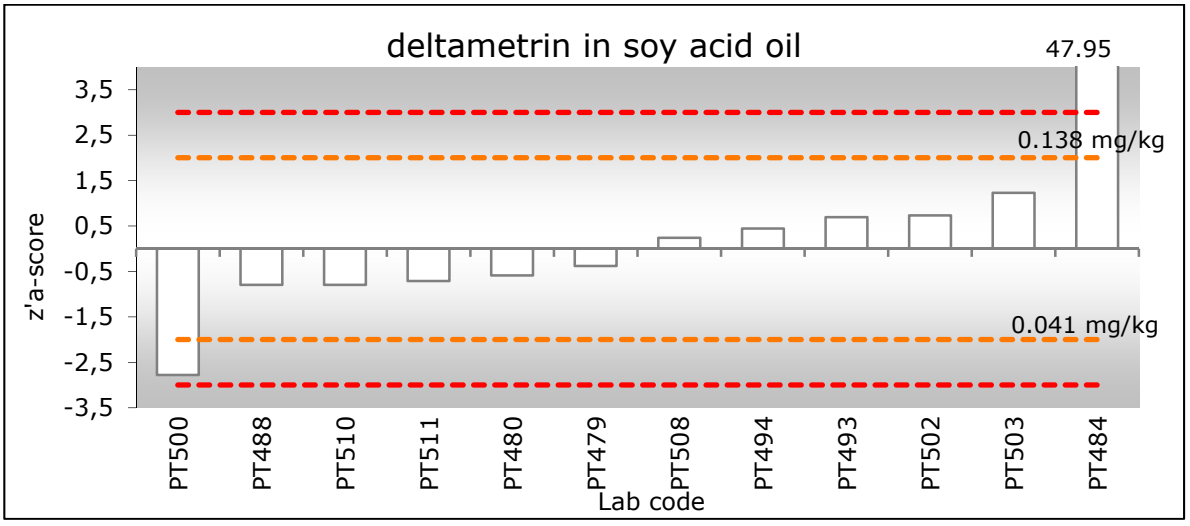

Figure f *Graphical representation of the z'_a-scores for cis-deltamethrin. The X ± 2σ_P lines (dotted) are calculated according to equation II in §3.4.*

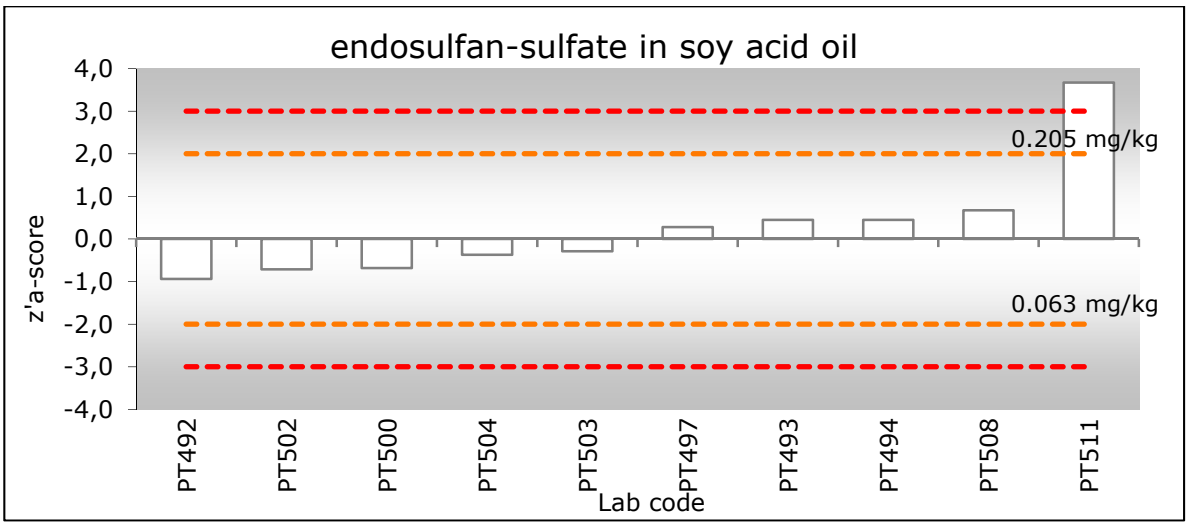

Figure g *Graphical representation of the z'_a-scores for endosulfan-sulfate. The X ± 2σ_P lines (dotted) are calculated according to equation II in §3.4.*

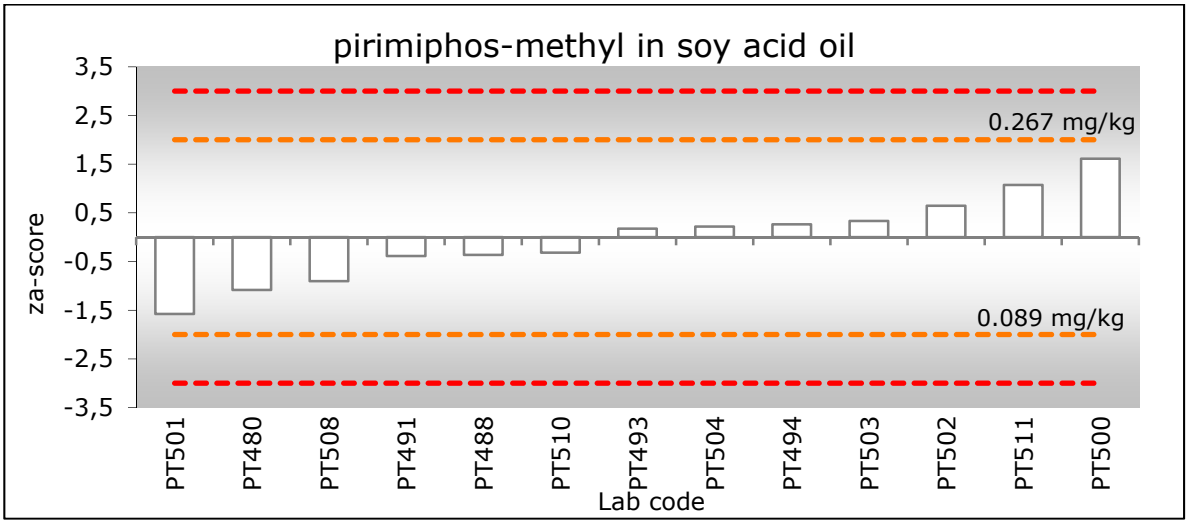

Figure h *Graphical representation of the z_a-scores for pirimiphos-methyl. The X ± 2σ_P lines (dotted) are calculated according to equation I in §3.4.*

Annex 7 Results material B

	azoxystrobin CV: 0.379 mg/kg u: 0.017 mg/kg σ_p: 0.095 mg/kg robust σ: 0.065 mg/kg		boscalid CV: 0.999 mg/kg u: 0.070 mg/kg σ_p: 0.250 mg/kg robust σ: 0.262 mg/kg		chlorpyrifos CV: 0.039 mg/kg u: 0.003 mg/kg σ_p: 0.010 mg/kg robust σ: 0.010 mg/kg	
Lab code	Result (mg/kg)	z_a-score	Result (mg/kg)	z_a-score	Result (mg/kg)	z_a-score
PT479	0.28	-1.05	0.8	-0.80	0.038	-0.11
PT480	0.289	-0.95	0.855	-0.58	0.042	0.30
PT481	0.427	0.50	0.841	-0.63	0.0526	1.38
PT483	0.404	0.26	1.006	0.03	0.036	-0.32
PT484	0.407	0.29	1.09	0.36	0.032	-0.73
PT485	nt		nt		nt	
PT486	nt		nt		nt	
PT487	0.127	**-2.66**	0.818	-0.72	0.03	-0.93
PT488	0.258	-1.28	0.75	-1.00	0.032	-0.73
PT489	0.358	-0.22	1.179	0.72	0.05	1.12
PT490	nt		nt		nt	
PT491	0.424	0.47	1.282	1.13	0.054	1.52
PT492	nt		nt		nt	
PT493	0.447	0.71	1.186	0.75	0.049	1.01
PT494	0.41	0.32	1.3	1.20	0.048	0.91
PT497	nt		nt		nt	
PT498	0.408	0.30	0.798	-0.80	0.035	-0.42
PT499	0.45	0.75	1.1	0.40	0.044	0.50
PT500	0.3	-0.84	0.99	-0.04	0.047	0.81
PT501	0.426	0.49	1.38	1.53	0.0275	-1.19
PT502	0.369	-0.11	1.232	0.93	0.043	0.40
PT503	0.397	0.19	1.07	0.28	0.038	-0.11
PT504	0.41	0.32	1.35	1.41	0.012	**-2.77**
PT505						
PT506	0.429	0.52	0.813	-0.74	nd	
PT508	0.026	**-3.73**	0.136	**-3.46**	0.012	**-2.77**
PT509	0.489	1.16	nt		0.047	0.81
PT510	0.255	-1.31	0.749	-1.00	0.035	-0.42
PT511	0.21	-1.79	0.775	-0.90	0.033	-0.62

CV = consensus value.

u = uncertainty of consensus value.

nt = not tested.

nd = not detected

Lab code	cypermethrin CV: 0.070 mg/kg u: 0.008 mg/kg σ_p: 0.017 mg/kg robust σ: 0.030 mg/kg		cyproconazole CV: 0.070 mg/kg u: 0.004 mg/kg σ_p: 0.018 mg/kg robust σ: 0.013 mg/kg		ortho-phenylphenol CV: 0.144 mg/kg u: 0.012 mg/kg σ_p: 0.036 mg/kg robust σ: 0.043 mg/kg	
	Result (mg/kg)	z'_a-score	Result (mg/kg)	z_a-score	Result (mg/kg)	z'_a-score
PT479	0.073	0.18	0.054	-0.93	0.115	-0.76
PT480	0.069	-0.03	0.07	-0.02	0.139	-0.13
PT481	0.0293	**-2.10**	0.0627	-0.43	0.206	1.64
PT483	0.0927	1.20	0.0704	0.00	nt	
PT484	0.119	**2.57**	0.0977	1.56	0.255	**2.93**
PT485	nt		nt		nt	
PT486	nt		nt		0.182	1.00
PT487	0.022	**-2.48**	0.022	**-2.75**	nt	
PT488	0.05	-1.02	0.064	-0.36	0.12	-0.63
PT489	0.076	0.33	0.075	0.27	0.158	0.37
PT490	nt		nt		nt	
PT491	0.135	**3.41**	0.099	1.63	0.103	-1.08
PT492	nt		nt		nt	
PT493	0.13	**3.15**	0.074	0.21	0.161	0.45
PT494	0.098	1.48	0.079	0.49	0.11	-0.89
PT497	nt		nt		nt	
PT498	nd		0.057	-0.76	nt	
PT499	0.067	-0.14	0.063	-0.42	0.15	0.16
PT500	0.073	0.18	0.27	**11.36**	0.15	0.16
PT501	0.067	-0.14	0.0711	0.04	0.172	0.74
PT502	0.074	0.23	0.074	0.21	0.152	0.21
PT503	0.086	0.85	0.08	0.55	0.15	0.16
PT504	0.063	-0.35	0.1	1.69	nd	
PT505						
PT506	nt		0.028	**-2.41**	0.117	-0.71
PT508	0.012	**-3.00**	nd		0.017	**-3.35**
PT509	0.042	-1.44	nt		0.2	1.48
PT510	0.049	-1.07	0.063	-0.42	0.119	-0.66
PT511	0.067	-0.14	0.064	-0.36	0.086	-1.53

CV = consensus value.

u = uncertainty of consensus value.

nt = not tested.

nd = not detected

Lab code	pirimiphos-methyl CV: 0.224 mg/kg u: 0.016 mg/kg σ_p: 0.056 mg/kg robust σ: 0.061 mg/kg		tebuconazole CV: 0.168 mg/kg u: 0.010 mg/kg σ_p: 0.042 mg/kg robust σ: 0.038 mg/kg	
	Result (mg/kg)	z_a-score	Result (mg/kg)	z_a-score
PT479	0.21	-0.25	0.15	-0.42
PT480	0.214	-0.18	0.153	-0.35
PT481	0.349	**2.23**	0.177	0.22
PT483	0.209	-0.27	0.197	0.70
PT484			0.186	0.44
PT485	nt		nt	
PT486	0.326	1.82	nt	
PT487	0.156	-1.22	0.145	-0.54
PT488	0.16	-1.15	0.129	-0.92
PT489	0.241	0.30	0.192	0.58
PT490	nt		nt	
PT491	0.273	0.87	0.203	0.84
PT492	Nt		nt	
PT493	0.258	0.60	0.198	0.72
PT494	0.26	0.64	0.19	0.53
PT497	nt		nt	
PT498	0.218	-0.11	0.159	-0.21
PT499	0.28	1.00	0.12	-1.14
PT500	0.21	-0.25	0.23	1.49
PT501	0.215	-0.16	0.137	-0.73
PT502	0.262	0.67	0.162	-0.14
PT503	0.247	0.41	0.192	0.58
PT504	0.047	**-3.16**	0.21	1.01
PT505				
PT506	0.251	0.48	0.167	-0.02
PT508	0.051	**-3.09**	0.021	-**3.50**
PT509	0.269	0.80	0.204	0.87
PT510	0.157	-1.20	0.129	-0.92
PT511	0.17	-0.97	0.122	-1.09

CV = consensus value.

u = uncertainty of consensus value.

nt: = not tested.

nd = not detected.

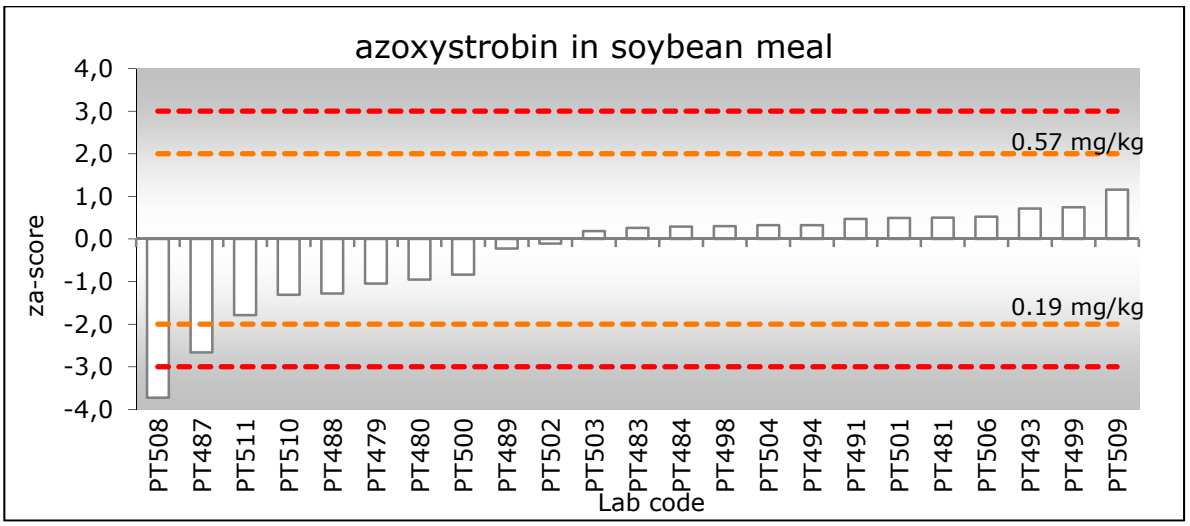

Figure i *Graphical representation of the z_a-scores for azoxystrobin. The X ± 2σ_P lines (dotted) are calculated according to equation I in §3.4.*

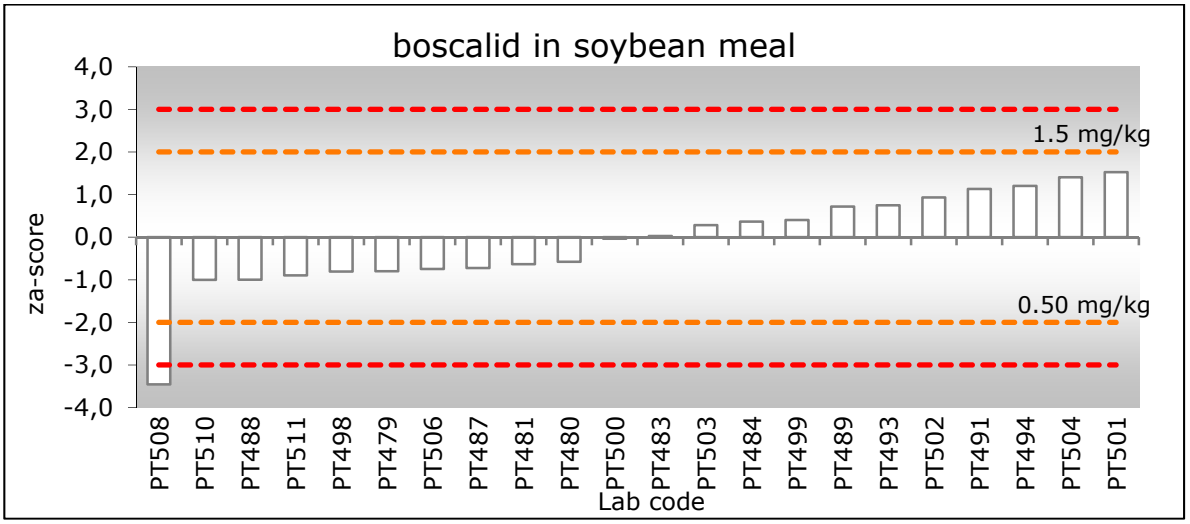

Figure j *Graphical representation of the z_a-scores for boscalid. The X ± 2σ_P lines (dotted) are calculated according to equation I in §3.4.*

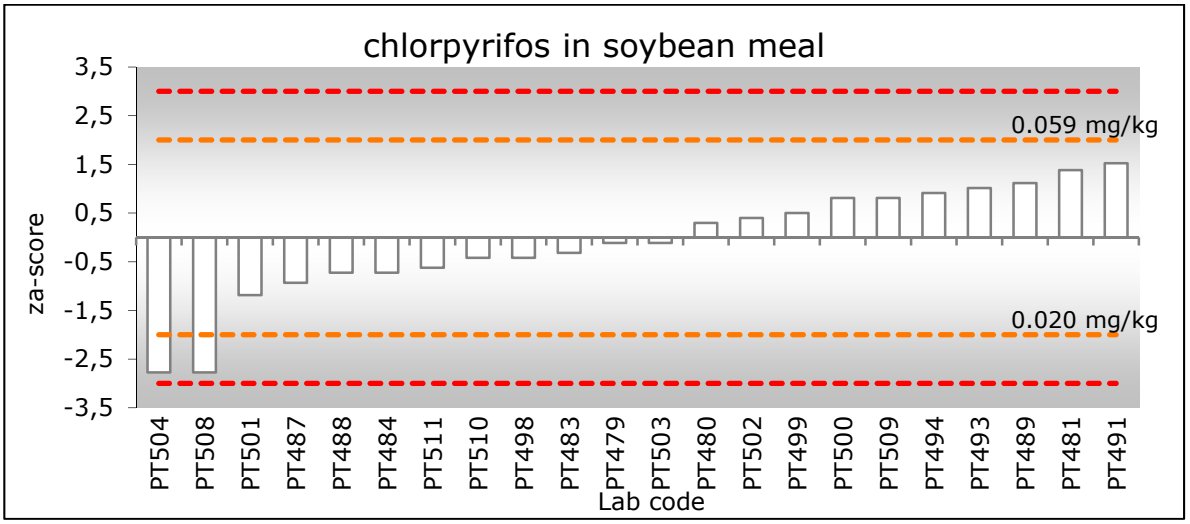

Figure k *Graphical representation of the z_a-scores for chlorpyrifos. The X ± 2σ_P lines (dotted) are calculated according to equation I in §3.4.*

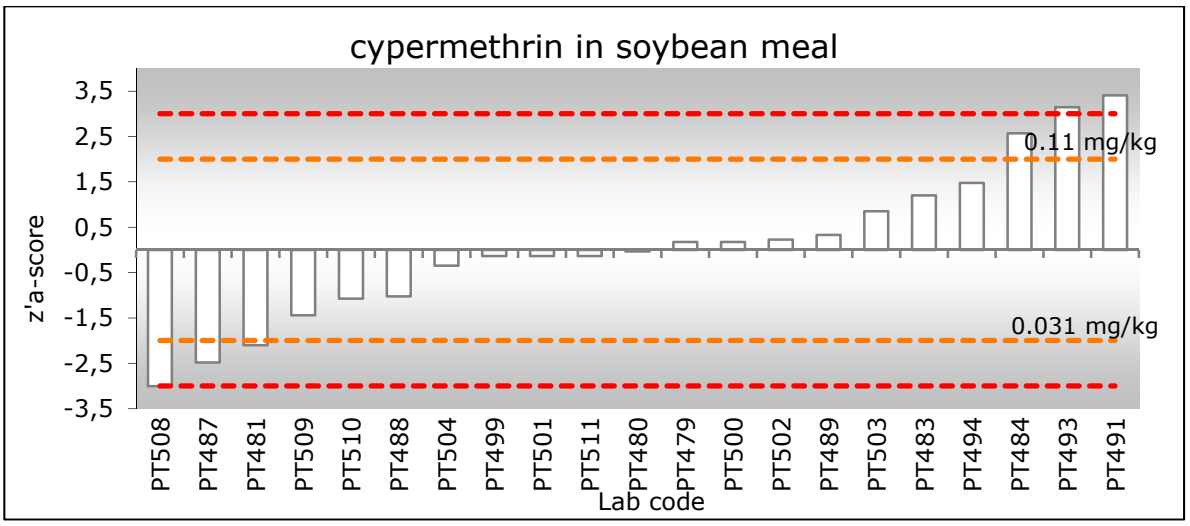

Figure l *Graphical representation of the z'_a-scores for cypermethrin. The X ± 2σ_P lines (dotted) are calculated according to equation II in §3.4.*

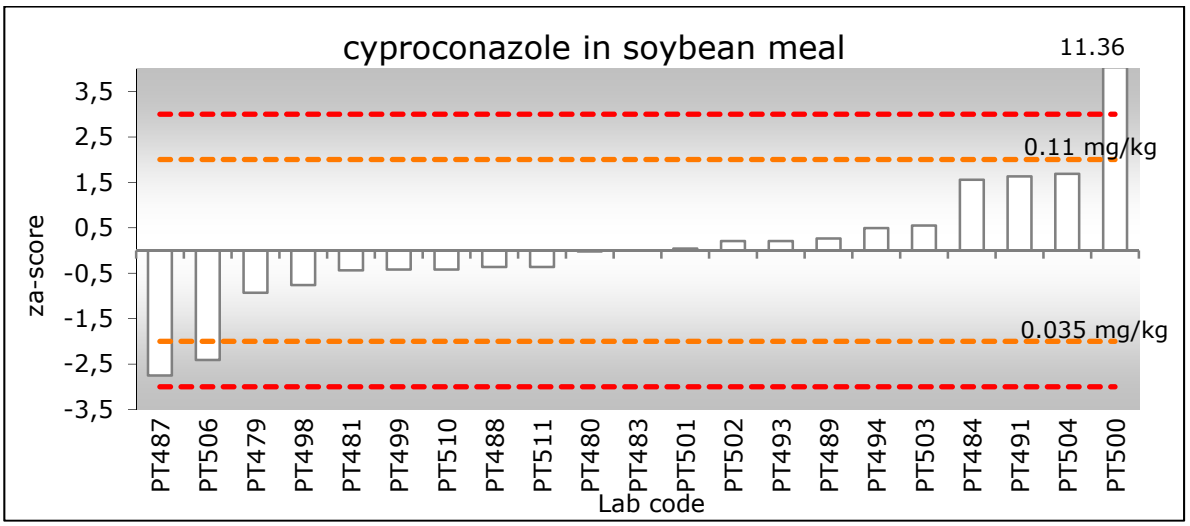

Figure m *Graphical representation of the z_a-scores for cyproconazole. The X ± 2σ_P lines (dotted) are calculated according to equation I in §3.4.*

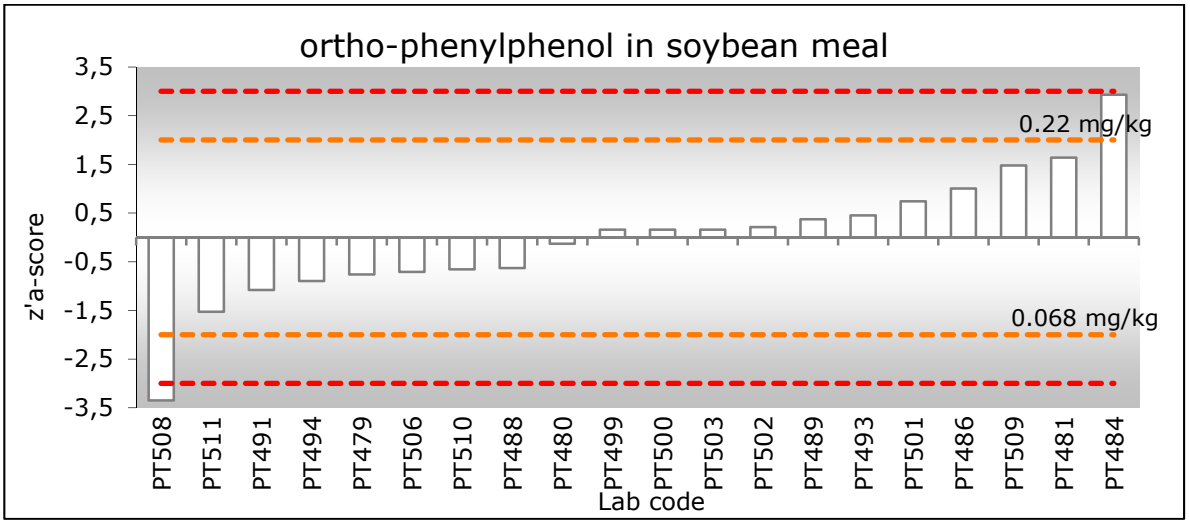

Figure n *Graphical representation of the z'_a-scores for ortho-phenylphenol. The X ± 2σ_P lines (dotted) are calculated according to equation II in §3.4.*

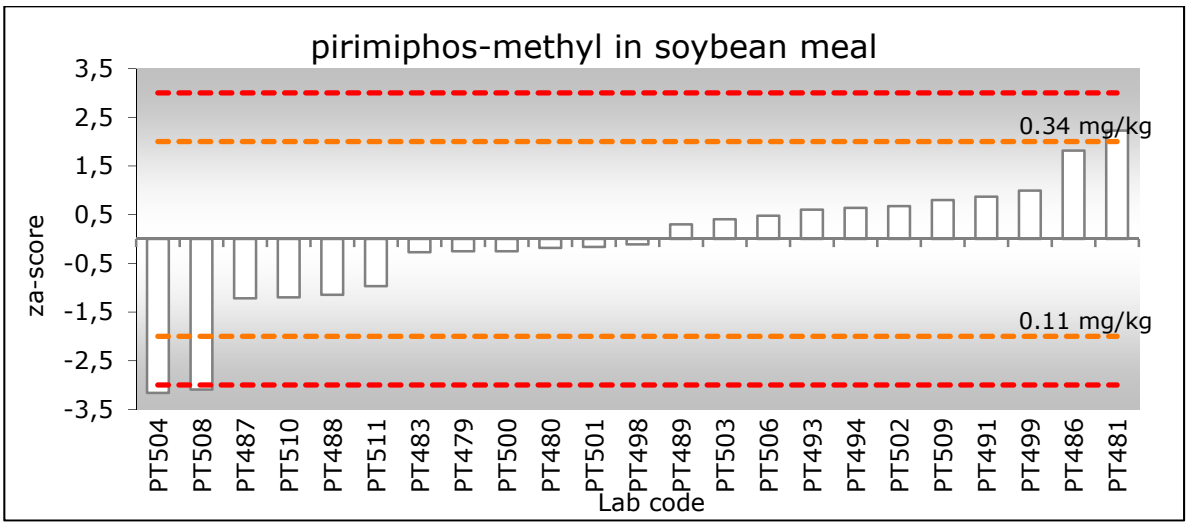

Figure o *Graphical representation of the z_a-scores for pirimiphos-methyl. The X ± 2σ_P lines (dotted) are calculated according to equation I in §3.4.*

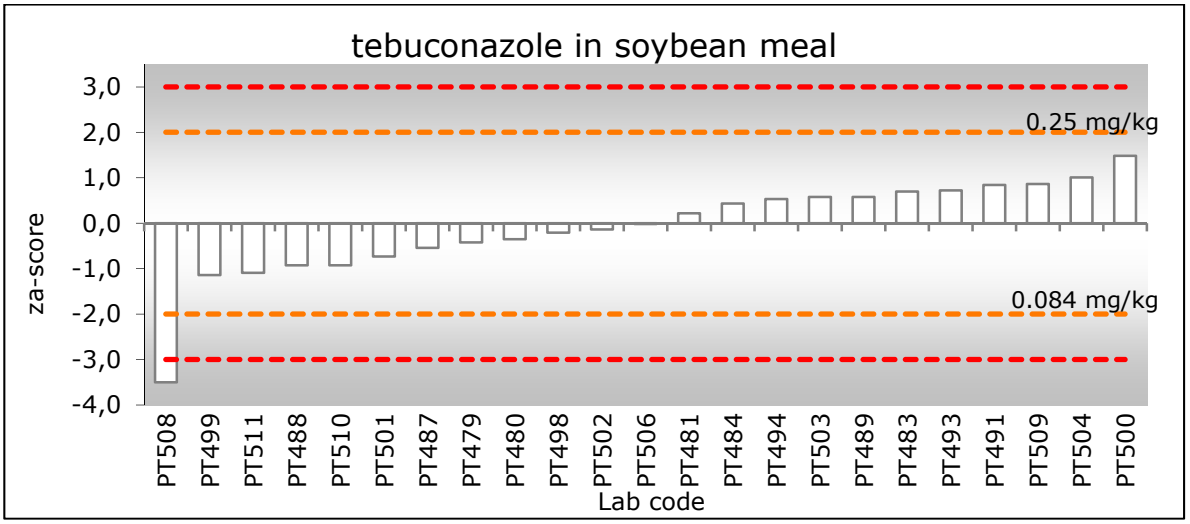

Figure p *Graphical representation of the z_a-scores for tebuconazole. The X ± 2σ_P lines (dotted) are calculated according to equation I in §3.4.*

Annex 8 False positive and false negative results

False positive results

Lab code	Material	Compound reported	Concentration mg/kg
PT481	B	cyfluthrin	0.0839
PT484	A	imazalil	0.149
PT500	B	carbendazim	0.087
PT501	A	İmazalil	0.184

False negative results

Lab code	Material	Compound missed	Lab code	Material	Compound missed
PT479	A	endosulfan-sulfate	PT489	A	endosulfan-sulfate
PT479	A	pirimiphos-methyl	PT489	A	pirimiphos-methyl
PT480	A	endosulfan-sulfate	PT494	A	cis-chlordane
PT484	A	biphenyl	PT494	A	p,p'-DDE
PT484	A	alpha-endosulfan	PT494	A	alpha-endosulfan
PT484	A	endosulfan-sulfate	PT498	B	cypermethrin
PT484	A	pirimiphos-methyl	PT501	A	cis-chlordane
PT484	B	pirimiphos-methyl	PT501	A	p,p'-DDE
PT485	A	cis-chlordane	PT501	A	cis-deltamethrin
PT485	A	p,p'-DDE	PT501	A	alpha-endosulfan
PT485	A	alpha-endosulfan	PT501	A	endosulfan-sulfate
PT485	A	endosulfan-sulfate	PT503	A	cis-chlordane
PT486	A	endosulfan-sulfate	PT504	A	cis-chlordane
PT486	A	pirimiphos-methyl	PT504	A	cis-deltamethrin
PT488	A	endosulfan-sulfate	PT504	A	alpha-endosulfan
PT489	A	biphenyl	PT504	B	ortho-phenylphenol
PT489	A	cis-chlordane	PT508	A	cis-chlordane
PT489	A	chlorpyrifos	PT508	A	p,p'-DDE
PT489	A	p,p'-DDE	PT508	B	cyproconazole
PT489	A	cis-deltamethrin	PT510	A	endosulfan-sulfate
PT489	A	alpha-endosulfan	PT511	A	cis-chlordane

Annex 9 Overview performance per laboratory

Laboratory code	Performance
PT479	2 FN
PT480	1 FN
PT481	Material A not analysed, 2 questionable z-scores for material B, 1 FP
PT483	**Optimal performance for material B,** material A not analysed
PT484	1 FP, 5 FN, 2 questionable z-scores, 2 unsatisfactory z-scores
PT485	4 FN, material A not analysed, pesticides in material B not in scope, reported too late
PT486	2 FN
PT487	Material A not analysed, 3 questionable z-scores for material B
PT488	1 FN
PT489	8 FN, material A not analysed
PT490	Material A not analysed, pesticides in material B not in scope,
PT491	2 unsatisfactory z-scores
PT492	**Optimal performance for material A,** pesticides in material B not in scope
PT493	3 unsatisfactory z-scores
PT494	3 FN
PT497	**Optimal performance for material A,** pesticides in material B not in scope
PT498	Material A not analysed, 1 FN for material B
PT499	**Optimal performance for material B,** material A not analysed
PT500	1 FP, 1 questionable z-scores, 2 unsatisfactory z-scores
PT501	1 FP, 5 FN
PT502	Optimal performance
PT503	1 FN
PT504	4 FN, 1 questionable z-score, 1 unsatisfactory z-score
PT505	**Optimal performance for material A,** pesticides in material B not in scope
PT506	Material A not analysed, 1 questionable z-score for material B
PT508	3 FN, 2 questionable z-scores, 6 unsatisfactory z-scores
PT509	**Optimal performance for material B,** material A not analysed
PT510	1 FN
PT511	1 FN, 1 unsatisfactory z-score

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The mission of Wageningen University and Research is "To explore the potential of nature to improve the quality of life". Under the banner Wageningen University & Research, Wageningen University and the specialised research institutes of the Wageningen Research Foundation have joined forces in contributing to finding solutions to important questions in the domain of healthy food and living environment. With its roughly 30 branches, 5,000 employees and 10,000 students, Wageningen University & Research is one of the leading organisations in its domain. The unique Wageningen approach lies in its integrated approach to issues and the collaboration between different disciplines.