

# ***Laboratory Performance Assessment***

## ***Analysis of Pesticides in Cereal Flour***

***Report***

December 2017

## Summary

The laboratory performance assessment related to pesticides in cereal flour was designed and organised by Lach & Bruns in cooperation with PROOF-ACS in November/December 2017 on behalf of BNN e.V. (Bundesverband Naturkost Naturwaren, Berlin, Germany) and SYNABIO (Syndicat Réseau Entreprises BIO Agroalimentaires, Paris, France).

The test material was prepared of organic cereal flour. Eight analytes were spiked to the cereal flour:

*Glyphosate, AMPA (main metabolite of Glyphosate), Trimethylsulfonium iodide ('Trimesium': as an important counter-ion of Glyphosate and regulated independently in reg. (EC) no. 396/2005), beta-Cyfluthrin, Diflufenican, Piperonylbutoxide, Pirimiphos-methyl, and Sulfoxaflor.*

The test material was distributed to twenty participants across six European countries (Belgium, France, Germany, Italy, Netherlands, and Spain). Each laboratory received 100 g of the homogenised cereal flour. No information with respect to the identity or the number of spiked multi-method analytes was provided to the laboratories in advance. In addition to analytes typically covered by the scope of multi-methods, the laboratories were instructed to analyse also for Glyphosate, AMPA and Trimethylsulfonium cation. Thus, the laboratories were requested to identify the five spiked multi-method analytes and to quantify eight analytes (multi-method analytes plus Glyphosate, AMPA and Trimethylsulfonium cation) in the test sample.

All participants kept the term of submission of results and were considered for evaluation.

The performance assessment considers the following test criteria:

- No *false positive results*.
- Correct *identification* of five multi-method analytes. The presence of Glyphosate, AMPA and Trimethylsulfonium cation in the test sample was to be expected by the labs since they were instructed to analyse the test sample for these parameters.
- Correct *quantification* of eight analytes in terms of 70 to 120 % recovery of the spiked values.

Summary of the performance of the laboratories with respect to the identification and quantification of the analytes:

<b>Criterion</b>	<b>Criterion passed</b>
Correct <i>identification</i> of all five multi-method analytes	15 out of 20 laboratories (75 %)
Correct <i>quantification</i> of all five multi-method analytes	14 out of 20 laboratories (70 %)
Correct <i>quantification</i> of Glyphosate	18 out of 20 laboratories (90 %)
Correct <i>quantification</i> of AMPA	16 out of 19* laboratories (84 %)
Correct <i>quantification</i> of Trimethylsulfonium cation	10 out of 13* laboratories (77 %)
Correct <i>quantification</i> of all eight analytes	7 out of 20 laboratories (35 %)

\* One lab (AMPA) resp. 7 labs (Trimethylsulfonium cation) do not cover the particular analyte within their analytical scope

## Assessment of quantification

Analytical results between 70 and 120 % recovery of the spiked levels are considered satisfying for the assessment of the correct quantification of the pesticides.

Pesticide	Spiked level [mg/kg]	Assigned value [mg/kg]	Number of results	Correct quantification
Cyfluthrin	0,037	0,0338	20	19 out of 20 (95 %)
Diflufenican	0,033	0,0314	20	20 out of 20 (100 %)
Piperonylbutoxide	0,10	0,0961	20	20 out of 20 (100 %)
Pirimiphos-methyl	0,023	0,0236	20	19 out of 20 (95 %)
Sulfoxaflor	0,067	0,0677	15*	14 out of 15 (93 %)
Glyphosate	0,042	0,0428	20	18 out of 20 (90 %)
AMPA	0,048	0,0408	19*	16 out of 19 (84 %)
Trimethylsulfonium cation ( <i>Trimesium</i> )	0,063	0,0660	13*	10 out of 13 (77 %)

\* One lab (AMPA) resp. 5 labs (Sulfoxaflor) resp. 7 labs (Trimethylsulfonium cation) do not cover the particular analyte within their analytical scope

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## 1. Test material preparation and design

The laboratory performance assessment was designed to verify the analytical competence related to BNN module-combination “A1 (pesticides) – B3/B4 (cereals, rice, oil seeds, vegetable oils and vegetable fats / tea, spices)”. As flour is a relevant product in the cereal market in the organic sector, cereal flour was chosen as test material.

Five analytes covered by multi-method analysis and three pesticides, which require single residue methods, were selected for the test:

*Glyphosate, AMPA (alpha-amino-3-hydroxy-5-methyl-4- isoxazole propionic acid, main metabolite of Glyphosate), Trimethylsulfonium iodide ('Trimesium': as an important counter-ion of Glyphosate and regulated independently in reg. (EC) no. 396/2005), beta-Cyfluthrin, Diflufenican, Piperonylbutoxide, Pirimiphos-methyl, and Sulfoxaflor.*

An external laboratory prepared the test material under supervision of PROOF-ACS.

A sample of the untreated material was bottled as blank material for analysis. No incurred residues of the spiked pesticides were identified.

The cereal flour was stirred in a Stephan cutter. The pesticides were added gradually, while the powder was continuously stirred. Stirring was continued after spiking to ensure a homogeneous distribution of all parameters.

Subsamples of 100 g were bottled and stored at -18 °C until shipment. Shipment was performed on dry ice in order to avoid any thawing of the test material, which might reduce the pourability of the material.

## 2. Statistical evaluation of results

### 2.1. Trueness criterion

The trueness criterion considers the correct quantification of the actual analyte concentration in the sample. The trueness of the results is assessed as the coverage of the spiked level in %. The coverage of the spiked level is calculated according to the equation below:

$$\text{coverage of the spiked level} = \frac{x}{sl} * 100$$

(x = reported result; sl = spiked level)

Accepted range:

Results, which correspond to a recovery of 70 to 120 % of the spiked level, are considered satisfying in this laboratory performance assessment in accordance with the guidelines of the BNN<sup>1</sup>. A non-commercial rounding is applied during the calculation of the accepted ranges (two significant figures).

Examples:

- A recovery of 70 % of the spiked level of Glyphosate (spiked level: 0.042 mg/kg) corresponds to an arithmetical value of 0.0294 mg/kg, which is rounded to the next lower figure: 0.029 mg/kg (slight increase of the accepted range).
- A recovery of 120 % of the spiked level of Pirimiphos-methyl (spiked level: 0.023 mg/kg) corresponds to an arithmetical value of 0.0276mg/kg. 0.0276 mg/kg is rounded to the next higher figure: 0.028 mg/kg (also slight increase of the accepted range).

## 2.2. Comparability criterion

The comparability criterion is for information only. The comparability of results is evaluated according to the z-score model based on an assigned value and the target standard deviation (acc. to Horwitz).

### Assigned value

The assigned value  $x_{pt}$  is the robust mean, which is derived from the results of the participants according to ISO13528, Algorithm A<sup>2</sup>. The Winsorisation algorithm is applied to minimise the influence of outliers.

The assigned values are subject to commercial rounding and are presented with an accuracy of three significant figures.

### z-score

The z-score is derived of the result  $x_i$  of each participant, the assigned value  $x_{pt}$  and the target standard deviation according to Horwitz  $\sigma_H^{2,3}$ :

$$z - score = \frac{x_i - x_{pt}}{\sigma_H}$$

The z-scores are provided for information purposes only (see table 2 to 9).

<sup>1</sup> BNN, Guidelines for laboratory approval by Bundesverband Naturkost Naturwaren (BNN) e. V. (Federal Association for Natural Foods and Natural Products inc. soc.), <http://n-bnn.de/sites/default/dateien/GuidelinesBNNLabApprovalSeptember2015.pdf>.

<sup>2</sup> Statistical methods for use in proficiency testing by interlaboratory comparison. ISO 13528:2015. Corrected version 2016-10-15.

<sup>3</sup> Horwitz W. Evaluation of Analytical Methods Used for Regulation of Foods and Drugs. Anal Chem. 1982;54(1):67A–76A.

### 3. Results

The laboratories received the test samples without prior announcement. Upon receipt of the parcel, the laboratories were informed about the test, the type of test material and the scope of the test by an enclosed instruction letter. The laboratories were requested to apply the pesticide multi residue methods (with GC and LC modules) plus single residue methods for the quantification of Glyphosate, AMPA and Trimethylsulfonium cation.

Twenty laboratories across six European countries (Belgium, France, Germany, Italy, Netherlands, and Spain) took part in the laboratory performance assessment. All participants kept the term of results submission and were considered for evaluation. Each laboratory was given a randomly selected identifier, hereinafter referred to as laboratory code.

The laboratories reported all sought and found pesticides, the corresponding recoveries, the reporting limits (RL) as well as the scope of the applied analytical methods.

A summary of the overall performance of the labs is provided in table 1. A more detailed evaluation of the results of the participants is presented in tables 2 to 9 (pp. 11-18) and in figures 1 to 8 (pp. 19-26).

All laboratories identified Cyfluthrin, Diflufenican, Piperonyl butoxide, and Pirimiphos-methyl correctly. None of the labs reported false positive results. Sulfoxaflor was out of the scope of 5 laboratories (lab 7, 9, 13, 14 and 20). Glyphosate was below the reporting limit of one laboratory (lab 6). AMPA was out of the scope of one laboratory (lab 6), and Trimethylsulfonium cation was out of the scope of 7 laboratories (lab 4, 6, 8, 12, 13, 14 and 17).

More than 90 % of the laboratories (at least 18 out of 20 labs) quantified Cyfluthrin, Diflufenican, Piperonyl butoxide, Pirimiphos-methyl and Glyphosate correctly and passed the trueness criterion.

#### Cyfluthrin

Only one laboratory (lab 9) did not quantify Cyfluthrin with a satisfying recovery of the spiked level (249 %). All other 19 participants (95 %) reported results within the target recovery range of 70 – 120 % of the spiked level. The recoveries vary between 70 and 108 %. The assigned value is slightly below the actually spiked level (91 %).

#### Diflufenican

The general result of the analytical performance here is brilliant. All participants (100 %) reported satisfying results in terms of the target recovery of 70 – 120 % of the spiked level. The recoveries vary between 82 and 118 %. The assigned value is slightly below the actually spiked level (95 %).

#### Piperonyl butoxide

The general result of the analytical performance here is also brilliant. All participants (100 %) reported satisfying results in terms of meeting the target recovery of 70 – 120 % of the spiked level. The recoveries vary between 78 and 110 %. The assigned value is slightly below the actually spiked level (96 %).

### Pirimiphos-methyl

19 out of 20 participants (95 %) reported satisfying results in terms of meeting the target recovery of 70 – 120 % of the spiked level. One laboratory (lab 5) reported too high results (135 % recovery). The recoveries of the participants vary between 70 and 135 %. The assigned value is slightly above the actually spiked level (103 %).

### Sulfoxaflor

14 laboratories (70 %) reported satisfying results in terms of meeting the target recovery of 70 – 120 % of the spiked level. 5 laboratories (lab 7, 9, 13, 14 and 20) did not include this pesticide within their analytical scope thus they reported no result for Sulfoxaflor. One laboratory (lab 5) reported too high results for Sulfoxaflor (154 % recovery of the actually spiked level). The assigned value is very closed to the actually spiked level (spiked level: 0,67 mg/kg, assigned value: 0,677 mg/kg).

### Glyphosate

18 out of 20 participants (90 %) reported satisfying results for Glyphosate in terms of meeting the target recovery of 70 – 120 % of the spiked level. One laboratory (lab 4) reported a too high result (152 % recovery of the spiked level). Another laboratory (lab 6) had a too high reporting limit (0,05 mg/kg) compared to the spiked level (0,042 mg/kg) for Glyphosate and therefore did not report a result for Glyphosate. The assigned value of Glyphosate is slightly above the spiked level (102 % of the spiked level).

### AMPA

16 laboratories (80 %) reported satisfying results in terms of meeting the target recovery of 70 – 120 % of the spiked level. Three laboratories (lab 12, 14 and 15) reported too low results (63, 50 respectively 65 % recovery of the spiked level), and one laboratory (lab 6) does not have AMPA within its analytical scope. The assigned value corresponds to 84 % recovery of the spiked level.

### Trimethylsulfonium cation (Trimesium)

This analyte was the most challenging of the ring test. 7 laboratories (lab 4, 6, 8, 12, 13, 14 and 17) did not have this analyte within their analytical scope. 3 other laboratories (lab 1, 5 and 7) reported too high results outside the target recovery of 70 – 120 % of the spiked level. As a conclusion, 10 laboratories reported satisfying results in terms of meeting the target recovery of 70 – 120 % of the spiked level. The assigned value corresponds to 105 % recovery of the spiked level.

#### Additional remarks of the participants:

- Lab 1: Trimethyl-sulfonium cation is not part of the routine scope yet.
- Lab 4: Trimethyl-sulfonium cation is not part of our analytical scope. The method for the determination of Glyphosate and AMPA is based on FMOC-derivatisation. Thus, a determination of the recovery is not possible.
- Lab 6: Traces of Cyanazin were detected (< 0,01 mg/kg).
- Lab 8: Trimethyl-sulfonium cation is not part of the analytical scope.
- Lab 12: Trimethyl sulfonium cation is not in our scope.
- Lab 13: Trimethyl-sulfonium cation is not part of our scope.
- Lab 17: Trimethyl-sulfonium cation was not analysed. It is not in the Scope of our laboratory.
- Lab 19: Hexaconazole: 0,003 mg/kg.

## 4. Conclusion

- All laboratories identified Cyfluthrin, Diflufenican, Piperonyl butoxide, and Pirimiphos-methyl correctly. None of the laboratories reported false positive results.
- Some pesticides (Sulfoxaflor, AMPA, and Trimethylsulfonium cation) were not within the analytical scope of all participating laboratories.
- One pesticide (Glyphosate) was spiked at a concentration level below the reporting limit of one laboratory.
- Each of the pesticides Cyfluthrin, Diflufenican, Piperonlyl butoxide, Pirimiphos-methyl and Glyphosate was quantified correctly by at least 90 % of the laboratories (at least 18 out of 20 labs).
- Diflufenican and Piperonyl butoxide are the analytes with the best analytical performance of the labs. All participants (100 %) reported satisfying results for these two pesticides.
- 84 % of the labs (16 out of 19) quantified AMPA correctly, 93 % of the labs (14 out of 15) reported satisfying results for Sulfoxaflor (one lab does not cover AMPA and 5 labs do not cover Sulfoxaflor in their analytical scopes).
- The most challenging parameter in the test is Trimethylsulfonium cation. Only 10 laboratories were able to report correct results of this parameter.
- A slight tendency towards an overestimation is observed for Trimethylsulfonium cation.
- Seven laboratories quantified all eight parameters correctly (labs 2, 3, 10, 11, 16, 18, and 19).

## 5. Tables and figures

Table 1: Summary of the overall performance

	Cyfluthrin	Diflufenican	Piperonyl butoxide	Pirimiphos-methyl	Sulfoxaflor	Glyphosate	AMPA	Trimethylsulfonium <sup>+</sup>
Lab code	Trueness							
1	yes	yes	yes	yes	yes	yes	yes	no
2	yes	yes	yes	yes	yes	yes	yes	yes
3	yes	yes	yes	yes	yes	yes	yes	yes
4	yes	yes	yes	yes	yes	no	yes	-
5	yes	yes	yes	no	no	yes	yes	no
6	yes	yes	yes	yes	yes	no	-	-
7	yes	yes	yes	yes	-	yes	yes	no
8	yes	yes	yes	yes	yes	yes	yes	-
9	no	yes	yes	yes	-	yes	yes	yes
10	yes	yes	yes	yes	yes	yes	yes	yes
11	yes	yes	yes	yes	yes	yes	yes	yes
12	yes	yes	yes	yes	yes	yes	no	-
13	yes	yes	yes	yes	-	yes	yes	-
14	yes	yes	yes	yes	-	yes	no	-
15	yes	yes	yes	yes	yes	yes	no	yes
16	yes	yes	yes	yes	yes	yes	yes	yes
17	yes	yes	yes	yes	yes	yes	yes	-
18	yes	yes	yes	yes	yes	yes	yes	yes
19	yes	yes	yes	yes	yes	yes	yes	yes
20	yes	yes	yes	yes	-	yes	yes	yes

Table 2: Results of Cyfluthrin

Cyfluthrin					
	Spiked level [mg/kg]	Assigned value [mg/kg]	Assigned value in % of spiked level	Accepted range [mg/kg]	
Lab code	Result [mg/kg]	RL [mg/kg]	z-score	Result in % of Spike	Trueness: passed
1	0,036	0,010	0,3	97	yes
2	0,036	0,01	0,3	97	yes
3	0,036	0,010	0,3	97	yes
4	0,034	0,01	0,0	92	yes
5	0,038	0,010	0,6	103	yes
6	0,031	0,01	-0,4	84	yes
7	0,040	0,005	0,8	108	yes
8	0,033	0,01	-0,1	89	yes
9	0,092	0,010	7,8	249	no
10	0,035	0,01	0,2	95	yes
11	0,033	0,01	-0,1	89	yes
12	0,030	0,01	-0,5	81	yes
13	0,034	0,010	0,0	92	yes
14	0,028	0,020	-0,8	76	yes
15	0,034	0,01	0,0	92	yes
16	0,035	0,005	0,2	95	yes
17	0,026	0,01	-1,1	70	yes
18	0,030	0,010	-0,5	81	yes
19	0,032	0,01	-0,2	86	yes
20	0,034	0,010	0,0	92	yes

RL: reporting limit

Cyfluthrin - trueness criterion: accepted range: 70 to 120 % of the spiked level

Table 3: Results of Diflufenican

Diflufenican					
	Spiked level [mg/kg]	Assigned value [mg/kg]	Assigned value in % of spiked level	Accepted range [mg/kg]	
Lab code	Result [mg/kg]	RL [mg/kg]	z-score	Result in % of Spike	Trueness: passed
1	0,036	0,010	0,7	109	yes
2	0,033	0,01	0,2	100	yes
3	0,027	0,010	-0,6	82	yes
4	0,033	0,01	0,2	100	yes
5	0,037	0,010	0,8	112	yes
6	0,032	0,01	0,1	97	yes
7	0,039	0,01	1,1	118	yes
8	0,032	0,01	0,1	97	yes
9	0,026	0,003	-0,8	79	yes
10	0,030	0,01	-0,2	91	yes
11	0,029	0,01	-0,3	88	yes
12	0,029	0,01	-0,3	88	yes
13	0,027	0,010	-0,6	82	yes
14	0,035	0,020	0,5	106	yes
15	0,033	0,01	0,2	100	yes
16	0,027	0,010	-0,6	82	yes
17	0,027	0,01	-0,6	82	yes
18	0,032	0,010	0,1	97	yes
19	0,031	0,01	-0,1	94	yes
20	0,034	0,010	0,4	103	yes

RL: reporting limit

Diflufenican - trueness criterion: accepted range: 70 to 120 % of the spiked level

Table 4: Results of Piperonyl butoxide

<b>Piperonyl butoxide</b>					
Lab code	Result [mg/kg]		RL [mg/kg]	z-score	Result in % of Spike
	Accepted range [mg/kg]	Assigned value [mg/kg]			
	Assigned value in % of spiked level				96
	0,070	-			0,12
1	0,090	0,010	0,010	-0,3	90
2	0,097	0,01	0,01	0,0	97
3	0,090	0,010	0,010	-0,3	90
4	0,109	0,01	0,01	0,6	109
5	0,098	0,010	0,010	0,1	98
6	0,10	0,01	0,01	0,2	100
7	0,078	0,005	0,005	-0,9	78
8	0,10	0,01	0,01	0,2	100
9	0,094	0,003	0,003	-0,1	94
10	0,098	0,01	0,01	0,1	98
11	0,094	0,01	0,01	-0,1	94
12	0,094	0,01	0,01	-0,1	94
13	0,11	0,010	0,010	0,7	110
14	0,085	0,010	0,010	-0,5	85
15	0,096	0,01	0,01	0,0	96
16	0,10	0,005	0,005	0,2	100
17	0,087	0,01	0,01	-0,4	87
18	0,096	0,010	0,010	0,0	96
19	0,103	0,01	0,01	0,3	103
20	0,101	0,010	0,010	0,2	101

RL: reporting limit

Piperonyl butoxide - trueness criterion: accepted range: 70 to 120 % of the spiked level

Table 5: Results of Pirimiphos-methyl

<b>Pirimiphos-methyl</b>					
	Spiked level [mg/kg]	Assigned value [mg/kg]	Assigned value in % of spiked level	Accepted range [mg/kg]	
Lab code	Result [mg/kg]	RL [mg/kg]	z-score	Result in % of the spiked level	Trueness: passed
1	0,024	0,010	0,1	104	yes
2	0,024	0,01	0,1	104	yes
3	0,024	0,010	0,1	104	yes
4	0,027	0,01	0,7	117	yes
5	0,031	0,010	1,4	135	no
6	0,016	0,01	-1,5	70	yes
7	0,028	0,005	0,9	122	yes
8	0,025	0,01	0,3	109	yes
9	0,021	0,003	-0,5	91	yes
10	0,025	0,01	0,3	109	yes
11	0,022	0,01	-0,3	96	yes
12	0,027	0,01	0,7	117	yes
13	0,024	0,010	0,1	104	yes
14	0,016	0,005	-1,5	70	yes
15	0,024	0,01	0,1	104	yes
16	0,024	0,005	0,1	104	yes
17	0,020	0,01	-0,7	87	yes
18	0,021	0,010	-0,5	91	yes
19	0,020	0,002	-0,7	87	yes
20	0,026	0,010	0,5	113	yes

RL: reporting limit

Pirimiphos-methyl - trueness criterion: accepted range: 70 to 120 % of the spiked level

Table 6: Results of Sulfoxaflor

<b>Sulfoxaflor</b>					
	Spiked level [mg/kg]	Assigned value [mg/kg]	Assigned value in % of spiked level	Accepted range [mg/kg]	
Lab code	Result [mg/kg]	RL [mg/kg]	z-score	Result in % of the Spike	Trueness: passed
1	0,060	0,010	-0,5	90	yes
2	0,061	0,01	-0,4	91	yes
3	0,063	0,010	-0,3	94	yes
4	0,073	0,01	0,4	109	yes
5	0,103	0,010	2,5	154	no
6	0,057	0,01	-0,7	85	yes
7	oos	-	-	-	-
8	0,067	0,01	0,0	100	yes
9	oos	-	-	-	-
10	0,070	0,01	0,2	104	yes
11	0,068	0,01	0,1	101	yes
12	0,076	0,01	0,6	113	yes
13	oos	-	-	-	-
14	oos	-	-	-	-
15	0,067	0,01	0,0	100	yes
16	0,060	0,010	-0,5	90	yes
17	0,075	0,01	0,6	112	yes
18	0,076	0,010	0,6	113	yes
19	0,063	0,01	-0,3	94	yes
20	oos	-	-	-	-

RL: reporting limit; oos: out of scope

Sulfoxaflor - trueness criterion: accepted range: 70 to 120 % of the spiked level

Table 7: Results of Glyphosate

Glyphosate					
	True value (spiked 0.037 + 0.005 incurred) [mg/kg]	Assigned value [mg/kg]	Assigned value in % of true value	Accepted range [mg/kg]*	
Lab code	Result [mg/kg]	RL [mg/kg]	z-score	Result in % of the Spike	Trueness: passed
1	0,040	0,010	-0,3	95	yes
2	0,042	0,01	-0,1	100	yes
3	0,047	0,010	0,4	112	yes
4	0,064	0,01	2,3	152	no
5	0,043	0,010	0,0	102	yes
6	n.d.	0,05	-4,5	-	no
7	0,041	0,01	-0,2	98	yes
8	0,044	0,01	0,1	105	yes
9	0,045	0,010	0,2	107	yes
10	0,035	0,01	-0,8	83	yes
11	0,047	0,01	0,4	112	yes
12	0,047	0,01	0,4	112	yes
13	0,043	0,01	0,0	102	yes
14	0,032	0,020	-1,1	76	yes
15	0,047	0,01	0,4	112	yes
16	0,045	0,010	0,2	107	yes
17	0,043	0,01	0,0	102	yes
18	0,036	0,010	-0,7	86	yes
19	0,044	0,01	0,1	105	yes
20	0,038	0,010	-0,5	90	yes

RL: reporting limit; n.d.: not detected

Glyphosate - trueness criterion: accepted range: 70 to 120 % of the spiked level

Table 8: Results of AMPA

AMPA					
Lab code	Result [mg/kg]	RL [mg/kg]	z-score	Result in % of Spike	Trueness passed
1	0,036	0,010	-0,5	75	yes
2	0,043	0,01	0,3	90	yes
3	0,048	0,010	0,9	100	yes
4	0,046	0,01	0,7	96	yes
5	0,048	0,010	0,9	100	yes
6	oos	-	-	-	-
7	0,037	0,01	-0,4	77	yes
8	0,043	0,01	0,3	90	yes
9	0,042	0,010	0,2	88	yes
10	0,053	0,01	1,4	110	yes
11	0,048	0,01	0,9	100	yes
12	0,030	0,01	-1,2	63	no
13	0,040	0,010	0,0	83	yes
14	0,024	0,020	-1,8	50	no
15	0,031	0,01	-1,0	65	no
16	0,043	0,020	0,3	90	yes
17	0,041	0,01	0,1	85	yes
18	0,036	0,010	-0,5	75	yes
19	0,039	0,01	-0,1	81	yes
20	0,033	0,01	-0,8	69	yes

RL: reporting limit; oos: out of scope

AMPA - trueness criterion: accepted range 70 to 120 % of the spiked level

Table 9: Results of Trimethyl sulfonium cation

Trimethyl sulfonium cation					
Lab code	Result [mg/kg]	RL [mg/kg]	z-score	Result in % of Spike	Trueness: passed
				Accepted range [mg/kg]	
1	0,094*	0,010	1,9	149	no
2	0,062	0,01	-0,3	98	yes
3	0,059	0,010	-0,5	94	yes
4	oos	-	-	-	-
5	0,31**	0,010	17	492	no
6	oos	-	-	-	-
7	0,083	0,01	1,2	132	no
8	oos	-	-	-	-
9	0,052	0,010	-1,0	83	yes
10	0,056	0,01	-0,7	89	yes
11	0,055	0,01	-0,8	87	yes
12	oos	-	-	-	-
13	oos	-	-	-	-
14	oos	-	-	-	-
15	0,060	0,01	-0,4	95	yes
16	0,064	0,020	-0,1	102	yes
17	oos	-	-	-	-
18	0,068	0,010	0,1	108	yes
19	0,074	0,01	0,5	117	yes
20	0,075	0,010	0,6	119	yes

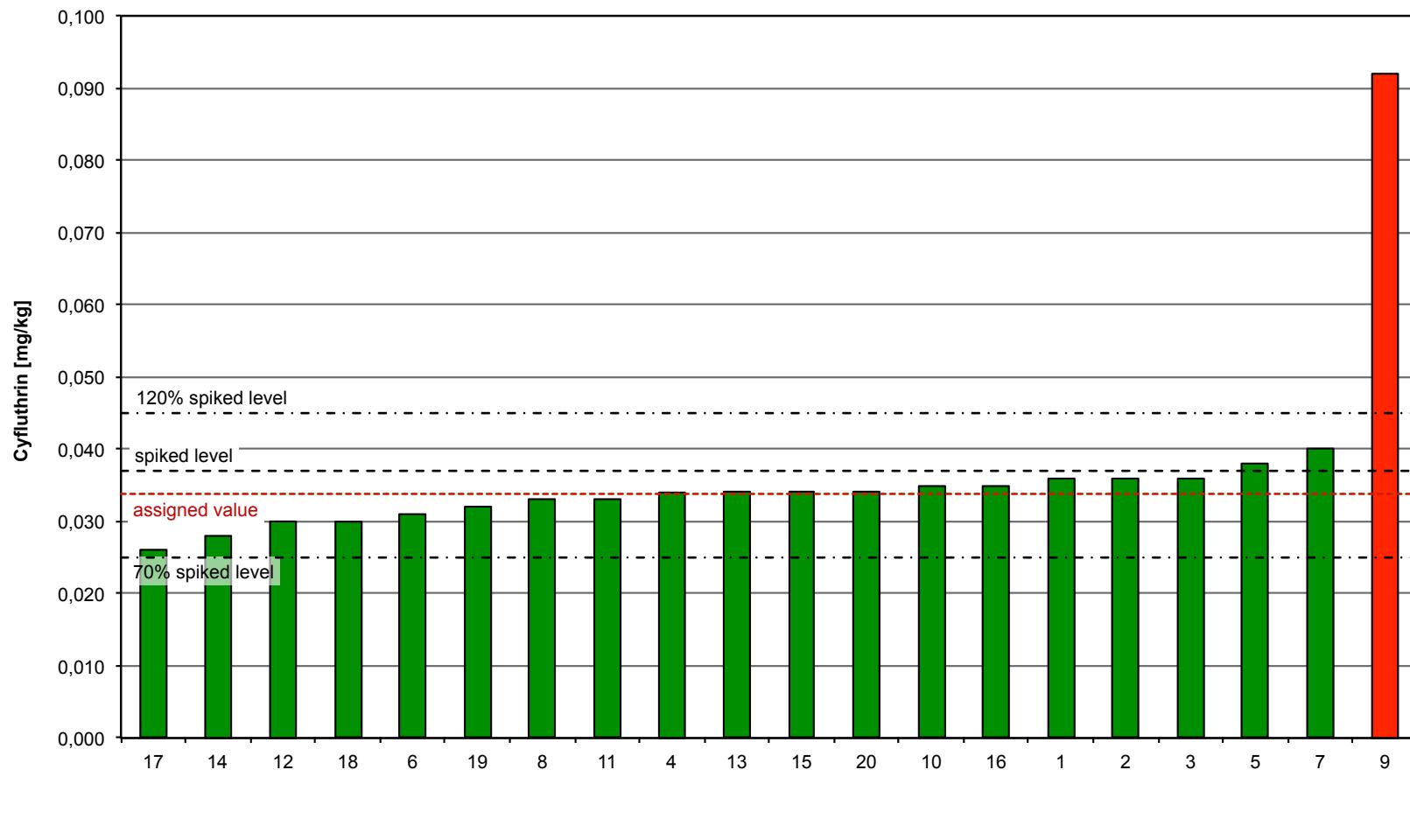
\* Trimethyl-sulfonium cation is not part of the routine scope yet.

\*\* The result of lab 5 was not considered for the calculation of the assigned value.

RL: reporting limit; oos: out of scope

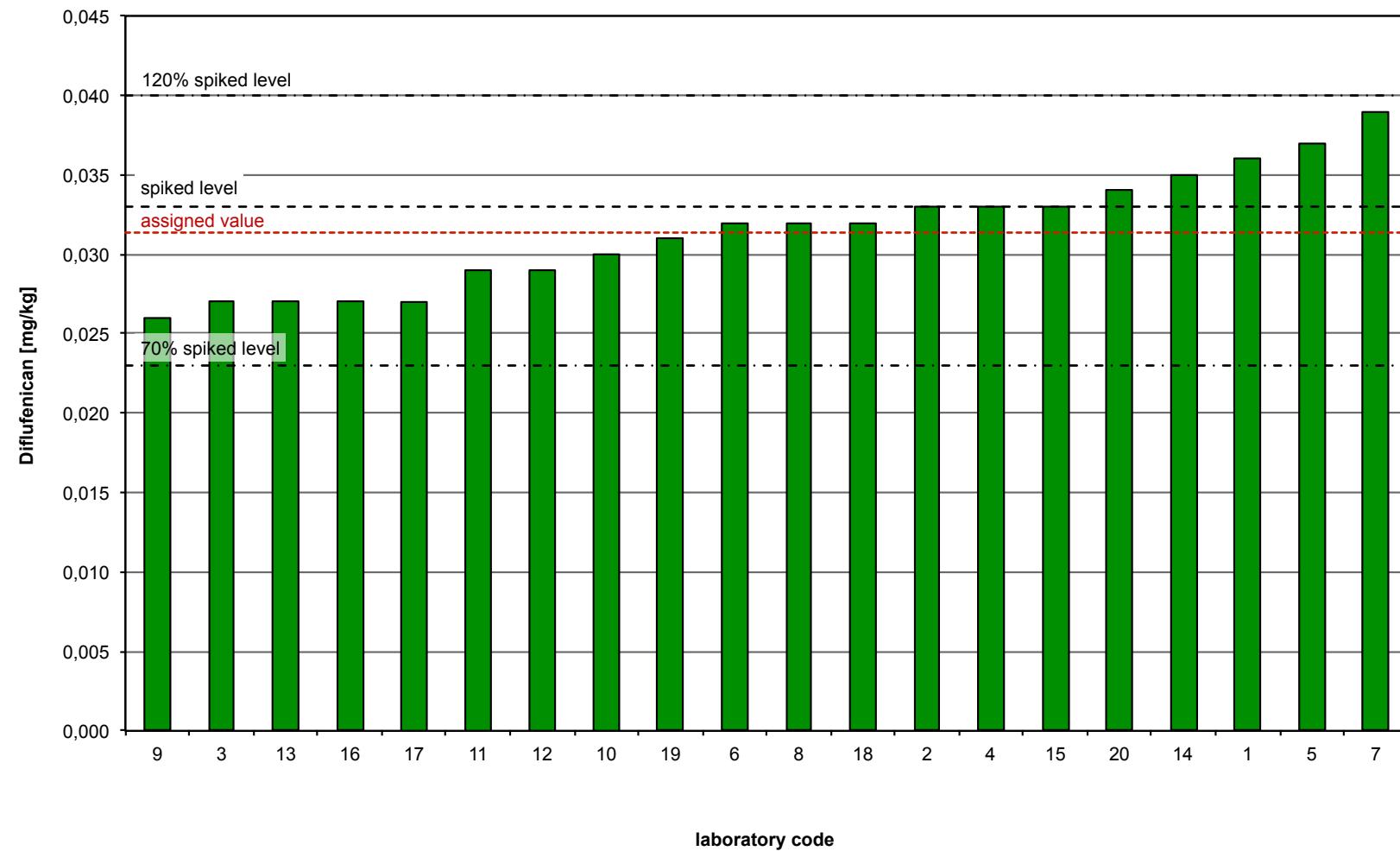
Trimethyl sulfonium cation - trueness criterion: accepted range 70 to 120 % of the spiked level

Figure 1: Assessment of Cyfluthrin (trueness)



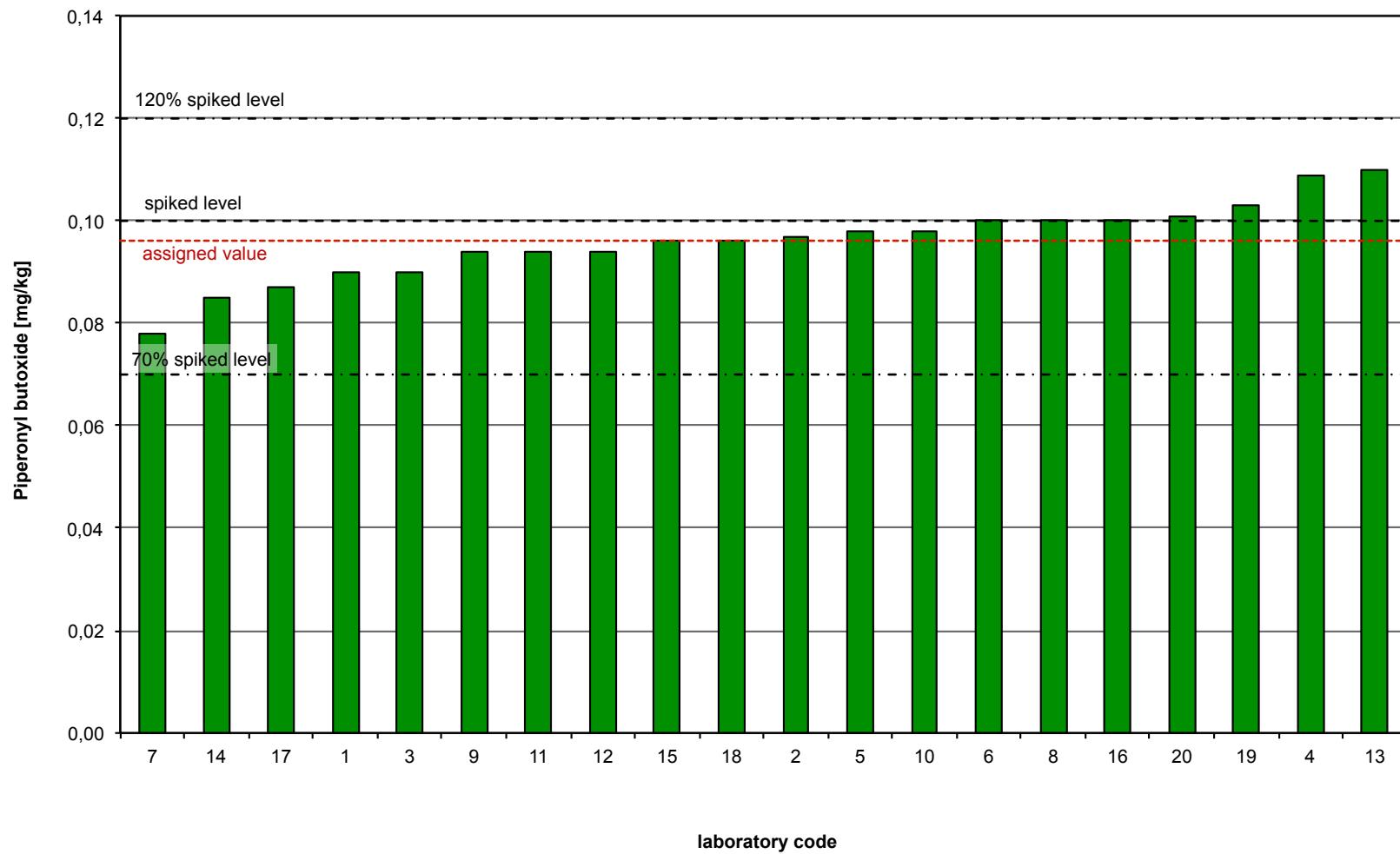
Green: satisfactory results, red: dissatisfactory results

Figure 2: Assessment of Diflufenican (trueness)



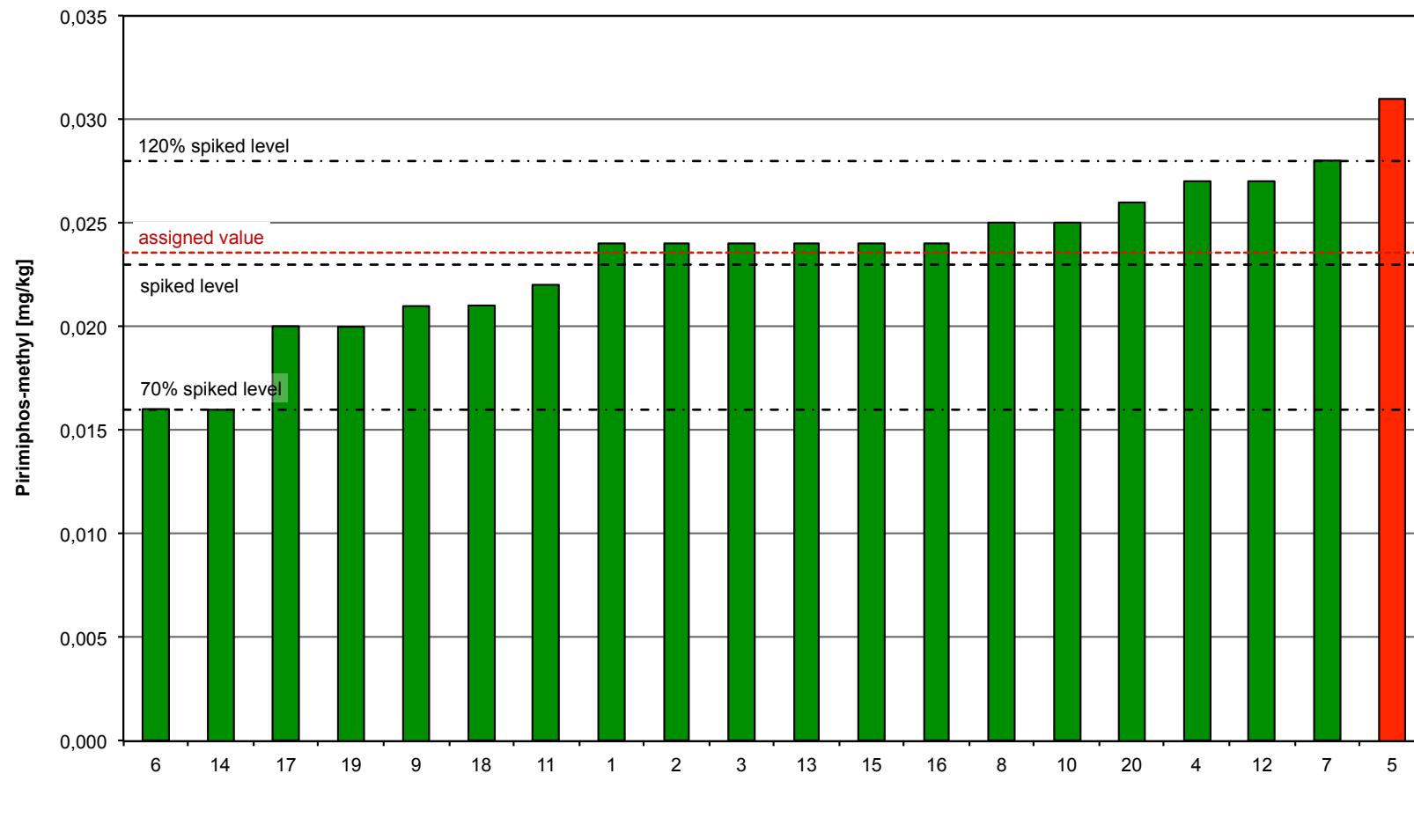
Green: satisfactory results, red: dissatisfactory results

Figure 3: Assessment of Piperonyl butoxide (trueness)



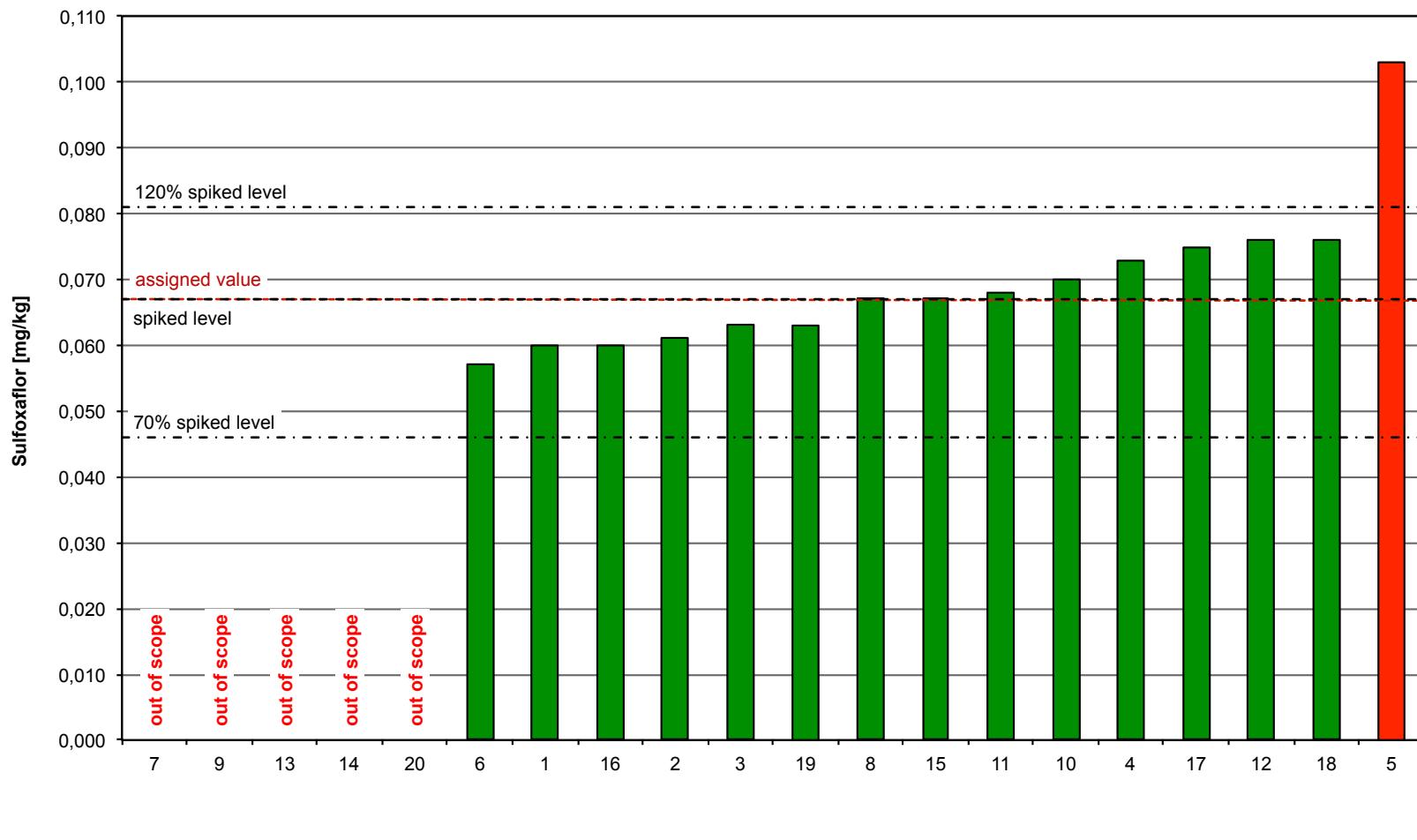
Green: satisfactory results, red: dissatisfactory results

Figure 4: Assessment of Pirimiphos-methyl (trueness)



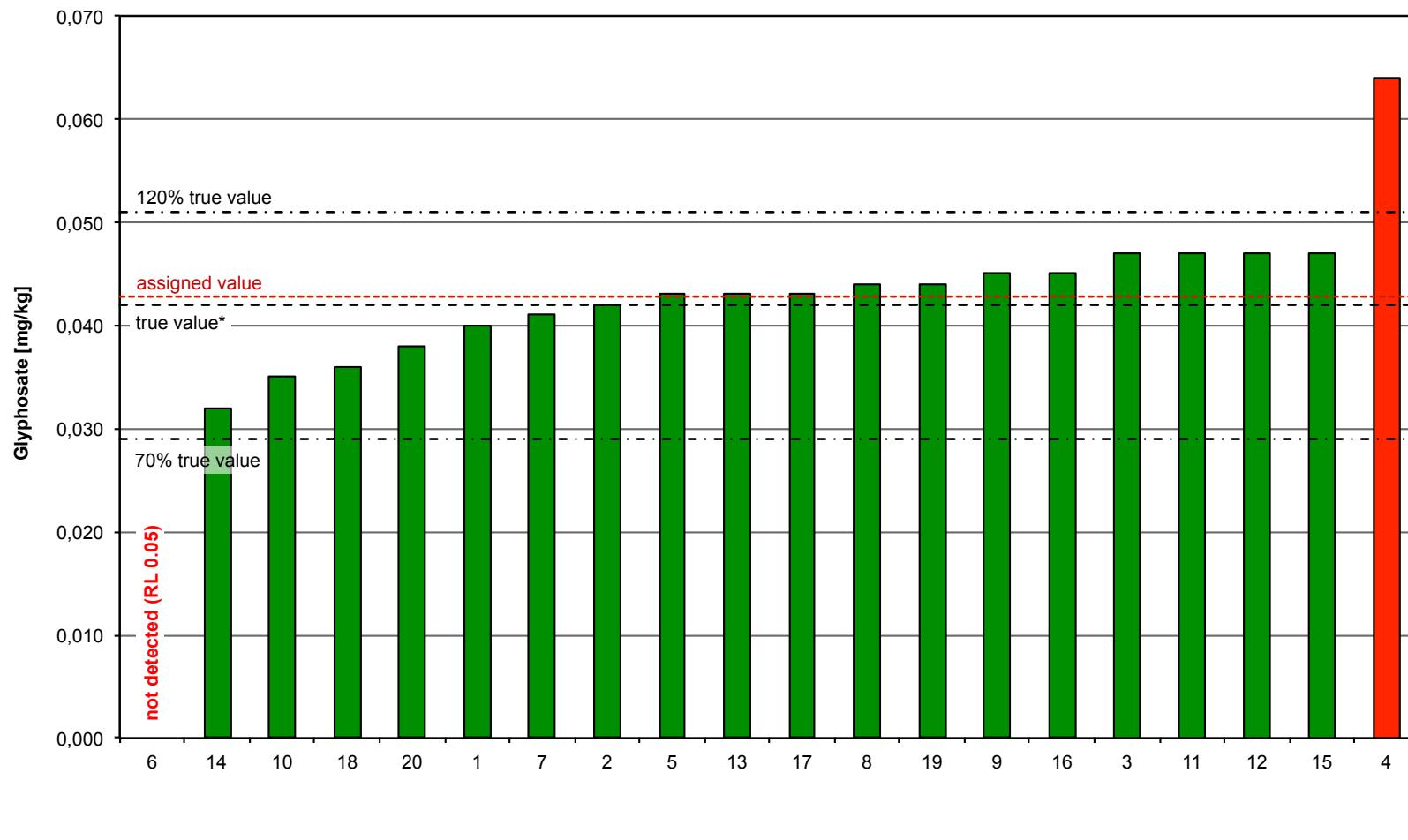
Green: satisfactory results, red: dissatisfactory results

Figure 5: Assessment of Sulfoxaflor (trueness)



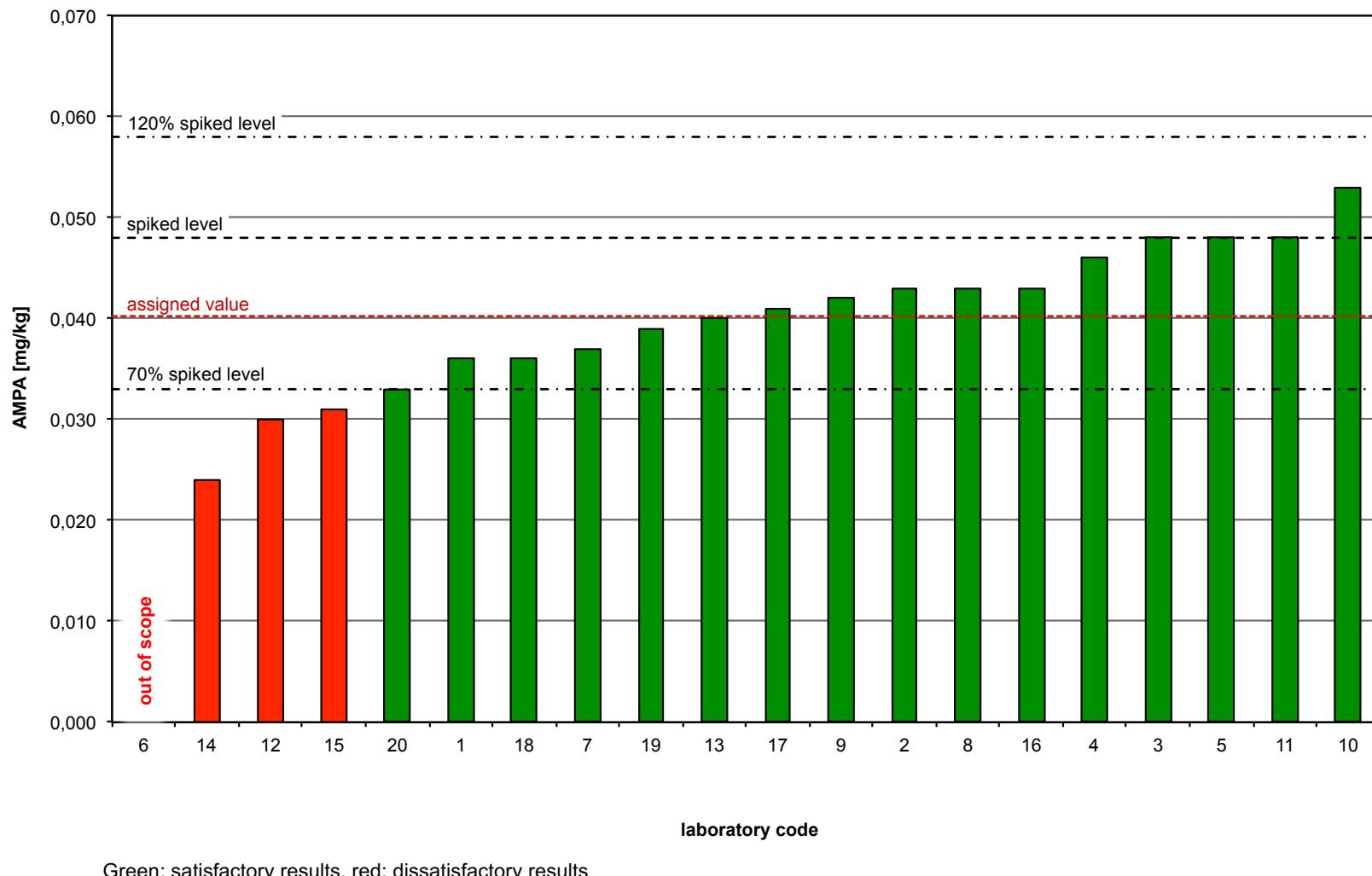
Green: satisfactory results, red: dissatisfactory results

Figure 6: Assessment of Glyphosate (trueness)

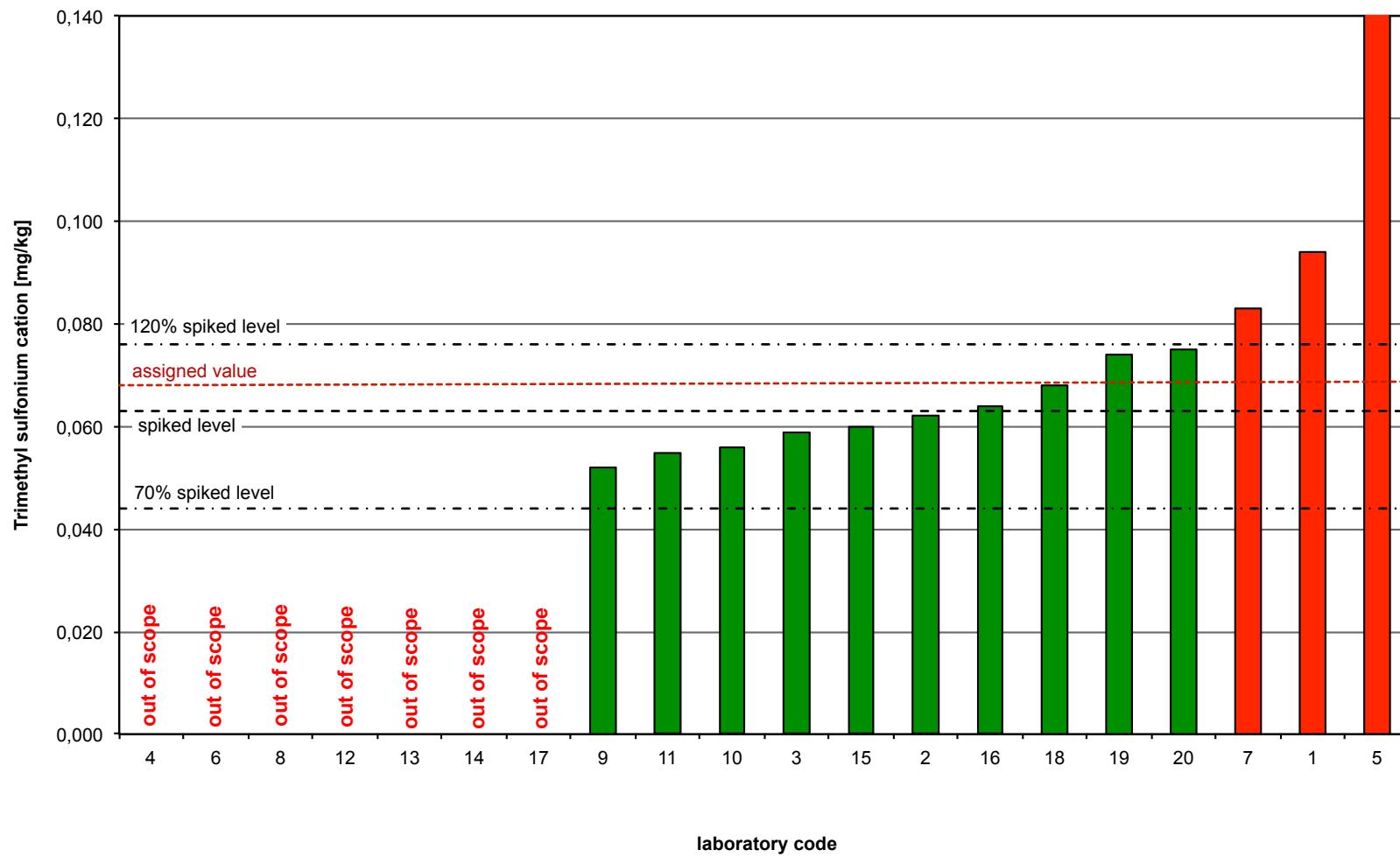


Green: satisfactory results, red: dissatisfactory results, RL: Reporting limit

Figure 7: Assessment of AMPA (trueness)



*Figure 8: Assessment of Trimethylsulfonium Cation (trueness)*



Green: satisfactory results, red: dissatisfactory results

## 6. Homogeneity testing

Seven randomly chosen test samples were used for homogeneity testing. Each subsample was analysed for all spiked pesticides in duplicate. The results confirm the homogeneous distribution of the pesticides in the test material and the spiked levels (tables 10 and 11).

*Table 10. Results of the homogeneity testing (part 1)*

Subsample No.	Replicate No.	beta-Cyfluthrin [mg/kg]	Diflufenican [mg/kg]	Pirimiphos-methyl [mg/kg]	Sulfoxaflor [mg/kg]
Blank	1	n.d.	n.d.	n.d.	n.d.
	2	n.d.	n.d.	n.d.	n.d.
1	1	0,037	0,036	0,028	0,066
	2	0,039	0,036	0,028	0,064
2	1	0,038	0,035	0,027	0,061
	2	0,037	0,031	0,025	0,057
3	1	0,039	0,034	0,025	0,060
	2	0,038	0,035	0,027	0,064
4	1	0,038	0,032	0,026	0,058
	2	0,040	0,037	0,029	0,067
5	1	0,038	0,036	0,026	0,062
	2	0,039	0,034	0,027	0,061
6	1	0,039	0,035	0,026	0,063
	2	0,040	0,035	0,026	0,064
7	1	0,039	0,034	0,027	0,064
	2	0,040	0,035	0,027	0,063
Mean [mg/kg]		0,039	0,035	0,027	0,062
Standard deviation [mg/kg]		0,0011	0,0015	0,0012	0,0028
Coefficient of variation [%]		2,8	4,4	4,5	4,5
Spiked level [mg/kg]		0,037	0,033	0,023	0,067
Recovery of the spiked level [%]		104	105	116	93

n.d. = not detected (LOD = 0,005 mg/kg)

Table 11. Results of the homogeneity testing (part 2)

Subsample No.	Replicate No.	Piperonyl butoxide [mg/kg]	Glyphosate [mg/kg]	AMPA [mg/kg]	Trimesium [mg/kg]
Blank	1	n.d.	0,005	n.d.	n.d.
	2	n.d.	0,005	n.d.	n.d.
1	1	0,097	0,041	0,042	0,063
	2	0,097	0,036	0,042	0,067
2	1	0,095	0,037	0,044	0,064
	2	0,093	0,035	0,042	0,065
3	1	0,093	0,034	0,045	0,064
	2	0,101	0,040	0,044	0,064
4	1	0,094	0,035	0,046	0,067
	2	0,107	0,040	0,043	0,066
5	1	0,105	0,035	0,042	0,067
	2	0,101	0,036	0,043	0,065
6	1	0,107	0,041	0,046	0,063
	2	0,107	0,036	0,046	0,063
7	1	0,112	0,036	0,045	0,063
	2	0,108	0,040	0,043	0,063
Mean [mg/kg]		0,101	0,037	0,044	0,065
Standard deviation [mg/kg]		0,0064	0,0026	0,0016	0,0015
Coefficient of variation [%]		6,3	6,9	3,6	2,3
Spiked level [mg/kg]		0,1	0,037	0,048	0,063
Recovery of the spiked level [%]		101	100	91	102

n.d. = not detected (LOD = 0,005 mg/kg)

Trimesium = Trimethyl sulfonium cation

## 7. Stability testing

After the closure of transmission of results the test material was re-analysed to confirm the stability of the pesticides over the period of the test. The mean of the re-analysis was compared to the mean result of the homogeneity testing (tables 10 and 11). The results confirm the stability of all analytes throughout the test (recoveries of 89 to 104 % of the homogeneity testing).

*Table 12. Results of the stability testing*

Pesticide	Mean result from homogeneity testing [mg/kg]	Mean level at closure of transmission of results [mg/kg]	Recovery compared to the mean of the homogeneity testing [%]
beta-Cyfluthrin	0,039	0,039	100
Diflufenican	0,035	0,035	100
Pirimiphos-methyl	0,027	0,025	92
Sulfoxaflor	0,062	0,062	100
Piperonyl butoxide	0,101	0,105	104
Glyphosate	0,037	0,038	103
AMPA	0,044	0,039	89
Trimesium	0,065	0,066	102

Trimesium = Trimethyl sulfonium cation