

Laboratory Performance Assessment

Analysis of Pesticides in Rice

(Module 2 of BNN lab approval system)

Report

September 2024



Summary

The laboratory performance assessment related to pesticides in rice was designed and organised by Lach & Bruns in September 2024 on behalf of BNN e.V. (Bundesverband Naturkost Naturwaren, Berlin, Germany).

The test material consists of white rice grains, which were spiked with 8 pesticides:

Clothianidin, Deltamethrin, Dimethomorph, Dinotefuran, Imidacloprid, Isoprothiolane, Metribuzin, and Tricyclazole. All eight substances were assessed by application of the **trueness criterion** (70% -120% of the spiking level).

The entire batch of the rice was thoroughly but carefully mixed avoiding any crushing or chopping of the grains. Subsamples of the test material were distributed to twenty (20) participants across four (4) European countries (Germany, Italy, The Netherlands, and Spain). Information with respect to the scope of analyses to be applied was provided to the laboratories in an instruction letter attached to the test sample.

All participants handed in their results before the deadline on 16th September 2024. Consequently, all results were considered for the assessment of results.

The performance assessment considers the following test criteria:

- No *false positive results*.
- Correct *identification* of the analytes with levels above 0,01 mg/kg (in total 8 analytes). Thus, no false negative results are accepted, independent whether an analyte is within the analytical scope of the laboratory or not.
- Correct *quantification* of at least 6 pesticides related to their residue definitions and the applied assessment criteria (trueness).

Based on these criteria, the laboratories were marked with one out of 3 marks, ranging from “*excellent*” to “*good*” to “*insufficient*”. Laboratories with an excellent (14 out of 20 participants) or good result (4 participants) satisfy the quality standards of BNN.

2 participants do not meet the expected requirements of BNN, as one lab reported 3 results outside the target range and one lab failed to identify Deltamethrin.

All in all, the outcome of the test is very good, as 18 of 20 laboratories (90 %) participated with good resp. excellent results.



Assessment of quantification

Analytical results within 70% - 120% of the spiked values are considered satisfying.

The overall performance is summarised as:

Substance	Spiked value [mg/kg]	Number of results	Correct quantification
Clothianidin	0.033	20	18 (90%)
Deltamethrin	0.041	19	17 (85%)
Dimethomorph	0.020	20	20 (100%)
Dinotefuran	0.046	20	19 (95%)
Imidacloprid	0.025	20	20 (100%)
Isoprothiolane	0.039	20	18 (90%)
Metribuzin	0.050	20	18 (90%)
Tricyclazole	0.032	20	20 (100%)
TOTAL		159 of 160 (99%)	150 of 160 (94%)



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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 M2 (Cereals and cereal products, rice, pulses), area pesticides.

Organic non-homogenised rice (milk-rice) was used for preparation of the test material. A sub-sample was taken and analysed (multi-method, polar pesticides, and acidic herbicides) to ensure that no incurred residues of pesticides (> 0,01 mg/kg) are present. The analysis of the sub-sample identified no levels of pesticides.

The organic rice was carefully mixed to avoid any crushing or chopping of the grains of rice. Subsamples of the non-spiked rice (ca. 200 g each) were also bottled as blank material (for internal analyses like homogeneity and stability testing only). Thereafter, the rice was spiked on the surface with *Clothianidin*, *Deltamethrin*, *Dimethomorph*, *Dinotefuran*, *Imidacloprid*, *Isoprothiolane*, *Metribuzin*, and *Tricyclazole*. For that purpose, a mix-solution of the analytes was added gradually while the grains of rice were carefully stirred to avoid crushing the grains. Careful stirring was continued after spiking to ensure a homogeneous distribution of the analytes in the test material. After spiking, subsamples of ca. 200 g were transferred into plastic bottles. The test materials were stored at -18°C in the dark until distribution.

The test samples were stored in Styrofoam boxes and cooled with dry ice during the transport to the participants of the ring test. The homogeneity and stability of the prepared test material was tested by an independent laboratory (homogeneity tests were performed one week before sample delivery date). Stability testing was performed after the last participant reported the results. The results showed sufficient stability across the entire test period. The results for homogeneity testing also confirm the homogeneity of the test material.

The samples were sent to the participating labs on September 9th, 2024, thus arriving 10th/11th September at the participating laboratories (unannounced test). Reporting of results was scheduled for 16th September 2024.

Design of BNN flaxseed test material and homogeneity/stability testing

Analyte	Spiked level (mg/kg)	homogeneity / stability average results (mg/kg)	spike level recovery rate homogeneity (in %)	spike level recovery rate stability (in %)
<i>Clothianidin</i>	0.033	0.033 / 0.023	100	70
<i>Deltamethrin</i>	0.041	0.029 / 0.029	71	71
<i>Dimethomorph</i>	0.020	0.015 / 0.014	75	70
<i>Dinotefuran</i>	0.046	0.042 / 0.031	91	67
<i>Imidacloprid</i>	0.025	0.020 / 0.018	80	72
<i>Isoprothiolane</i>	0.039	0.031 / 0.035	79	90
<i>Metribuzin</i>	0.050	0.044 / 0.040	88	80
<i>Tricyclazole</i>	0.032	0.031 / 0.028	97	88



2. Evaluation of results

Accuracy (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.

3. Results

The laboratories received the test samples without prior announcement. Upon receipt of the test sample, 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 analyse for “pesticides multi method” only.

Twenty (20) participants across four European countries (Germany, Italy, The Netherlands, and Spain) took part in the laboratory performance assessment.

All participants handed in their results before end of the deadline. All results were considered for the evaluation of results. Each laboratory was given a randomly selected identifier, hereinafter referred to as laboratory code.

The laboratories were asked to report all sought and found pesticides, 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 2. A detailed evaluation of the results of the participants is presented in tables 3 to 10 and in figures 1 to 8.

The performance of the participants has been evaluated based on the BNN requirements using the following criteria:

- No false positive results.
- No false negative results.
- Correct quantification in terms of accuracy (trueness).



The performance is evaluated as:

excellent: all criteria fulfilled (8 out of 8 results in conformity with BNN criteria).

good: single slight error (at least 7 out of 8 results in conformity with BNN criteria) AND **no** false positive AND **no** false negative result.

insufficient: more than 2 quantification deviations OR false negative result(s) OR false positive result(s).

Results in detail

Accuracy (trueness) criterion:

- **Dimethomorph, Imidacloprid, and Tricyclazole** are reported within the accepted range related to the trueness criterion (70 - 120% recovery of spike) by 20 out of 20 participants, which is an **excellent overall performance**.
- **Clothianidin, Dinotefuran, Isoprothiolane, and Metribuzin** are reported within the accepted range related to the trueness criterion (70 - 120% recovery of spike) by 19 out of 20 participants (Dinotefuran) resp. by 18 out of 20 participants (Clothianidin, Isoprothiolane, Metribuzin), which is a **very good performance** as well.
- Just **Deltamethrin** causes some challenges in the correct quantification. However, 17 participants meet the target area of 70% to 120% recovery of the spiking level (85%), which still is considered as a good overall performance. One lab missed the identification of Deltamethrin.

Excellent results (14 labs, sorted by lab code):

4 / 5 / 6 / 8 / 9 / 10 / 11 / 12 / 13 / 14 / 15 / 18 / 19 / 20

Good results (4 labs, sorted by lab code):

1 / 2 / 3 / 16

Insufficient results (2 labs, sorted by lab code):

7 / 17



4. Overview of laboratory evaluation

Table 1: laboratory evaluation

lab code	false negative	false positive	Quantification (recovery) achieved	Final evaluation based on reported results*
1	0	0	7 / 8	good
2	0	0	7 / 8	good
3	0	0	7 / 8	good
4	0	0	8 / 8	excellent
5	0	0	8 / 8	excellent
6	0	0	8 / 8	excellent
7	1	0	5 / 8	insufficient
8	0	0	8 / 8	excellent
9	0	0	8 / 8	excellent
10	0	0	8 / 8	excellent
11	0	0	8 / 8	excellent
12	0	0	8 / 8	excellent
13	0	0	8 / 8	excellent
14	0	0	8 / 8	excellent
15	0	0	8 / 8	excellent
16	0	0	7 / 8	good
17	0	0	5 / 8	insufficient
18	0	0	8 / 8	excellent
19	0	0	8 / 8	excellent
20	0	0	8 / 8	excellent

***excellent:** all criteria fulfilled (8 out of 8 results in conformity with BNN criteria);

***good:** single slight error (at least 7 out of 8 results in conformity with BNN criteria)
AND **no** false positive AND **no** false negative result;

***insufficient:** more than 2 quantification deviations OR false negative result(s) OR false positive result(s).



5. Tables and figures

Table 2: Summary of the overall performance - *recovery of spike* (1 of 3)

Lab No.	Clothianidin		Deltamethrin		Dimethomorph	
	result relative to spike [%]	criterion passed	result relative to spike [%]	criterion passed	result relative to spike [%]	criterion passed
1	94	Yes	59	No	100	Yes
2	76	Yes	80	Yes	75	Yes
3	85	Yes	98	Yes	115	Yes
4	88	Yes	95	Yes	110	Yes
5	94	Yes	73	Yes	85	Yes
6	73	Yes	73	Yes	80	Yes
7	130	No	n.r.	No	90	Yes
8	103	Yes	80	Yes	95	Yes
9	79	Yes	73	Yes	85	Yes
10	82	Yes	80	Yes	75	Yes
11	85	Yes	95	Yes	85	Yes
12	76	Yes	76	Yes	80	Yes
13	106	Yes	71	Yes	90	Yes
14	85	Yes	88	Yes	90	Yes
15	73	Yes	90	Yes	80	Yes
16	127	No	100	Yes	105	Yes
17	109	Yes	144	No	100	Yes
18	85	Yes	83	Yes	85	Yes
19	82	Yes	83	Yes	90	Yes
20	79	Yes	83	Yes	80	Yes



Table 2 (continued): Summary of the overall performance - **recovery of spike** (2 of 3)

Lab No.	Dinotefuran		Imidacloprid		Isoprothiolane	
	result relative to spike [%]	criterion passed	result relative to spike [%]	criterion passed	result relative to spike [%]	criterion passed
1	83	Yes	88	Yes	72	Yes
2	70	Yes	84	Yes	128	No
3	93	Yes	92	Yes	67	No
4	93	Yes	88	Yes	87	Yes
5	100	Yes	72	Yes	72	Yes
6	80	Yes	76	Yes	79	Yes
7	100	Yes	104	Yes	100	Yes
8	83	Yes	80	Yes	103	Yes
9	91	Yes	80	Yes	85	Yes
10	83	Yes	72	Yes	79	Yes
11	83	Yes	84	Yes	92	Yes
12	74	Yes	76	Yes	72	Yes
13	96	Yes	88	Yes	97	Yes
14	102	Yes	88	Yes	97	Yes
15	91	Yes	76	Yes	97	Yes
16	107	Yes	108	Yes	105	Yes
17	135	No	104	Yes	97	Yes
18	87	Yes	76	Yes	95	Yes
19	85	Yes	84	Yes	85	Yes
20	87	Yes	76	Yes	90	Yes



Table 2 (continued): Summary of the overall performance - **recovery of spike** (3 of 3)

Lab No.	Metribuzin		Tricyclazole	
	result relative to spike [%]	criterion passed	result relative to spike [%]	criterion passed
1	82	Yes	103	Yes
2	84	Yes	100	Yes
3	92	Yes	88	Yes
4	100	Yes	88	Yes
5	74	Yes	78	Yes
6	82	Yes	81	Yes
7	122	No	100	Yes
8	90	Yes	97	Yes
9	74	Yes	84	Yes
10	88	Yes	81	Yes
11	88	Yes	81	Yes
12	78	Yes	72	Yes
13	98	Yes	97	Yes
14	88	Yes	88	Yes
15	82	Yes	88	Yes
16	102	Yes	113	Yes
17	50	No	94	Yes
18	76	Yes	81	Yes
19	96	Yes	81	Yes
20	72	Yes	88	Yes



Table 3: Results of Clothianidin

Clothianidin			
spiked value [mg/kg]: 0.033			
Accepted range [%]: 70 - 120		Accepted range [mg/kg]: 0.0231 - 0.0396	
Lab code	result [mg/kg]	relative to spike [%]	satisfactory
1	0.031	94	Yes
2	0.025	76	Yes
3	0.028	85	Yes
4	0.029	88	Yes
5	0.031	94	Yes
6	0.024	73	Yes
7	0.043	130	No
8	0.034	103	Yes
9	0.026	79	Yes
10	0.027	82	Yes
11	0.028	85	Yes
12	0.025	76	Yes
13	0.035	106	Yes
14	0.028	85	Yes
15	0.024	73	Yes
16	0.042	127	No
17	0.036	109	Yes
18	0.028	85	Yes
19	0.027	82	Yes
20	0.026	79	Yes



Table 4: Results of Deltamethrin

Deltamethrin			
spiked value [mg/kg]: 0.041			
Accepted range [%]: 70 - 120		Accepted range [mg/kg]: 0.0287 - 0.0492	
Lab code	result [mg/kg]	relative to spike [%]	satisfactory
1	0.024	59	No
2	0.033	80	Yes
3	0.040	98	Yes
4	0.039	95	Yes
5	0.030	73	Yes
6	0.030	73	Yes
7	n.r.	n.r.	No
8	0.033	80	Yes
9	0.030	73	Yes
10	0.033	80	Yes
11	0.039	95	Yes
12	0.031	76	Yes
13	0.029	71	Yes
14	0.036	88	Yes
15	0.037	90	Yes
16	0.041	100	Yes
17	0.059	144	No
18	0.034	83	Yes
19	0.034	83	Yes
20	0.034	83	Yes

n.r.: not reported



Table 5: Results of Dimethomorph

Dimethomorph			
spiked value [mg/kg]: 0.020			
Accepted range [%]: 70 - 120		Accepted range [mg/kg]: 0.0140 - 0.0240	
Lab code	result [mg/kg]	relative to spike [%]	satisfactory
1	0.020	100	Yes
2	0.015	75	Yes
3	0.023	115	Yes
4	0.022	110	Yes
5	0.017	85	Yes
6	0.016	80	Yes
7	0.018	90	Yes
8	0.019	95	Yes
9	0.017	85	Yes
10	0.015	75	Yes
11	0.017	85	Yes
12	0.016	80	Yes
13	0.018	90	Yes
14	0.018	90	Yes
15	0.016	80	Yes
16	0.021	105	Yes
17	0.020	100	Yes
18	0.017	85	Yes
19	0.018	90	Yes
20	0.016	80	Yes



Table 6: Results of Dinotefuran

Dinotefuran			
spiked value [mg/kg]: 0.046			
Accepted range [%]: 70 - 120		Accepted range [mg/kg]: 0.0322 - 0.0552	
Lab code	result [mg/kg]	relative to spike [%]	satisfactory
1	0.038	83	Yes
2	0.032	70	Yes
3	0.043	93	Yes
4	0.043	93	Yes
5	0.046	100	Yes
6	0.037	80	Yes
7	0.046	100	Yes
8	0.038	83	Yes
9	0.042	91	Yes
10	0.038	83	Yes
11	0.038	83	Yes
12	0.034	74	Yes
13	0.044	96	Yes
14	0.047	102	Yes
15	0.042	91	Yes
16	0.049	107	Yes
17	0.062	135	No
18	0.040	87	Yes
19	0.039	85	Yes
20	0.040	87	Yes



Table 7: Results of Imidacloprid

Imidacloprid			
spiked value [mg/kg]: 0.025			
Accepted range [%]: 70 - 120		Accepted range [mg/kg]: 0.0175 - 0.0300	
Lab code	result [mg/kg]	relative to spike [%]	satisfactory
1	0.022	88	Yes
2	0.021	84	Yes
3	0.023	92	Yes
4	0.022	88	Yes
5	0.018	72	Yes
6	0.019	76	Yes
7	0.026	104	Yes
8	0.020	80	Yes
9	0.020	80	Yes
10	0.018	72	Yes
11	0.021	84	Yes
12	0.019	76	Yes
13	0.022	88	Yes
14	0.022	88	Yes
15	0.019	76	Yes
16	0.027	108	Yes
17	0.026	104	Yes
18	0.019	76	Yes
19	0.021	84	Yes
20	0.019	76	Yes



Table 8: Results of Isoprothiolane

Isoprothiolane			
spiked value [mg/kg]: 0.039			
Accepted range [%]: 70 - 120		Accepted range [mg/kg]: 0.0273 - 0.0468	
Lab code	result [mg/kg]	relative to spike [%]	satisfactory
1	0.028	72	Yes
2	0.050	128	No
3	0.026	67	No
4	0.034	87	Yes
5	0.028	72	Yes
6	0.031	79	Yes
7	0.039	100	Yes
8	0.040	103	Yes
9	0.033	85	Yes
10	0.031	79	Yes
11	0.036	92	Yes
12	0.028	72	Yes
13	0.038	97	Yes
14	0.038	97	Yes
15	0.038	97	Yes
16	0.041	105	Yes
17	0.038	97	Yes
18	0.037	95	Yes
19	0.033	85	Yes
20	0.035	90	Yes



Table 9: Results of Metribuzin

Metribuzin			
spiked value [mg/kg]: 0.050			
Accepted range [%]: 70 - 120		Accepted range [mg/kg]: 0.0350 - 0.0600	
Lab code	result [mg/kg]	relative to spike [%]	satisfactory
1	0.041	82	Yes
2	0.042	84	Yes
3	0.046	92	Yes
4	0.050	100	Yes
5	0.037	74	Yes
6	0.041	82	Yes
7	0.061	122	No
8	0.045	90	Yes
9	0.037	74	Yes
10	0.044	88	Yes
11	0.044	88	Yes
12	0.039	78	Yes
13	0.049	98	Yes
14	0.044	88	Yes
15	0.041	82	Yes
16	0.051	102	Yes
17	0.025	50	No
18	0.038	76	Yes
19	0.048	96	Yes
20	0.036	72	Yes



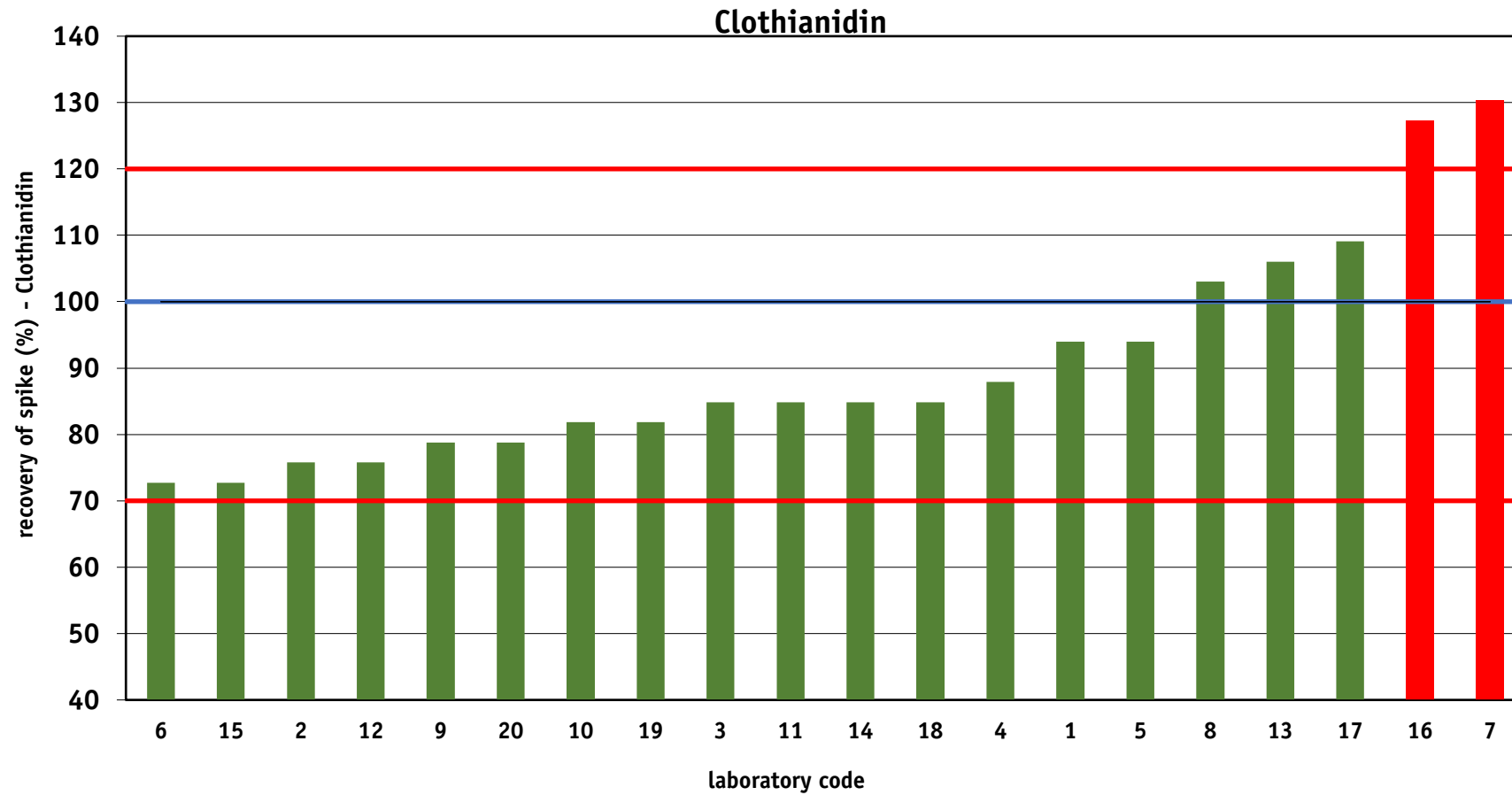
Table 10: Results of Tricyclazole

Tricyclazole			
spiked value [mg/kg]: 0.032			
Accepted range [%]: 70 - 120		Accepted range [mg/kg]: 0.0224 - 0.0384	
Lab code	result [mg/kg]	relative to spike [%]	satisfactory
1	0.033	103	Yes
2	0.032	100	Yes
3	0.028	88	Yes
4	0.028	88	Yes
5	0.025	78	Yes
6	0.026	81	Yes
7	0.032	100	Yes
8	0.031	97	Yes
9	0.027	84	Yes
10	0.026	81	Yes
11	0.026	81	Yes
12	0.023	72	Yes
13	0.031	97	Yes
14	0.028	88	Yes
15	0.028	88	Yes
16	0.036	113	Yes
17	0.030	94	Yes
18	0.026	81	Yes
19	0.026	81	Yes
20	0.028	88	Yes

n.r.: not reported



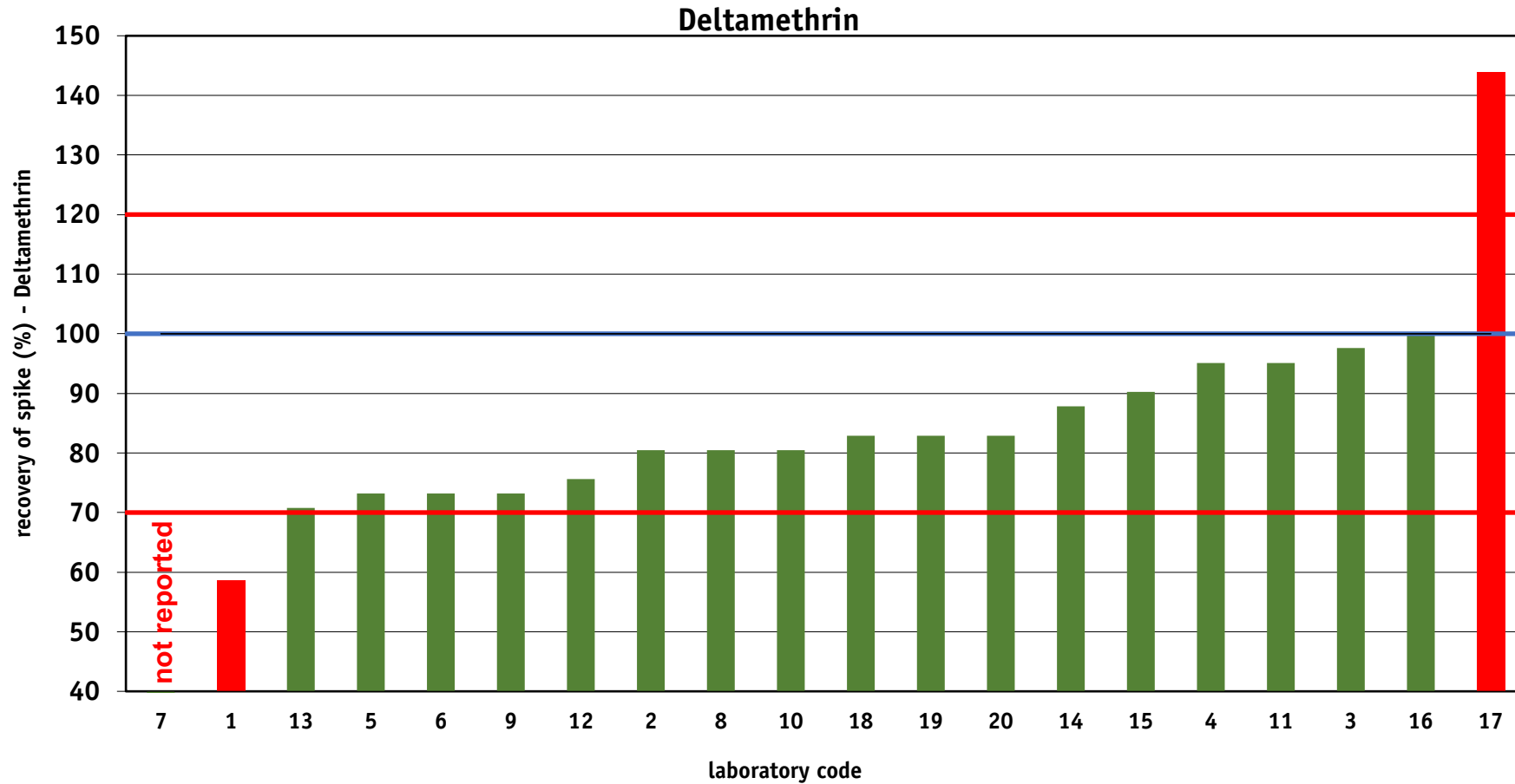
Figure 1: Assessment of Clothianidin - recovery of spike



Green: satisfactory results, red: dissatisfactory results



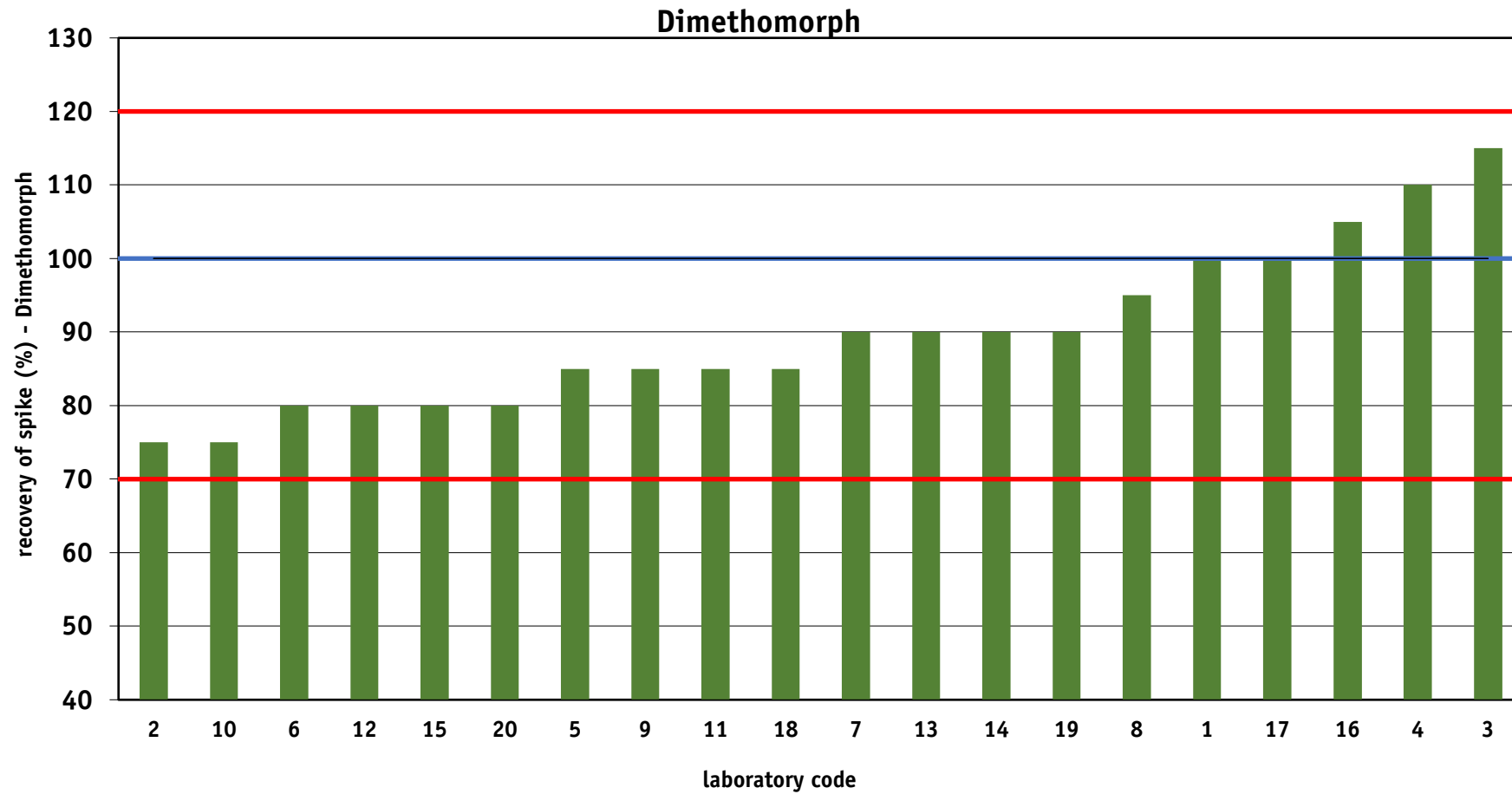
Figure 2: Assessment of Deltamethrin - recovery of spike



Green: satisfactory results, red: dissatisfactory results



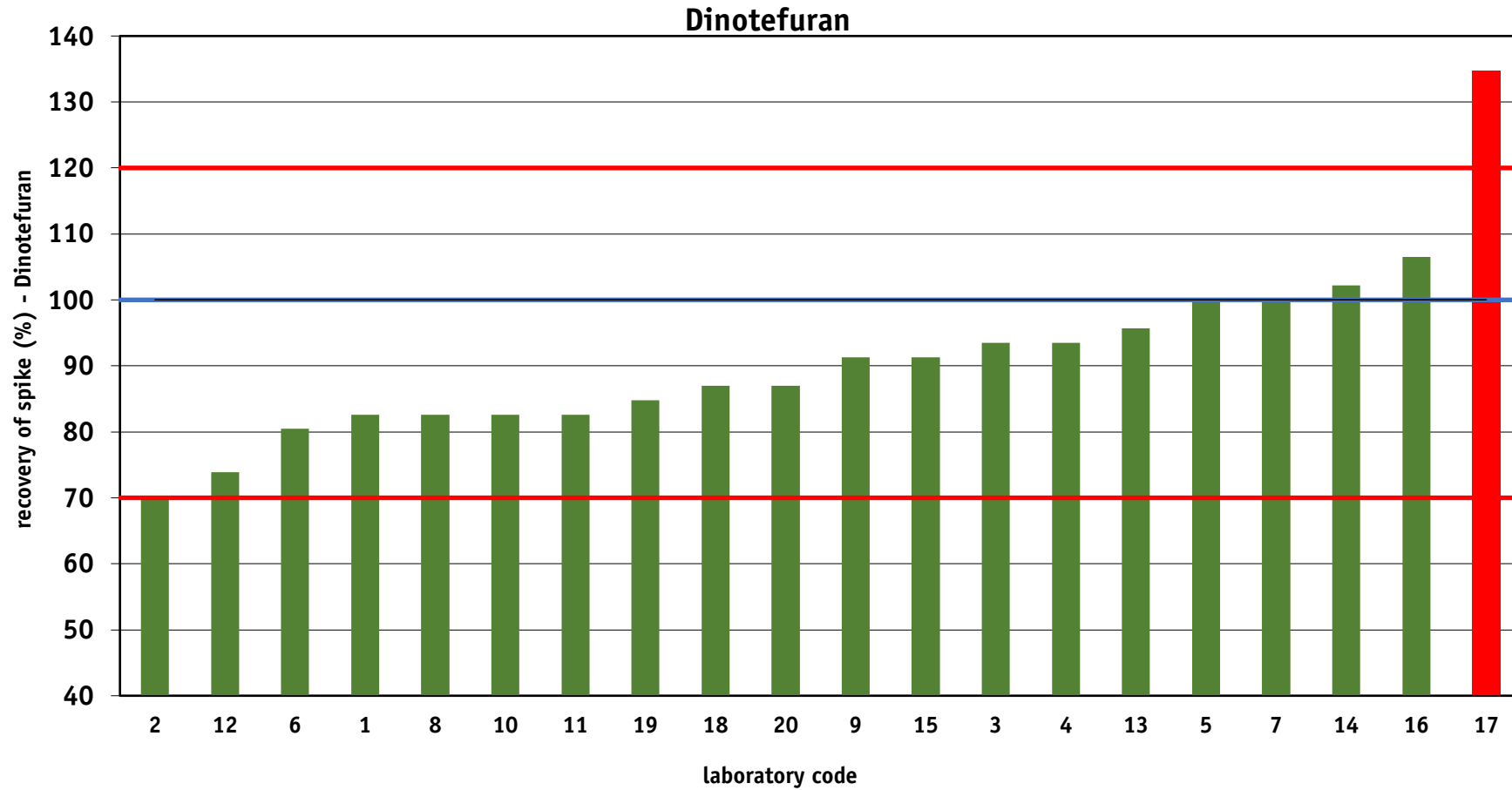
Figure 3: Assessment of Dimethomorph - recovery of spike



Green: satisfactory results, red: dissatisfactory results



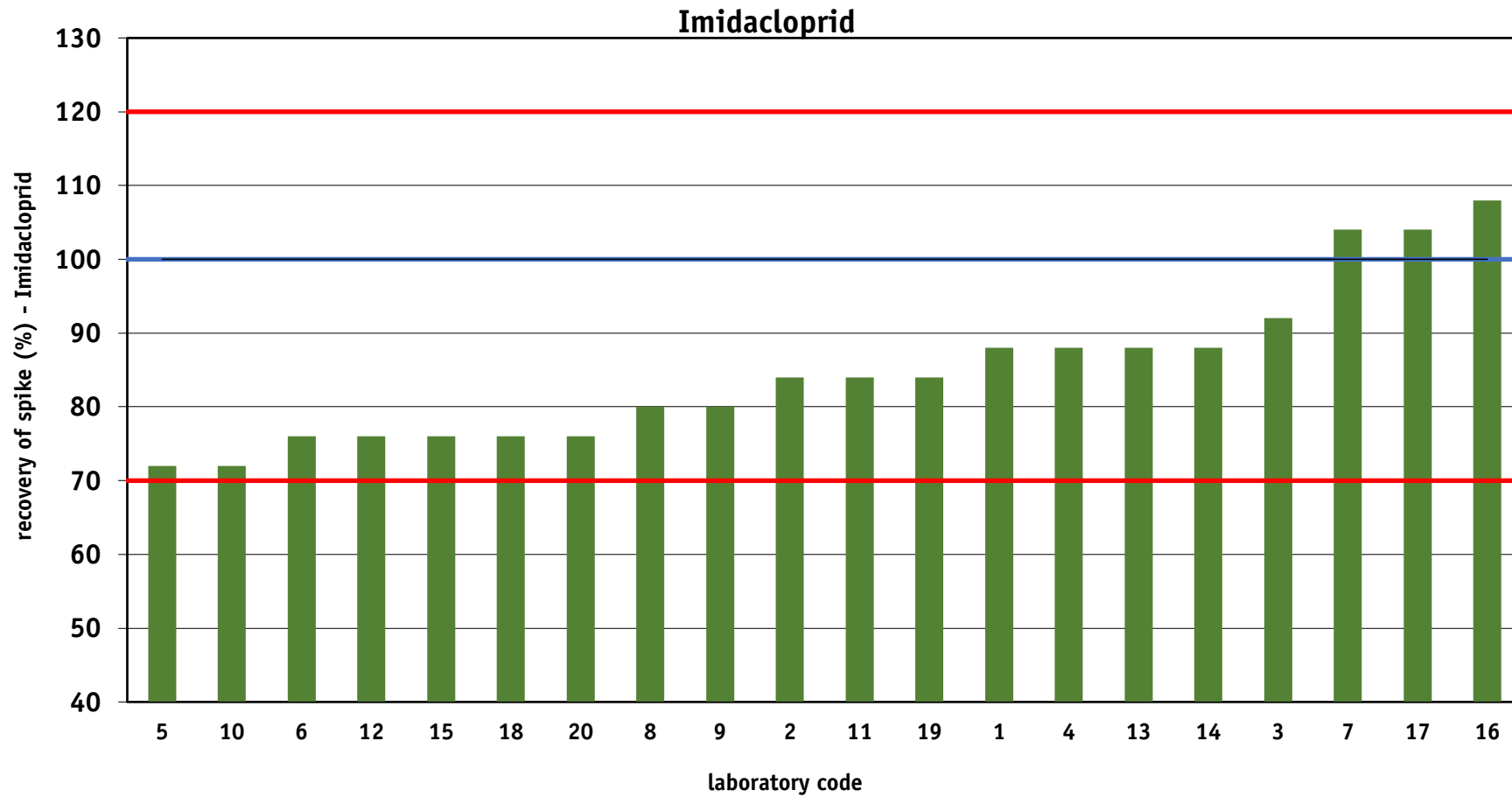
Figure 4: Assessment of Dinotefuran - recovery of spike



Green: satisfactory results, red: dissatisfactory results; n.r.: not reported



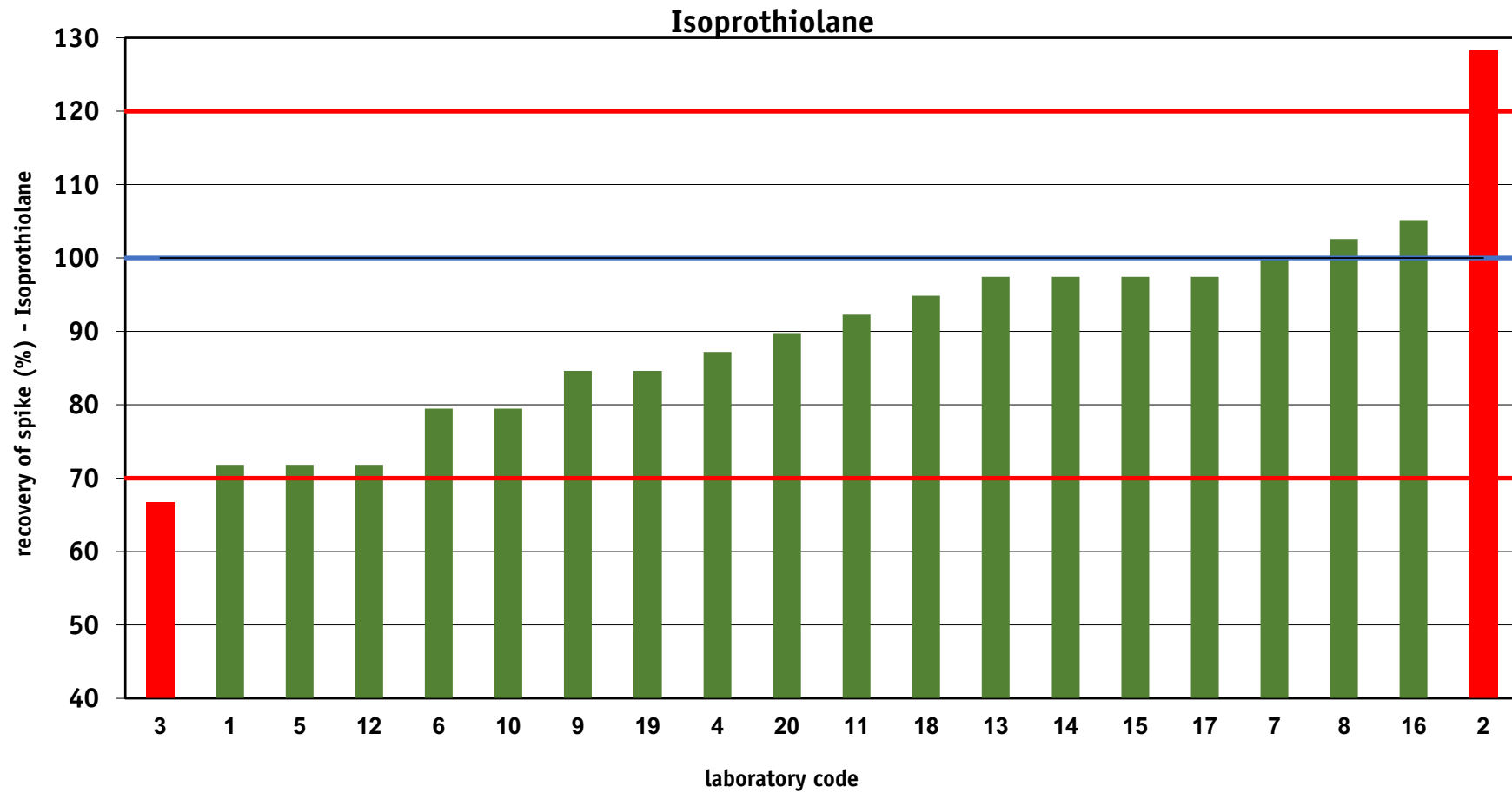
Figure 5: Assessment of Imidacloprid – recovery of spike



Green: satisfactory results, red: dissatisfactory results



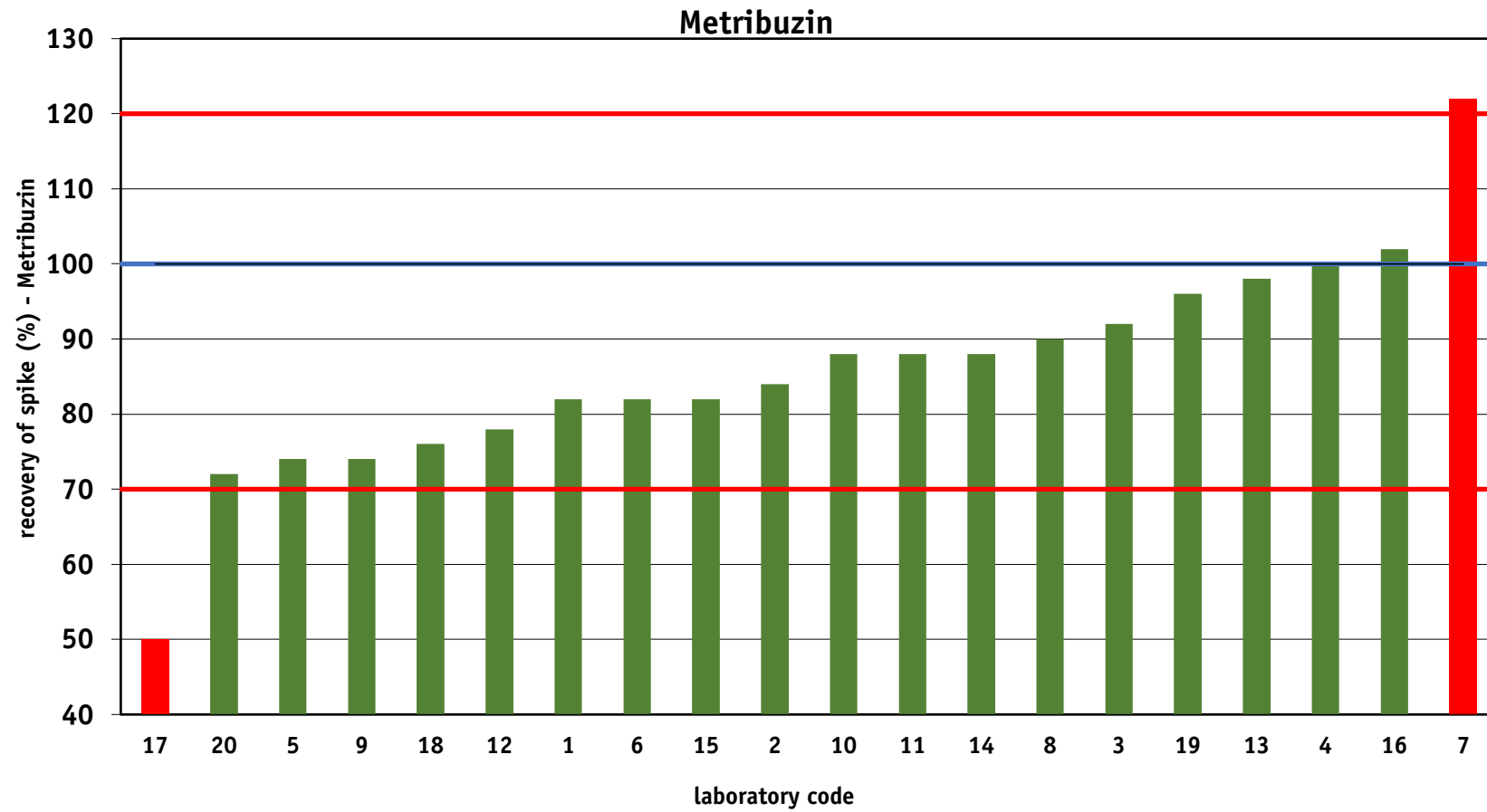
Figure 6: Assessment of Isoprothiolane – recovery of spike



Green: satisfactory results, red: dissatisfactory results



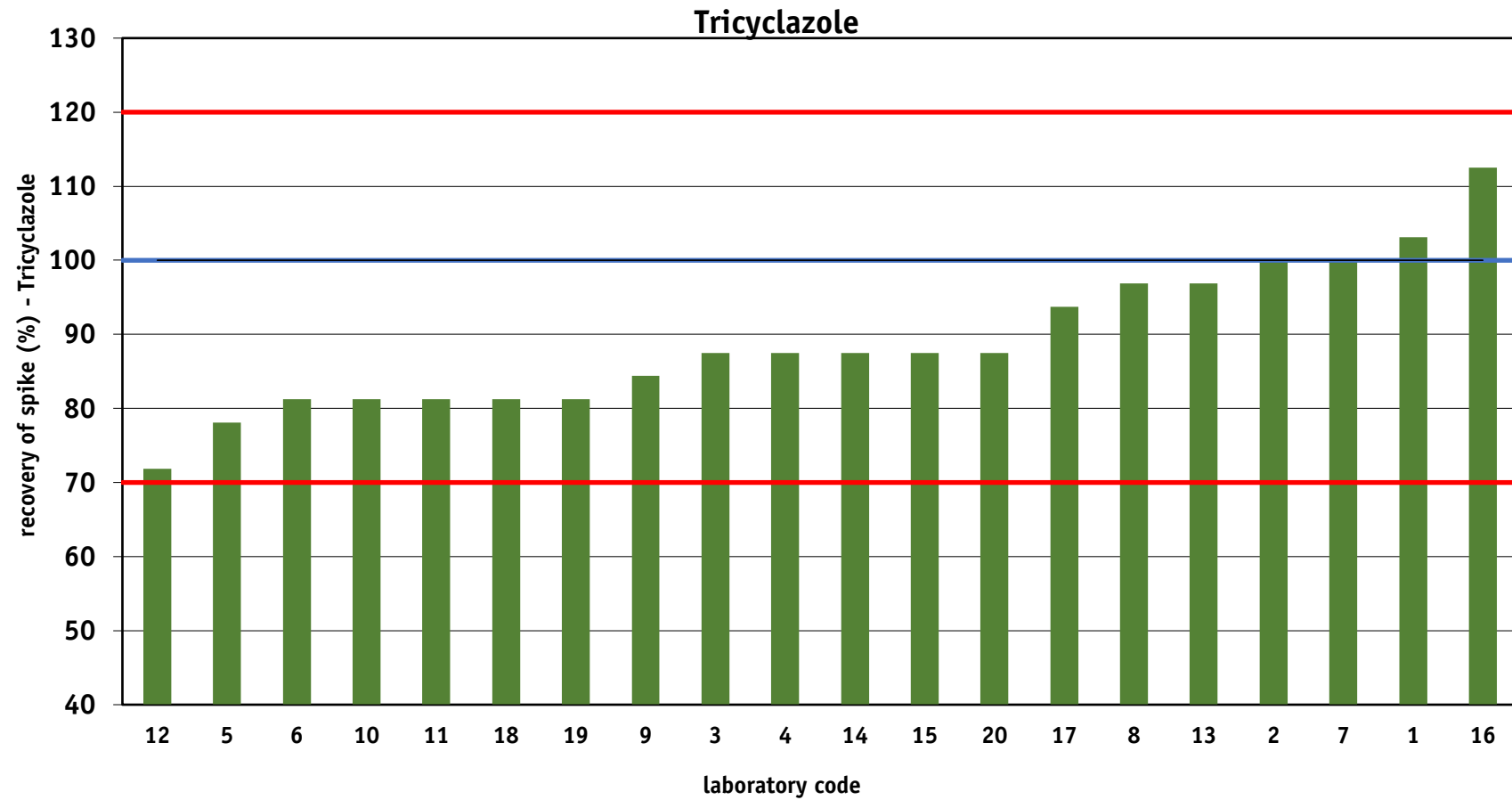
Figure 7: Assessment of Metribuzin – recovery of spike



Green: satisfactory results, red: dissatisfactory results



Figure 8: Assessment of Tricyclazole – recovery of spike



Green: satisfactory results, red: dissatisfactory results