Bundesverband Naturkost Naturwaren

lach bruns

Laboratory Performance Assessment

Analysis of incurred Pesticides in Cherries

Report

June 2018

Summary

The laboratory performance assessment related to pesticides in fresh cherries was designed and organised by Lach & Bruns in June 2018 on behalf of BNN e.V. (Bundesverband Naturkost Naturwaren, Berlin, Germany).

The test material consists of freshly harvested cherries (variety “Christiana”). Twelve pesticides were applied during the growing season of the cherries (some of the pesticides were applied twice):

Acetamiprid, Boscalid, Cyantraniliprole, Dodine, Fenpyroximate, Fluopyram, Myclobutanil, Pirimicarb, Pyraclostrobin, Spinosad, Tebuconazole, and Thiacloprid.

The entire batch of cherries (ca. 100 kg) was thoroughly mixed and the test material samples (ca. 1,6 kg each) were distributed to thirty-six (36) participants across eight (8) European countries (Austria, Belgium, France, Germany, Greece, Italy, the Netherlands, and Spain). No information with respect to the identity or the number of spiked multi-method analytes was provided to the laboratories in advance.

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* multi-method pesticides with an assigned value above 0,01 mg/kg (in total 10 pesticides). Thus, no false negative results, except a pesticide is not within the analytical scope of the particular laboratory. This is mainly related to Cyantraniliprole, as 8 laboratories do not cover this pesticide within their scope yet.
- Correct *quantification* of minimum eight (8) out of ten (10, including Cyantraniliprol), resp. seven (7) out of nine (9, without Cyantraniliprol, if out of scope) pesticides in terms of comparability (z-score evaluation).

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

Criterion	**Criterion passed**
Correct *identification* of all 10 resp. 9 pesticides	34* out of 36 laboratories (94 %)
Correct *quantification* of all 10 resp. 9 pesticides	27 out of 36 laboratories (75 %)
Correct quantification of minimum 8 resp. 7 pesticides	36 out of 36 laboratories (100 %)

* one lab missed one pesticide (false negative); one lab reported one false positive result

Assessment of quantification

Analytical results with a z-score of |z| ≤ 2 are considered satisfying for the assessment of the correct quantification of the pesticides.

Pesticide	Assigned value [mg/kg]	Number of results	Correct quantification
Acetamiprid	0,039	36	35 out of 36 (97 %)
Boscalid	0,073	36	35 out of 36 (97 %)
Cyantraniliprole *	0,027	28	28 out of 28 (100 %)
Dodine	0,133	36	35 out of 36 (97 %)
Fenpyroximate	0,043	36	33 out of 36 (92 %)
Fluopyram	0,063	36	36 out of 36 (100 %)
Myclobutanil	traces < 0,01	26	not applicable
Pirimicarb	traces <0,01	26	not applicable
Pyraclostrobin	0,016	35	33 out of 35 (94 %)
Spinosad	0,050	36	34 out of 36 (94 %)
Tebuconazole	0,043	36	36 out of 36 (100 %)
Thiacloprid	0,025	36	35 out of 36 (97 %)

* Eight (8) labs 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) – B1 (fresh fruits and vegetables)”. As cherries are a relevant seasonal product in the market, they were chosen as test material samples.

The cherries (variety “Christiana”) have been cultivated at a fruit tree growing area close to Hamburg (“Altes Land”). The trees selected are located at a research centre focussing on agriculture practices related to all kind of fruit trees (pomiculture). Twelve pesticides were applied during the growing season of the cherries (some of the pesticides were applied twice) by the research centre:

Acetamiprid, Boscalid, Cyantraniliprole, Dodine, Fenpyroximate, Fluopyram, Myclobutanil, Pirimicarb, Pyraclostrobin, Spinosad, Tebuconazole, and Thiacloprid.

The used pesticide formulations are:
Systhane 20 EW (Myclobutanil), 1 application
Calypso (Thiacloprid), 2 applications
Pirimor Granulate (Pirimicarb), 1 application
Mospilan SG (Acetamiprid), 1 application
Signum (Boscalid + Pyrclostrobin), 1 application
Kiron (Fenpyroximate), 1 application
Syllit (Dodine), 1 application
Exirel (Cyantraniliprol), 1 application
SpinTor (Spinosad), 2 applications
Luna Experience (Fluopyram + Tebuconazole), 1 application.

The entire batch of cherries (ca. 100 kg) was harvested by the research centre and picked up by Lach&Bruns. All cherries were thoroughly mixed and carefully selected to ensure a homogeneous distribution of the cherries across the 50 test material samples (ca. 1,6 kg each). The samples were distributed to thirty-six (36) participants across eight (8) European countries (Austria, Belgium, France, Germany, Greece, Italy, the Netherlands, and Spain). No information with respect to the identity or the number of spiked multi-method analytes was provided to the laboratories in advance.

11 randomly selected samples were forwarded to a pesticide laboratory, not participating in the ring test. 10 samples were analysed in duplicate to prove the homogeneous distribution of the cherries throughout all test material samples and 1 sample was analysed in duplicate after the results of the participants were reported to Lach&Bruns, to prove the stability of the pesticides in/on the test material after storing it in a fridge during the time of the ring test trial.

2. Statistical evaluation of results

Comparability criterion

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 [1]. 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 σ_H[2,2]:

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

Analytical results with a z-score of |z| ≤ 2 are considered satisfying for the assessment of the correct quantification of the pesticides.

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 a pesticide multi residue method (with GC and LC modules).

Thirty-six (36) participants across eight (8) European countries (Austria, Belgium, France, Germany, Greece, Italy, the Netherlands, and Spain) took part in the laboratory performance assessment. Twenty-nine (29) labs participated as they are listed as BNN approved labs, while additional seven (7) labs took part because of other reasons (f.ex. voluntarily to check the analytical competence before applying for BNN approval). 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.

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[1] Statistical methods for use in proficiency testing by interlaboratory comparison. ISO 13528:2015. Corrected version 2016-10-15.

[2] Horwitz W. Evaluation of Analytical Methods Used for Regulation of Foods and Drugs. Anal Chem. 1982;54(1):67A–76A.

The laboratories reported all sought and found pesticides, the reporting limits (RL) as well as the scope of the applied analytical methods. Many labs reported additionally pesticide findings below their reporting limit. These findings are taken as informative and are listed separately on the next page.

A summary of the overall performance of the labs is provided in table 1 (pp. 9-10). A more detailed evaluation of the results of the participants is presented in tables 2 to 14 (pp. 11-23) and in figures 1 to 11 (pp. 24-34).

Results in detail

- All laboratories identified Acetamiprid, Boscalid, Dodine, Fenpyroximate, Fluopyram, Spinosad, Tebuconazole, and Thiacloprid correctly.
- One lab missed the identification of Pyraclostrobin (lab 30; **false negative**), while Cyantraniliprol is out of the scope of 8 laboratories (labs 7, 9, 16, 23 - 27; not considered as false negative).
- One lab (lab 27) reported a **false positive** result of Pyrethrins (0,057 mg/kg).
- All of the pesticides applied to the cherries and evaluated with assigned values above 0,01 mg/kg are quantified pretty well by the participants. Only a very small number of results are outside the z-score corridor of $|z| \leq 2$. In total, 340 z-scores out of 352 meet the z-score criterion, just 12 z-scores are outside (3,4%). This is a fantastic result, especially when taking into consideration, that not a homogenised test material was distributed to the participants but original unprocessed cherries.

Several additional pesticides, which are common to be used in fruit tree cultivation - thus also in the area where the cherries are cultivated - were reported with **trace levels** by the participating labs:

Captan and/or THPI (21 labs), Dithianon (4), **Flonicamid (20)** and TNFA (2), **MCPA (27)**, Phosphonic acid (5), Phthalimid (1), see table below.

As Captan was not applied actively to the cherries but is frequently detected by the participants, the evaluation of Captan (as the sum of Captan and its' metabolite THPI) is included to this report, but just for information purposes. Captan can be considered as a contaminant as this fungicide is the most important and widely used pesticide in conventional apple tree cultivation. The findings of Myclobutanil and Pirimicarb as traces below, at or just slightly above the related reporting limits are also presented just for information.

Additional (trace) findings of the participants:

1	MCPA 0,006
2	Captan 0,014; THPI 0,006; MCPA 0,006
3	MCPA 0,007; Flonicamid <0,005; Dithianone detcted
4	Captan 0,010; THPI 0,010; MCPA <0,01; Flonicamid <0,01
5	Captan 0,006; THPI 0,008; Spinosyn A 0,039; Spinosyn D 0,013; MCPA <0,01; Flonicamid <0,01
6	Captan 0,01; THPI 0,007
7	THPI 0,006; MCPA 0,006
8	THPI 0,012; MCPA 0,006; Myclobutanil 0,005; Flonicamid 0,003
9	MCPA <0,01; Flonicamid <0,01
10	Spinosyn A 0,042; Spinosyn D 0,011
11	THPI <0,01; Spinosyn A 0,036; Spinosyn D 0,010; MCPA <0,01; Flonicamid <0,01
12	Captan 0,013; THPI 0,009; Spinosyn A 0,036; Spinosyn D <0,005; MCPA 0,006
13	Captan <0,01; THPI 0,013; Spinosyn A 0,064; MCPA <0,01; Phosphonic acid 0,037
14	Captan <0,01; THPI 0,015; MCPA <0,01; Flonicamid <0,01; Phosphonic acid 0,010
15	THPI <0,01; Spinosyn A 0,036; Spinosyn D <0,01; MCPA <0,01; Flonicamid <0,01
16	MCPA <0,01; Flonicamid <0,01
17	Spinosyn A 0,040; Spinosyn D 0,016; MCPA <0,01; Flonicamid <0,01
18	Captan 0,003; THPI 0,007; Spinosyn A 0,042; Spinosyn D 0,016; MCPA 0,006; Flonicamid 0,003; TFNA 0,002, Phosphonic acid 0,008
19	THPI 0,010; Spinosyn A 0,052; Spinosyn D 0,019; MCPA 0,0066; Flonicamid 0,0076
21	THPI <0,01
22	MCPA 0,013
24	Dithianon detected < RL; MCPA <0,01
25	Dithianon (qualitativ)
27	Spinosyn A 0,045; Spinosyn D 0,019; MCPA 0,011; **Pyrethrine 0,057**
28	THPI <0,01; Flonicamid <0,01; MCPA <0,01
29	THPI 0,010; Flonicamid <0,01; MCPA <0,01; Phosphonic acid <0,01; Dithianon (qualitativ)
30	Spinosyn A 0,035
31	Captan 0,007; THPI 0,008; Spinosyn A 0,032; Spinosyn D 0,014; MCPA 0,008; Flonicamid 0,004
32	MCPA <0,01; Flonicamid <0,01; Phosphonic acid <0,01; Dithianon (qualitativ)
33	Captan < 0,01; THPI <0,01; Spinosyn A 0,043; Spinosyn D 0,017; MCPA <0,01; Flonicamid <0,01
34	Captan 0,011; THPI <0,01; Spinosyn A 0,043; Spinosyn D 0,010; MCPA <0,01; Flonicamid <0,01, Dithianon 0,079*
35	Captan 0,012; THPI 0,005; Spinosyn A 0,052; Spinosyn D 0,013; MCPA 0,006; Flonicamid 0,003; TFNA 0,003
36	Captan <0,01; THPI 0,01; Phthalimid < 0,01; Flonicamid <0,02; MCPA <0,01

Lab code / findings in mg/kg

* As Dithianon was reported by several participants and also is intensively applied in the area of cultivation, this result is not considered as false-positive.

4. Tables and figures

Table 1: Summary of the overall performance

	Acetamiprid	Boscalid	Cyantra-niliprole	Dodine	Fenpyroximate	Fluopyram	Pyraclo-strobin	Spinosad	Tebucon-azole	Thiacloprid
Lab code	**Comparability**									
1	yes	yes	(oos)	yes	yes	yes	yes	yes	yes	yes
2	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes
3	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes
4	yes	yes	yes	yes	yes	yes	yes	yes	yes	no
5	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes
6	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes
7	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes
8	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes
9	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes
10	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes
11	yes	yes	(oos)	yes	yes	yes	yes	yes	yes	yes
12	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes
13	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes
14	yes	yes	yes	yes	no	yes	yes	yes	yes	yes
15	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes
16	yes	yes	(oos)	yes	yes	yes	yes	yes	yes	yes
17	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes
18	yes	no	yes	yes	yes	yes	yes	yes	yes	yes

Remark: For Myclobutanil and Pirimicarb, a z-score evaluation could not be applied.
oos: out of scope

Table 1 (continued): Summary of the overall performance

	Acetamiprid	Boscalid	Cyantra-niliprole	Dodine	Fenpyroximate	Fluopyram	Pyraclo-strobin	Spinosad	Tebucon-azole	Thiacloprid
Lab code	**Comparability**									
19	yes	yes	yes	yes	no	yes	no	yes	yes	yes
20	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes
21	yes	yes	yes	yes	no	yes	yes	no	yes	yes
22	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes
23	yes	yes	(oos)	yes	yes	yes	yes	yes	yes	yes
24	yes	yes	(oos)	yes	yes	yes	yes	yes	yes	yes
25	yes	yes	(oos)	no	yes	yes	yes	yes	yes	yes
26	yes	yes	(oos)	yes	yes	yes	yes	yes	yes	yes
27	yes	yes	(oos)	yes	yes	yes	yes	yes	yes	yes
28	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes
29	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes
30	yes	yes	yes	yes	yes	yes	no	yes	yes	yes
31	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes
32	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes
33	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes
34	no	yes	yes	yes	yes	yes	no	yes	yes	yes
35	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes
36	yes	yes	yes	yes	yes	yes	yes	no	yes	yes

Remark: For Myclobutanil and Pirimicarb, a z-score evaluation could not be applied
oos: out of scope

Table 2: Results of Acetamiprid

	Acetamiprid			
	Assigned value [mg/kg]			0,039 mg/kg
Lab code	**Result [mg/kg]**	**RL [mg/kg]**	**z-score**	**z-score: passed**
1	0,042	0,003	0,3	yes
2	0,037	0,005	-0,3	yes
3	0,036	0,005	-0,4	yes
4	0,048	0,010	1,0	yes
5	0,040	0,010	0,1	yes
6	0,042	0,010	0,3	yes
7	0,041	0,010	0,2	yes
8	0,047	0,010	0,9	yes
9	0,042	0,010	0,3	yes
10	0,037	0,010	-0,3	yes
11	0,035	0,010	-0,5	yes
12	0,053	0,010	1,6	yes
13	0,039	0,010	0,0	yes
14	0,037	0,010	-0,3	yes
15	0,038	0,010	-0,2	yes
16	0,039	0,005	0,0	yes
17	0,037	0,010	-0,3	yes
18	0,038	0,005	-0,2	yes
19	0,044	0,010	0,5	yes
20	0,033	0,010	-0,7	yes
21	0,037	0,010	-0,3	yes
22	0,050	0,005	1,2	yes
23	0,040	0,010	0,1	yes
24	0,041	0,010	0,2	yes
25	0,033	0,010	-0,7	yes
26	0,028	0,010	-1,3	yes
27	0,038	0,010	-0,2	yes
28	0,041	0,010	0,2	yes
29	0,036	0,010	-0,4	yes
30	0,033	0,010	-0,7	yes
31	0,036	0,010	-0,4	yes
32	0,044	0,010	0,5	yes
33	0,040	0,010	0,1	yes
34	0,063	0,010	2,7	no
35	0,040	0,005	0,1	yes
36	0,038	0,010	-0,2	yes

RL: reporting limit
Acetamiprid (comparability criterion): Accepted range z-score of $|z| \leq 2$

Table 3: Results of Boscalid

	Boscalid			
	Assigned value [mg/kg]			0,073 mg/kg
Lab code	**Result [mg/kg]**	**RL [mg/kg]**	**z-score**	**z-score: passed**
1	0,080	0,003	0,5	yes
2	0,077	0,005	0,3	yes
3	0,074	0,005	0,1	yes
4	0,080	0,010	0,5	yes
5	0,081	0,010	0,5	yes
6	0,084	0,010	0,7	yes
7	0,083	0,010	0,7	yes
8	0,080	0,010	0,5	yes
9	0,068	0,010	-0,3	yes
10	0,100	0,010	1,7	yes
11	0,070	0,010	-0,2	yes
12	0,070	0,005	-0,2	yes
13	0,066	0,010	-0,4	yes
14	0,084	0,010	0,7	yes
15	0,070	0,010	-0,2	yes
16	0,076	0,005	0,2	yes
17	0,076	0,010	0,2	yes
18	0,039	0,005	-2,1	no
19	0,105	0,010	2,0	Yes
20	0,056	0,010	-1,0	yes
21	0,052	0,010	-1,3	yes
22	0,095	0,005	1,4	yes
23	0,065	0,010	-0,5	yes
24	0,071	0,010	-0,1	yes
25	0,080	0,010	0,5	yes
26	0,049	0,010	-1,5	yes
27	0,044	0,010	-1,8	yes
28	0,078	0,010	0,3	yes
29	0,050	0,010	-1,4	yes
30	0,065	0,010	-0,5	yes
31	0,062	0,010	-0,7	yes
32	0,064	0,010	-0,5	yes
33	0,078	0,010	0,3	yes
34	0,090	0,010	1,1	yes
35	0,081	0,005	0,5	yes
36	0,061	0,010	-0,7	yes

RL: reporting limit
Boscalid (comparability criterion): Accepted range z-score of $|z| \leq 2$

Table 4: Results of Captan

	Captan (sum)		
	Assigned value [mg/kg]		0,021 mg/kg
Lab code	**Result [mg/kg]**	**RL [mg/kg]**	**z-score**
1	*0,025*	*0,010*	*0,8*
2	*0,026*	*0,005*	*1,0*
3	*0,018*	*0,005*	*-0,7*
4	*0,030*	*0,010*	*1,9*
5	*0,022*	*0,010*	*0,2*
6	*0,010*	*0,010*	*-2,4*
7	*0,024*	*0,010*	*0,6*
8	*0,023*	*0,010*	*0,4*
9	*0,010*	*0,010*	*-2,4*
10	*0,025*	*0,010*	*0,8*
11	*< 0,01*	*0,010*	*/*
12	*0,028*	*0,010*	*1,5*
13	*0,025*	*0,010*	*0,8*
14	*0,030*	*0,010*	*1,9*
15	*0,011*	*0,010*	*-2,2*
16	*0,010*	*0,010*	*-2,4*
17	*n.d.*	*0,030*	*/*
18	*< 0,02*	*0,020*	*/*
19	*0,020*	*0,010*	*-0,3*
20	*n.d.*	*0,010*	*/*
21	*n.d.*	*0,010*	*/*
22	*0,032*	*0,005*	*2,3*
23	*n.d.*	*0,010*	*/*
24	*< 0,01*	*0,010*	*/*
25	*n.d.*	*0,010*	*/*
26	*n.d.*	*0,010*	*/*
27	*n.d.*	*0,010*	*/*
28	*< 0,01*	*0,010*	*/*
29	*0,020*	*0,010*	*-0,3*
30	*n.d.*	*0,010*	*/*
31	*0,023*	*0,010*	*0,4*
32	*0,022*	*0,010*	*0,2*
33	*< 0,01*	*0,010*	*/*
34	*0,011*	*0,010*	*-2,2*
35	*0,022*	*0,005*	*0,2*
36	*0,020*	*0,020*	*-0,3*

RL: reporting limit
n.d.: not detected

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Table 5: Results of Cyantraniliprole

	Cyantraniliprole			
	Assigned value [mg/kg]			0,027 mg/kg
Lab code	**Result [mg/kg]**	**RL [mg/kg]**	**z-score**	**z-score: passed**
1	oos		/	(oos)
2	0,027	0,005	-0,1	yes
3	0,025	0,005	-0,4	yes
4	0,032	0,010	0,7	yes
5	0,027	0,010	-0,1	yes
6	0,030	0,010	0,4	yes
7	0,025	0,010	-0,4	yes
8	0,030	0,010	0,4	yes
9	0,023	0,010	-0,8	yes
10	0,024	0,010	-0,6	yes
11	oos		/	(oos)
12	0,024	0,010	-0,6	yes
13	0,030	0,010	0,4	yes
14	0,025	0,010	-0,4	yes
15	0,024	0,010	-0,6	yes
16	oos		/	(oos)
17	0,033	0,010	0,9	yes
18	0,023	0,010	-0,8	yes
19	0,029	0,010	0,2	yes
20	0,019	0,010	-1,4	yes
21	0,018	0,010	-1,6	yes
22	0,035	0,005	1,2	yes
23	oos		/	(oos)
24	oos		/	(oos)
25	oos		/	(oos)
26	oos		/	(oos)
27	oos		/	(oos)
28	0,034	0,010	1,0	yes
29	0,027	0,010	-0,1	yes
30	0,028	0,010	0,1	yes
31	0,024	0,010	-0,6	yes
32	0,039	0,010	1,9	yes
33	0,032	0,010	0,7	yes
34	0,035	0,010	1,2	yes
35	0,033	0,005	0,9	yes
36	0,020	0,010	-1,3	yes

RL: reporting limit
oos: out of scope
Cyantraniliprole (comparability criterion): Accepted range z-score of |z| ≤ 2

Table 6: Results of Dodine

	Dodine			
	Assigned value [mg/kg]			0,133 mg/kg
Lab code	**Result [mg/kg]**	**RL [mg/kg]**	**z-score**	**z-score: passed**
1	0,136	0,005	0,1	yes
2	0,082	0,005	-1,8	yes
3	0,108	0,005	-0,9	yes
4	0,140	0,010	0,2	yes
5	0,120	0,010	-0,5	yes
6	0,150	0,010	0,6	yes
7	0,125	0,010	-0,3	yes
8	0,140	0,010	0,2	yes
9	0,120	0,010	-0,5	yes
10	0,120	0,010	-0,5	yes
11	0,108	0,010	-0,9	yes
12	0,161	0,010	1,0	yes
13	0,130	0,010	-0,1	yes
14	0,160	0,010	0,9	yes
15	0,140	0,010	0,2	yes
16	0,130	0,010	-0,1	yes
17	0,140	0,010	0,2	yes
18	0,075	0,010	-2,0	yes
19	0,143	0,010	0,3	yes
20	0,120	0,010	-0,5	yes
21	0,108	0,010	-0,9	yes
22	0,147	0,005	0,5	yes
23	0,172	0,010	1,3	yes
24	0,140	0,010	0,2	yes
25	0,250	0,010	4,0	no
26	0,120	0,010	-0,5	yes
27	0,110	0,010	-0,8	yes
28	0,154	0,010	0,7	yes
29	0,120	0,010	-0,5	yes
30	0,120	0,010	-0,5	yes
31	0,100	0,010	-1,2	yes
32	0,150	0,010	0,6	yes
33	0,150	0,010	0,6	yes
34	0,170	0,010	1,3	yes
35	0,150	0,005	0,6	yes
36	0,140	0,010	0,2	yes

RL: reporting limit
Dodine (comparability criterion): Accepted range z-score of $|z| \leq 2$

Table 7: Results of Fenpyroximate

	Fenpyroximate			
	Assigned value [mg/kg]			0,043 mg/kg
Lab code	**Result [mg/kg]**	**RL [mg/kg]**	**z-score**	**z-score: passed**
1	0,045	0,003	0,2	yes
2	0,036	0,005	-0,8	yes
3	0,037	0,005	-0,7	yes
4	0,053	0,010	1,0	yes
5	0,040	0,010	-0,3	yes
6	0,048	0,010	0,5	yes
7	0,045	0,010	0,2	yes
8	0,055	0,010	1,2	yes
9	0,052	0,010	0,9	yes
10	0,042	0,010	-0,1	yes
11	0,049	0,010	0,6	yes
12	0,059	0,005	1,6	yes
13	0,033	0,010	-1,1	yes
14	0,020	0,010	-2,4	no
15	0,045	0,010	0,2	yes
16	0,049	0,010	0,6	yes
17	0,055	0,010	1,2	yes
18	0,037	0,010	-0,7	yes
19	0,076	0,010	3,4	no
20	0,036	0,010	-0,8	yes
21	0,023	0,010	-2,1	no
22	0,046	0,005	0,3	yes
23	0,041	0,010	-0,2	yes
24	0,035	0,010	-0,9	yes
25	0,037	0,010	-0,7	yes
26	0,027	0,010	-1,7	yes
27	0,050	0,010	0,7	yes
28	0,055	0,010	1,2	yes
29	0,036	0,010	-0,8	yes
30	0,033	0,010	-1,1	yes
31	0,038	0,010	-0,6	yes
32	0,045	0,010	0,2	yes
33	0,050	0,010	0,7	yes
34	0,053	0,010	1,0	yes
35	0,056	0,005	1,3	yes
36	0,026	0,010	-1,8	yes

RL: reporting limit
Fenpyroximate (comparability criterion): Accepted range z-score of $|z| \leq 2$

Table 8: Results of Fluopyram

	Fluopyram			
	Assigned value [mg/kg]			0,063 mg/kg
Lab code	**Result [mg/kg]**	**RL [mg/kg]**	**z-score**	**z-score: passed**
1	0,061	0,005	-0,1	yes
2	0,060	0,005	-0,2	yes
3	0,063	0,005	0,0	yes
4	0,065	0,010	0,2	yes
5	0,061	0,010	-0,1	yes
6	0,060	0,010	-0,2	yes
7	0,064	0,010	0,1	yes
8	0,066	0,010	0,3	yes
9	0,068	0,010	0,4	yes
10	0,052	0,010	-0,8	yes
11	0,063	0,010	0,0	yes
12	0,084	0,010	1,6	yes
13	0,056	0,010	-0,5	yes
14	0,059	0,010	-0,3	yes
15	0,061	0,010	-0,1	yes
16	0,073	0,010	0,8	yes
17	0,079	0,010	1,2	yes
18	0,050	0,010	-0,9	yes
19	0,081	0,010	1,3	yes
20	0,049	0,010	-1,0	yes
21	0,056	0,010	-0,5	yes
22	0,071	0,005	0,6	yes
23	0,057	0,010	-0,4	yes
24	0,066	0,010	0,3	yes
25	0,069	0,010	0,5	yes
26	0,052	0,010	-0,8	yes
27	0,047	0,010	-1,1	yes
28	0,065	0,010	0,2	yes
29	0,068	0,010	0,4	yes
30	0,058	0,010	-0,3	yes
31	0,061	0,010	-0,1	yes
32	0,070	0,010	0,5	yes
33	0,062	0,010	0,0	yes
34	0,064	0,010	0,1	yes
35	0,073	0,005	0,8	yes
36	0,043	0,010	-1,4	yes

RL: reporting limit
Fluopyram (comparability criterion): Accepted range z-score of $|z| \leq 2$

Table 9: Results of Trimethyl sulfonium cation

	Myclobutanil	
Lab code	Result [mg/kg]	RL [mg/kg]
1	0,004	0,003
2	n.d.	0,005
3	< 0,005	0,005
4	< 0,01	0,010
5	n.d.	0,010
6	n.d.	0,010
7	n.d.	0,010
8	< 0,01	0,010
9	< 0,01	0,010
10	n.d.	0,010
11	< 0,01	0,010
12	< 0,005	0,005
13	< 0,01	0,010
14	< 0,01	0,010
15	< 0,01	0,010
16	< 0,005	0,005
17	< 0,01	0,010
18	0,005	0,005
19	< 0,01	0,010
20	n.d.	0,010
21	n.d.	0,010
22	0,006	0,005
23	< 0,01	0,010
24	< 0,01	0,010
25	n.d.	0,010
26	< 0,01	0,010
27	n.d.	0,010
28	< 0,01	0,010
29	< 0,01	0,010
30	n.d.	0,010
31	< 0,01	0,010
32	< 0,01	0,010
33	< 0,01	0,010
34	< 0,01	0,010
35	< 0,005	0,005
36	< 0,01	0,010

RL: reporting limit
n.d.: not detected

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Table 10: Results of Pirimicarb (sum)

	Pirimicarb (sum)	
Lab code	Result [mg/kg]	RL [mg/kg]
1	0,003	0,003
2	n.d.	0,005
3	< 0,005	0,005
4	< 0,010	0,010
5	< 0,010	0,010
6	n.d.	0,010
7	n.d.	0,010
8	0,003	0,010
9	< 0,010	0,010
10	n.d.	0,010
11	< 0,010	0,010
12	< 0,005	0,005
13	< 0,010	0,010
14	< 0,010	0,010
15	< 0,010	0,010
16	< 0,005	0,005
17	< 0,010	0,010
18	0,003	0,010
19	0,0033	0,010
20	n.d.	0,010
21	n.d.	0,010
22	< 0,005	0,005
23	< 0,010	0,010
24	< 0,010	0,010
25	n.d.	0,010
26	n.d.	0,010
27	n.d.	0,010
28	< 0,010	0,010
29	< 0,010	0,010
30	n.d.	0,010
31	0,003	0,010
32	< 0,010	0,010
33	< 0,010	0,010
34	< 0,010	0,010
35	0,003	0,010
36	< 0,010	0,010

RL: reporting limit
n.d.: not detected

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Table 11: Results of Pyraclostrobin

	Pyraclostrobin			
	Assigned value [mg/kg]			0,016 mg/kg
Lab code	**Result [mg/kg]**	**RL [mg/kg]**	**z-score**	**z-score: passed**
1	0,015	0,003	-0,4	yes
2	0,012	0,005	-1,2	yes
3	0,014	0,005	-0,6	yes
4	0,016	0,010	0,0	yes
5	0,014	0,010	-0,6	yes
6	0,018	0,010	0,5	yes
7	0,017	0,010	0,3	yes
8	0,021	0,010	1,4	yes
9	0,018	0,010	0,5	yes
10	0,016	0,010	0,0	yes
11	0,012	0,010	-1,2	yes
12	0,023	0,005	1,9	yes
13	0,019	0,010	0,8	yes
14	0,013	0,010	-0,9	yes
15	0,014	0,010	-0,6	yes
16	0,015	0,005	-0,3	yes
17	0,018	0,010	0,5	yes
18	0,014	0,005	-0,6	yes
19	0,024	0,010	2,2	no
20	0,012	0,010	-1,2	yes
21	0,010	0,010	-1,7	yes
22	0,015	0,005	-0,3	yes
23	0,016	0,010	0,0	yes
24	0,013	0,010	-0,9	yes
25	0,018	0,010	0,5	yes
26	0,010	0,010	-1,7	yes
27	0,018	0,010	0,5	yes
28	0,019	0,010	0,8	yes
29	0,014	0,010	-0,6	yes
30	n.d.	0,010	-4,5	no
31	0,015	0,010	-0,3	yes
32	0,020	0,010	1,1	yes
33	0,020	0,010	1,1	yes
34	0,024	0,010	2,2	no
35	0,017	0,005	0,3	yes
36	0,015	0,010	-0,3	yes

RL: reporting limit
Pyraclostrobin (comparability criterion): Accepted range z-score of $|z| \leq 2$

Table 12: Results of Spinosad

	Spinosad			
	Assigned value [mg/kg]			0,050 mg/kg
Lab code	**Result [mg/kg]**	**RL [mg/kg]**	**z-score**	**z-score: passed**
1	0,052	0,003	0,2	yes
2	0,050	0,005	0,0	yes
3	0,051	0,005	0,1	yes
4	0,070	0,010	1,8	yes
5	0,052	0,010	0,2	yes
6	0,060	0,010	0,9	yes
7	0,043	0,010	-0,7	yes
8	0,054	0,010	0,3	yes
9	0,051	0,010	0,1	yes
10	0,053	0,010	0,2	yes
11	0,046	0,010	-0,4	yes
12	0,033	0,005	-1,6	yes
13	0,064	0,010	1,2	yes
14	0,048	0,010	-0,2	yes
15	0,036	0,010	-1,3	yes
16	0,054	0,005	0,3	yes
17	0,055	0,010	0,4	yes
18	0,056	0,010	0,5	yes
19	0,071	0,010	1,9	yes
20	0,045	0,010	-0,5	yes
21	0,027	0,010	-2,1	no
22	0,058	0,005	0,7	yes
23	0,059	0,010	0,8	yes
24	0,044	0,010	-0,6	yes
25	0,034	0,010	-1,5	yes
26	0,032	0,010	-1,7	yes
27	0,064	0,010	1,2	yes
28	0,064	0,010	1,2	yes
29	0,034	0,010	-1,5	yes
30	0,035	0,010	-1,4	yes
31	0,046	0,010	-0,4	yes
32	0,058	0,010	0,7	yes
33	0,060	0,010	0,9	yes
34	0,053	0,010	0,2	yes
35	0,065	0,005	1,3	yes
36	0,027	0,010	-2,1	no

RL: reporting limit
Spinosad (comparability criterion): Accepted range z-score of $|z| \leq 2$

Table 13: Results of Tebuconazole

	Tebuconazole			
	Assigned value [mg/kg]			0,043 mg/kg
Lab code	**Result [mg/kg]**	**RL [mg/kg]**	**z-score**	**z-score: passed**
1	0,043	0,003	0,0	yes
2	0,042	0,005	-0,1	yes
3	0,037	0,005	-0,6	yes
4	0,045	0,010	0,2	yes
5	0,041	0,010	-0,2	yes
6	0,039	0,010	-0,4	yes
7	0,043	0,010	0,0	yes
8	0,047	0,010	0,5	yes
9	0,044	0,010	0,1	yes
10	0,034	0,010	-0,9	yes
11	0,042	0,010	-0,1	yes
12	0,052	0,010	1,0	yes
13	0,037	0,010	-0,6	yes
14	0,040	0,010	-0,3	yes
15	0,041	0,010	-0,2	yes
16	0,051	0,005	0,9	yes
17	0,048	0,010	0,6	yes
18	0,032	0,010	-1,1	yes
19	0,050	0,010	0,8	yes
20	0,031	0,010	-1,2	yes
21	0,038	0,010	-0,5	yes
22	0,039	0,005	-0,4	yes
23	0,045	0,010	0,2	yes
24	0,043	0,010	0,0	yes
25	0,045	0,010	0,2	yes
26	0,043	0,010	0,0	yes
27	0,056	0,010	1,4	yes
28	0,041	0,010	-0,2	yes
29	0,042	0,010	-0,1	yes
30	0,039	0,010	-0,4	yes
31	0,042	0,010	-0,1	yes
32	0,048	0,010	0,6	yes
33	0,044	0,010	0,1	yes
34	0,048	0,010	0,6	yes
35	0,050	0,005	0,8	yes
36	0,027	0,010	-1,7	yes

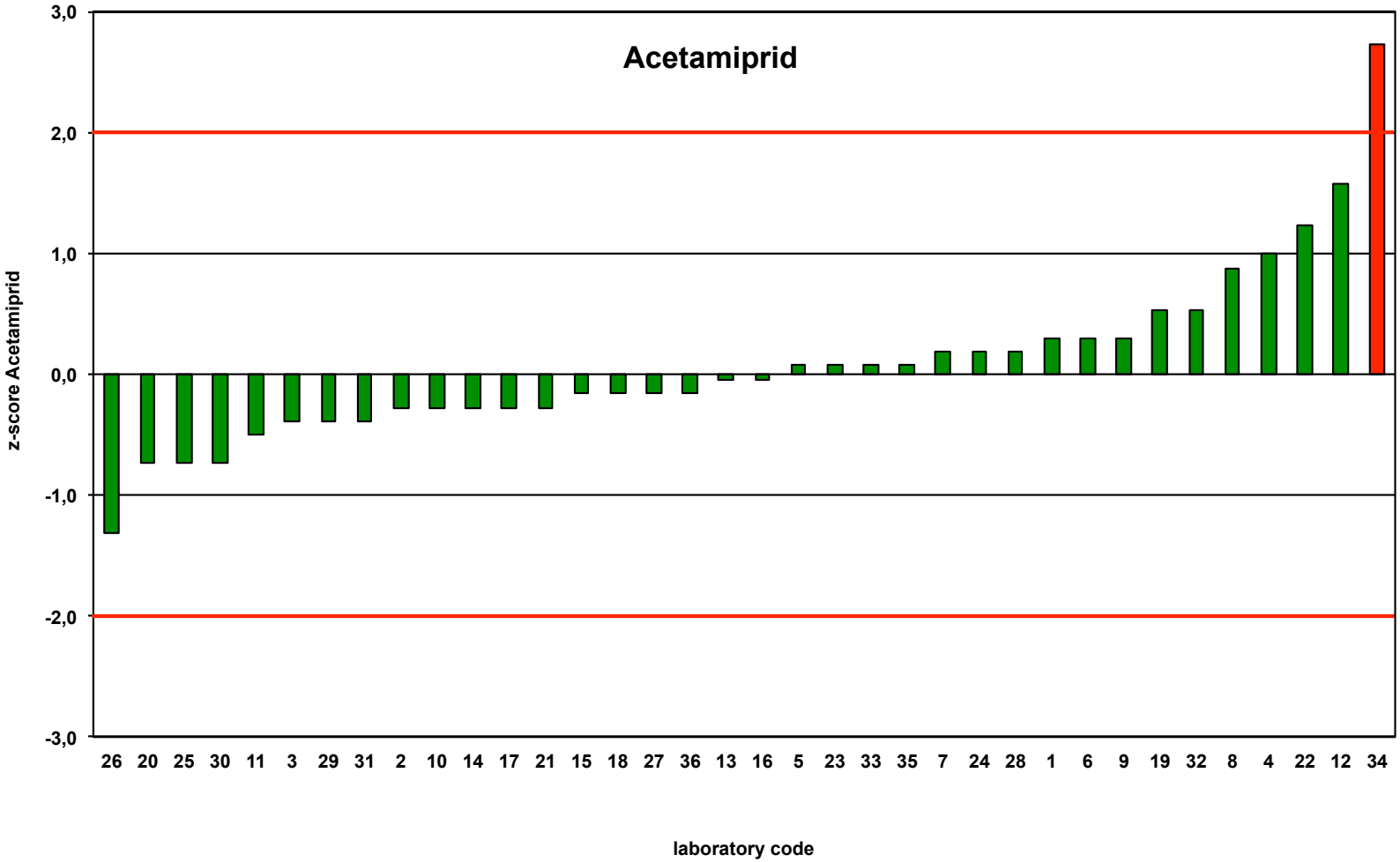
RL: reporting limit
Tebuconazole (comparability criterion): Accepted range z-score of $|z| \leq 2$

Table 14: Results of Thiacloprid

	Thiacloprid			
	Assigned value [mg/kg]			0,025 mg/kg
Lab code	**Result [mg/kg]**	**RL [mg/kg]**	**z-score**	**z-score: passed**
1	0,026	0,003	0,1	yes
2	0,025	0,005	-0,1	yes
3	0,024	0,005	-0,2	yes
4	0,037	0,010	2,1	no
5	0,026	0,010	0,1	yes
6	0,027	0,010	0,3	yes
7	0,026	0,010	0,1	yes
8	0,026	0,010	0,1	yes
9	0,024	0,010	-0,2	yes
10	0,030	0,010	0,8	yes
11	0,024	0,010	-0,2	yes
12	0,031	0,005	1,0	yes
13	0,023	0,010	-0,4	yes
14	0,023	0,010	-0,4	yes
15	0,025	0,010	-0,1	yes
16	0,025	0,005	-0,1	yes
17	0,025	0,010	-0,1	yes
18	0,022	0,005	-0,6	yes
19	0,035	0,010	1,7	yes
20	0,020	0,010	-1,0	yes
21	0,020	0,010	-1,0	yes
22	0,025	0,005	-0,1	yes
23	0,024	0,010	-0,2	yes
24	0,026	0,010	0,1	yes
25	0,018	0,010	-1,3	yes
26	0,021	0,010	-0,8	yes
27	0,029	0,010	0,7	yes
28	0,028	0,010	0,5	yes
29	0,020	0,010	-1,0	yes
30	0,020	0,010	-1,0	yes
31	0,029	0,010	0,7	yes
32	0,033	0,010	1,4	yes
33	0,028	0,010	0,5	yes
34	0,032	0,010	1,2	yes
35	0,025	0,005	-0,1	yes
36	0,020	0,010	-1,0	yes

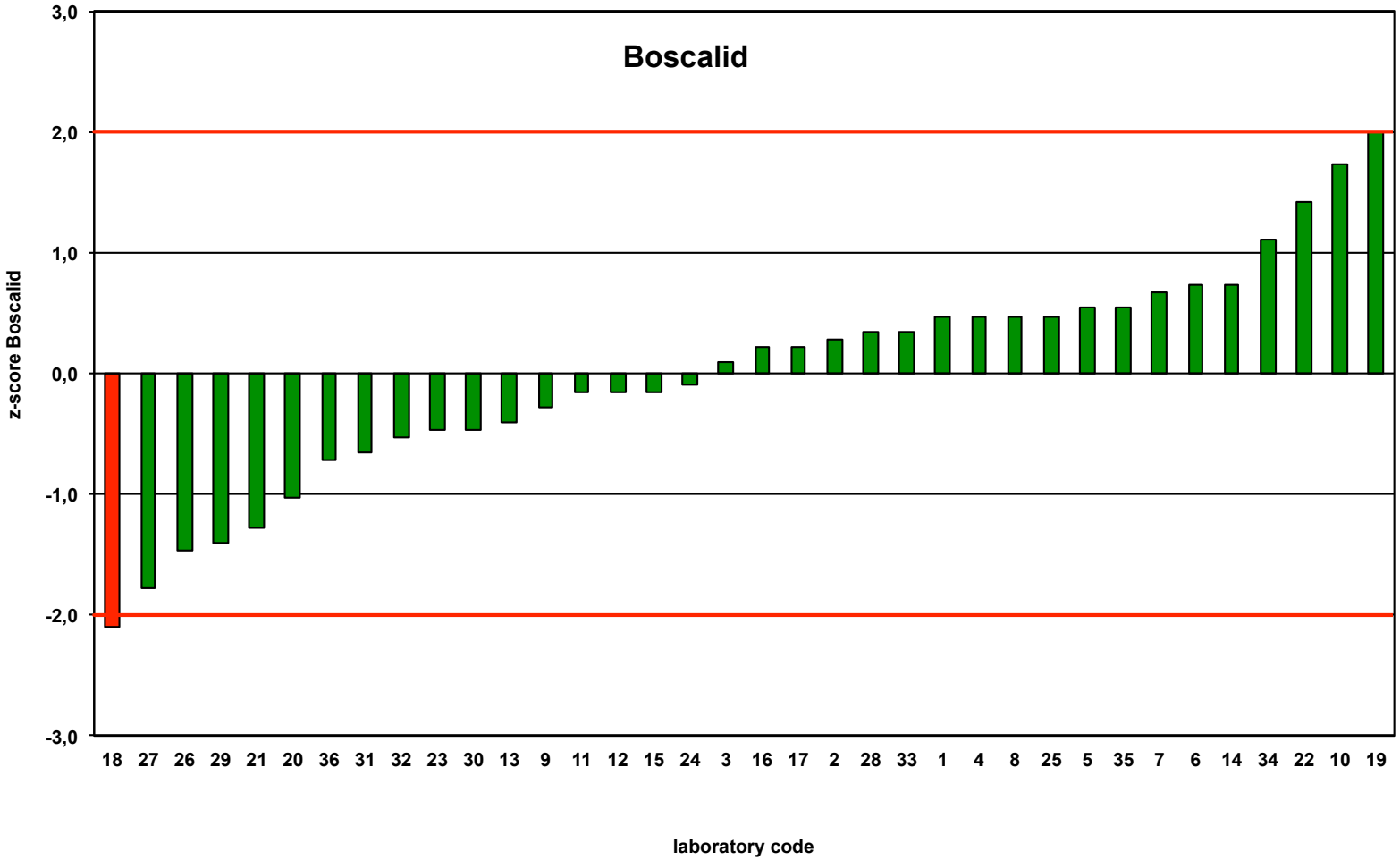
RL: reporting limit
Thiacloprid (comparability criterion): Accepted range z-score of |z| ≤ 2

Figure 1: Assessment of Acetamiprid (comparability)



Green: satisfactory results, red: dissatisfactory results

Figure 2: Assessment of Boscalid (comparability)



Green: satisfactory results, red: dissatisfactory results

Figure 3: Assessment of Captan (comparability)

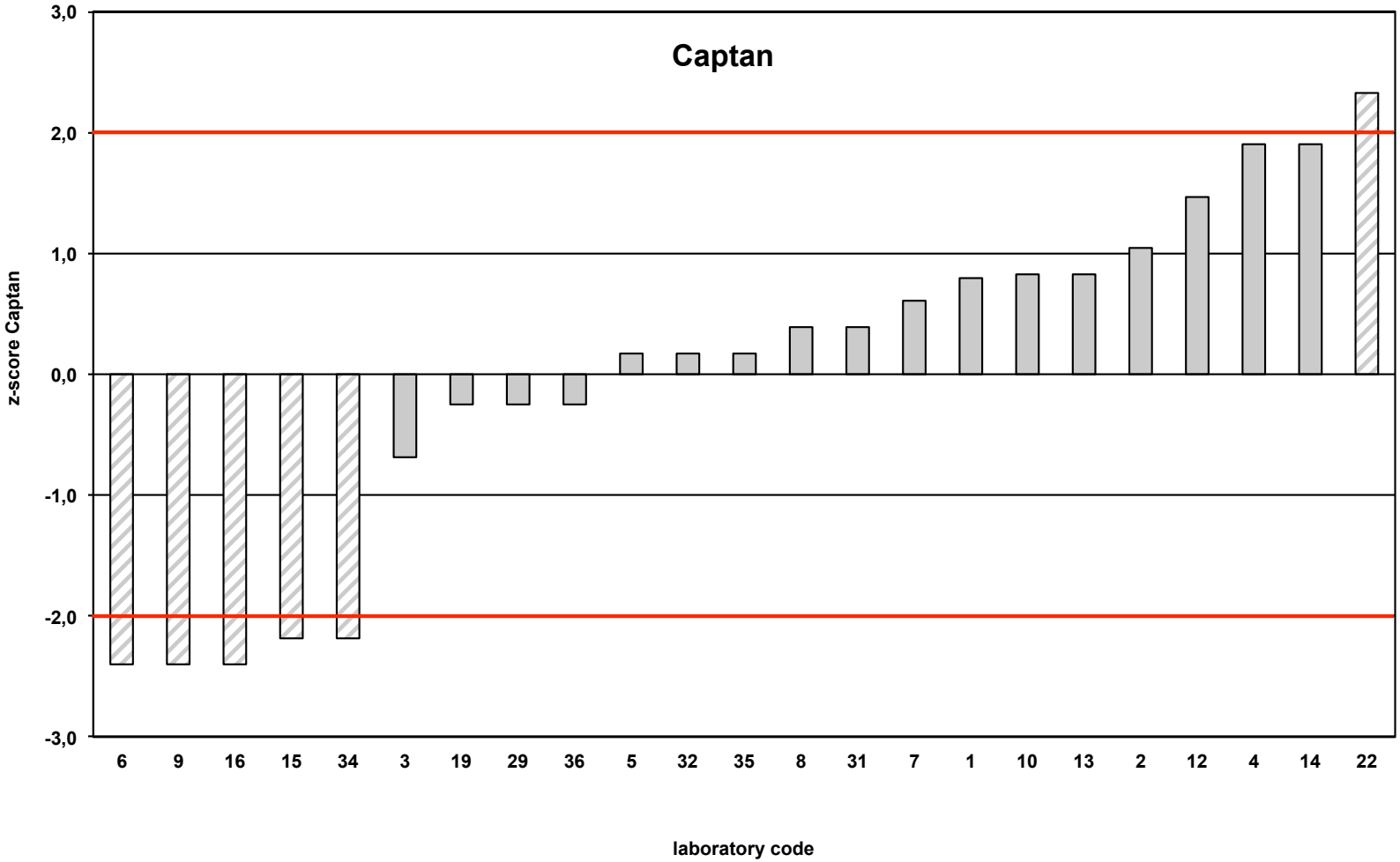


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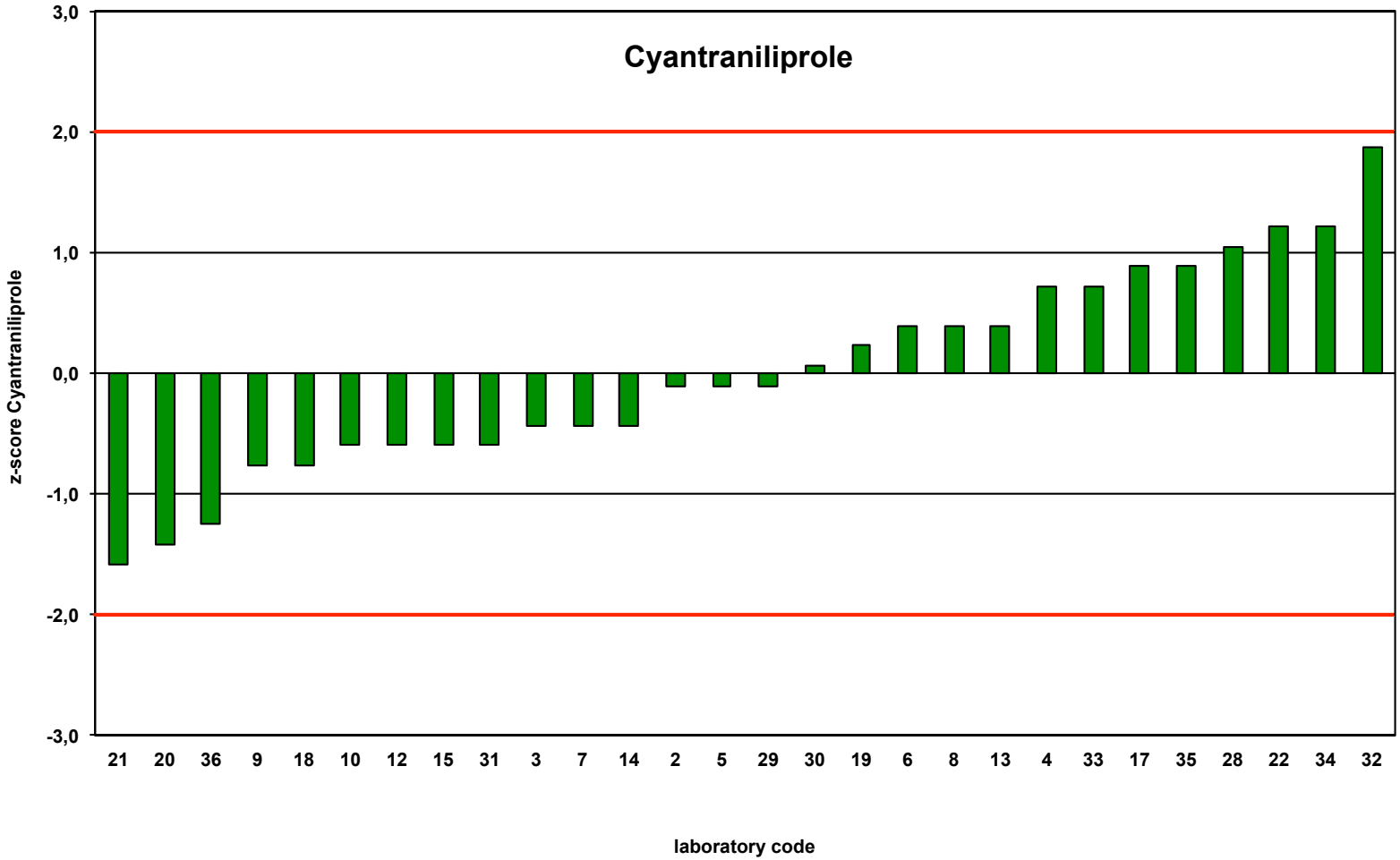
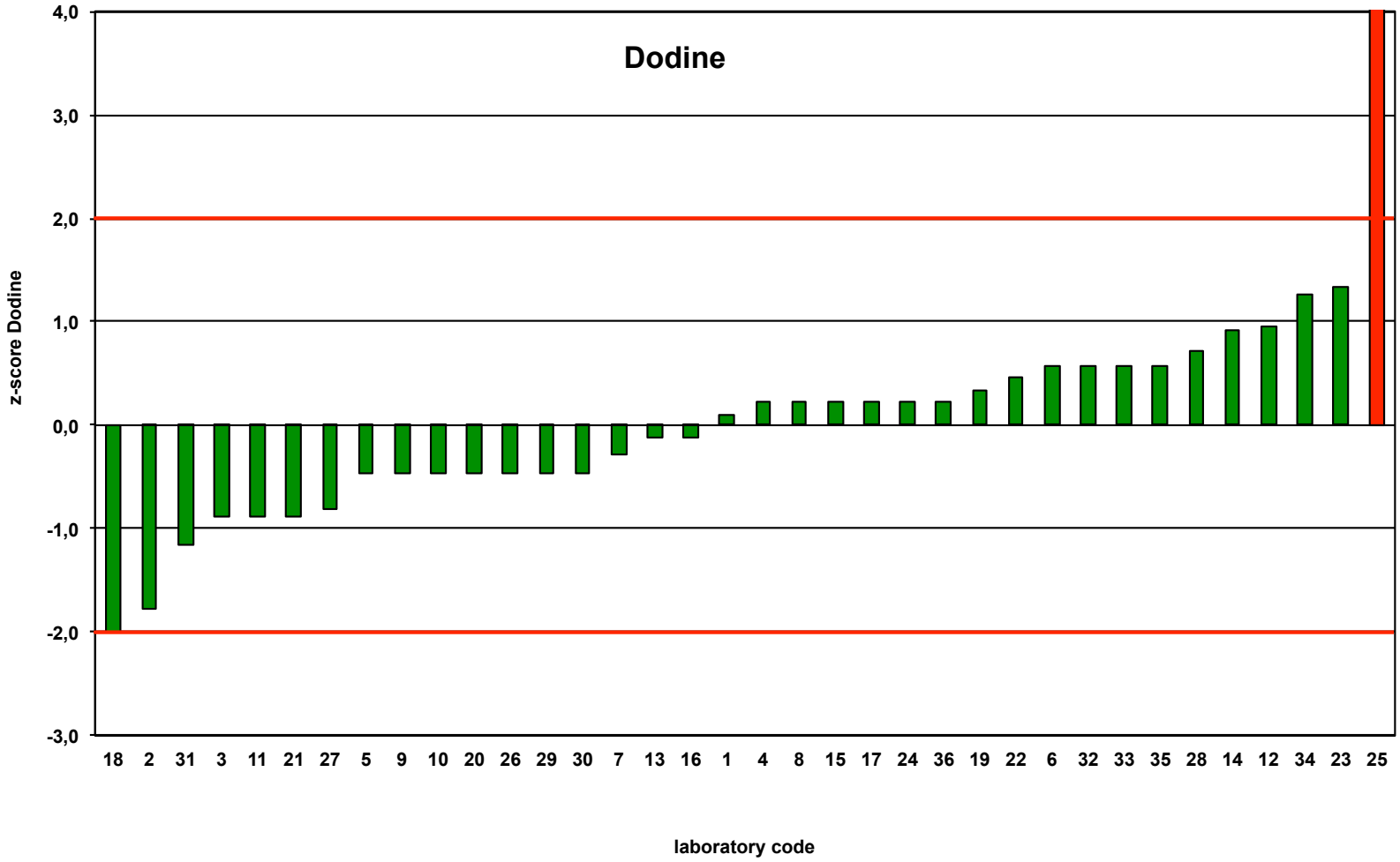
Figure 4: Assessment of Cyantraniliprole (comparability)



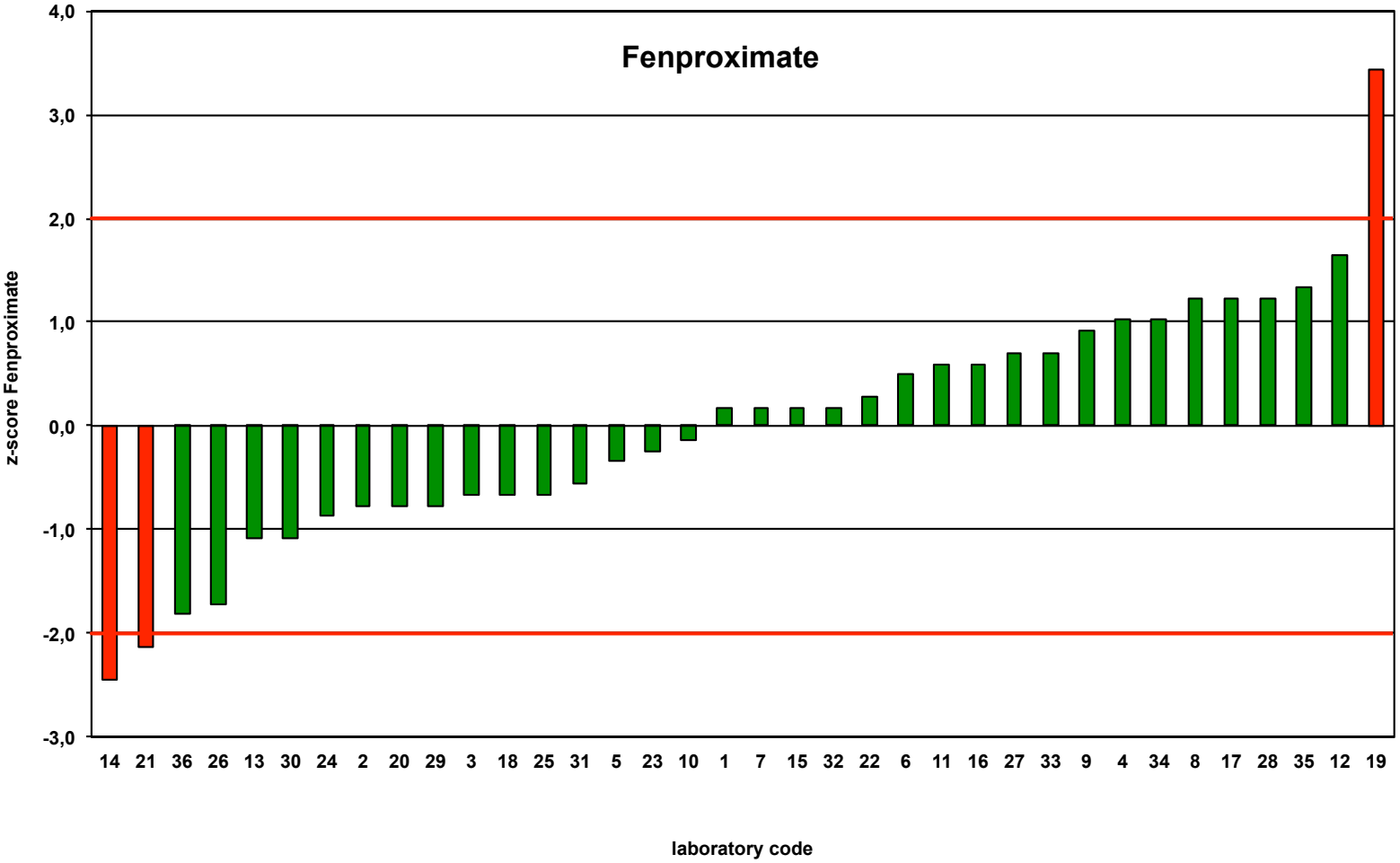
Green: satisfactory results, red: dissatisfactory results

Figure 5: Assessment of Dodine (comparability)



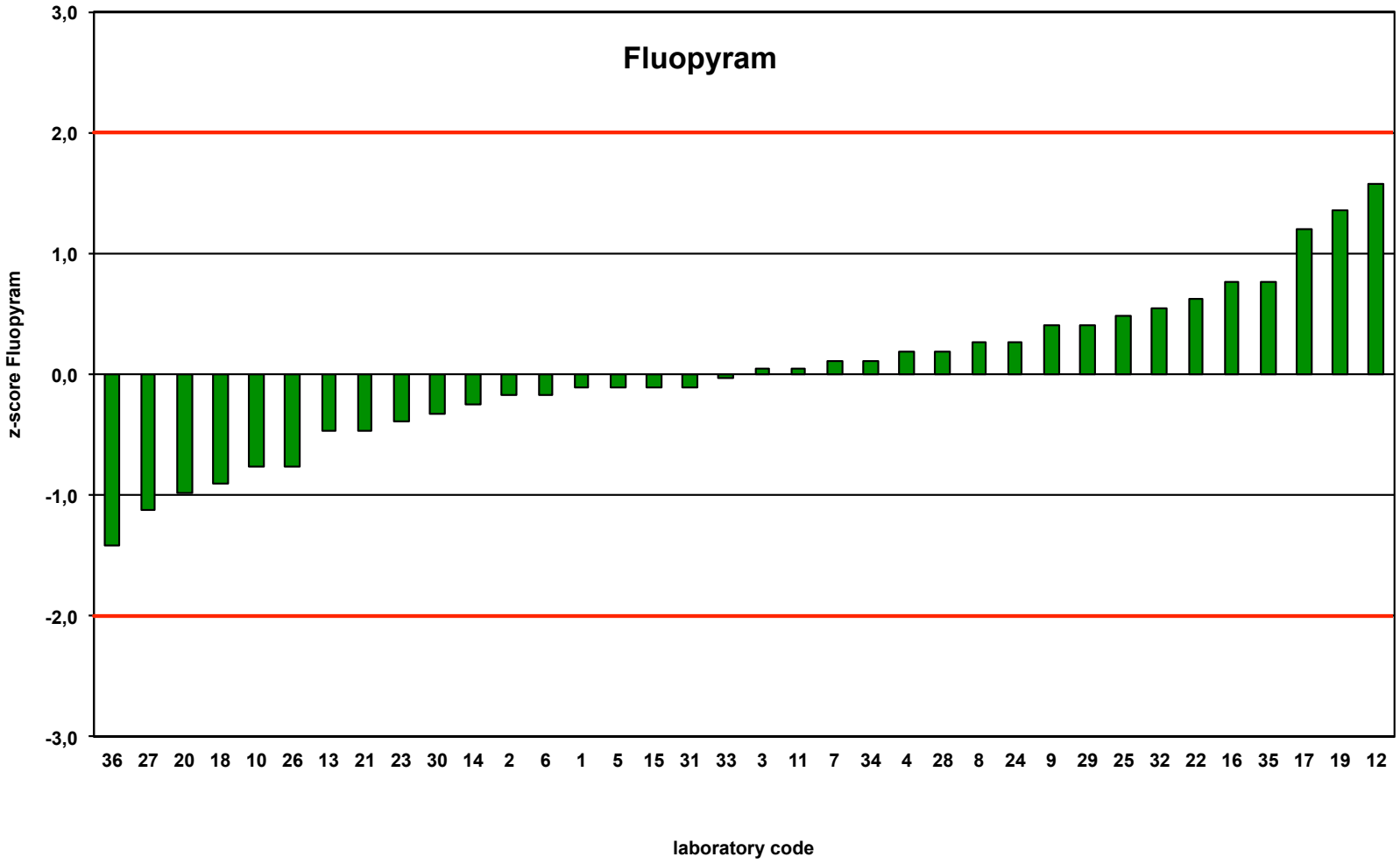
Green: satisfactory results, red: dissatisfactory results

Figure 6: Assessment of Fenproximate (comparability)



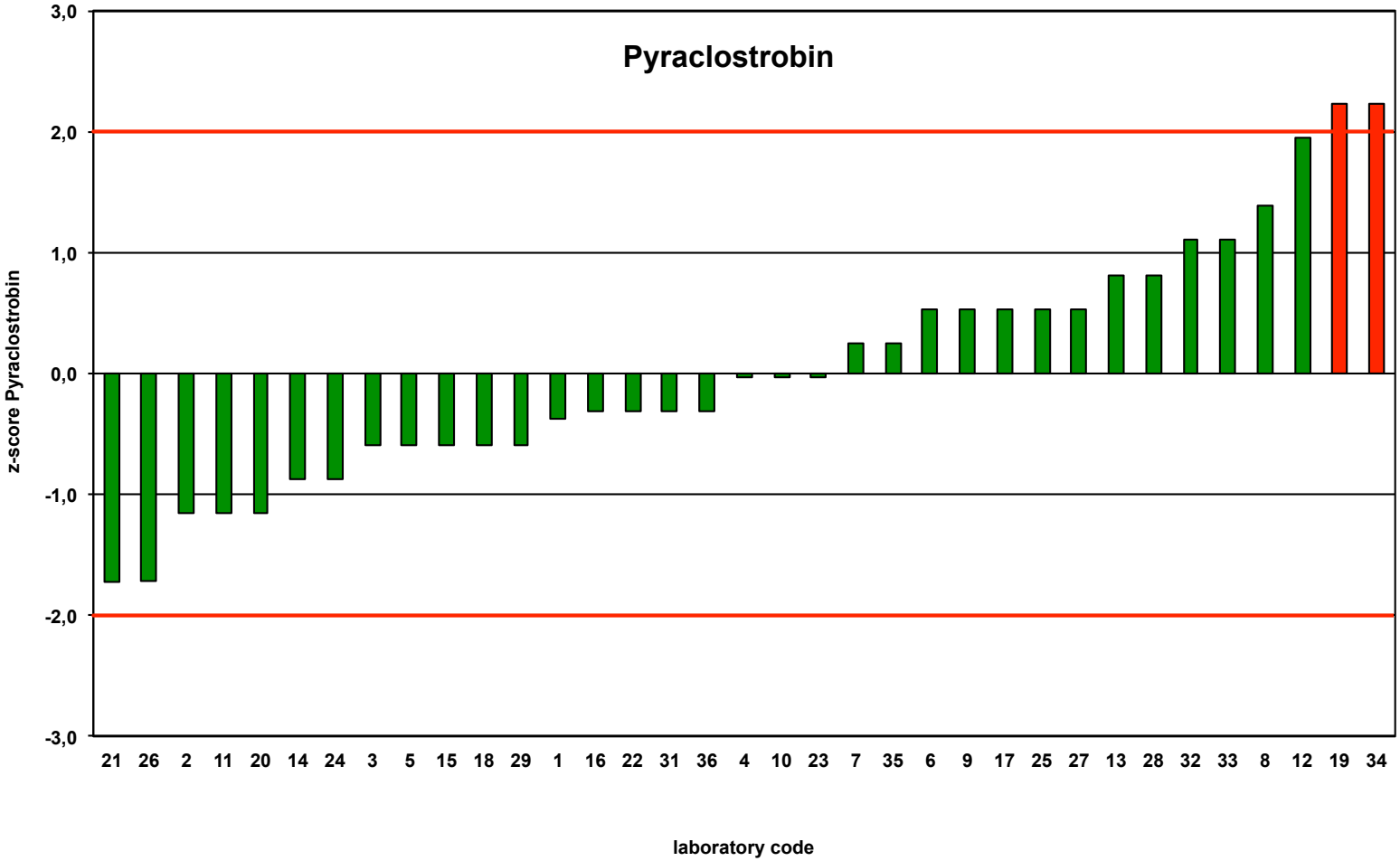
Green: satisfactory results, red: dissatisfactory results

Figure 7: Assessment of Fluopyram (comparability)



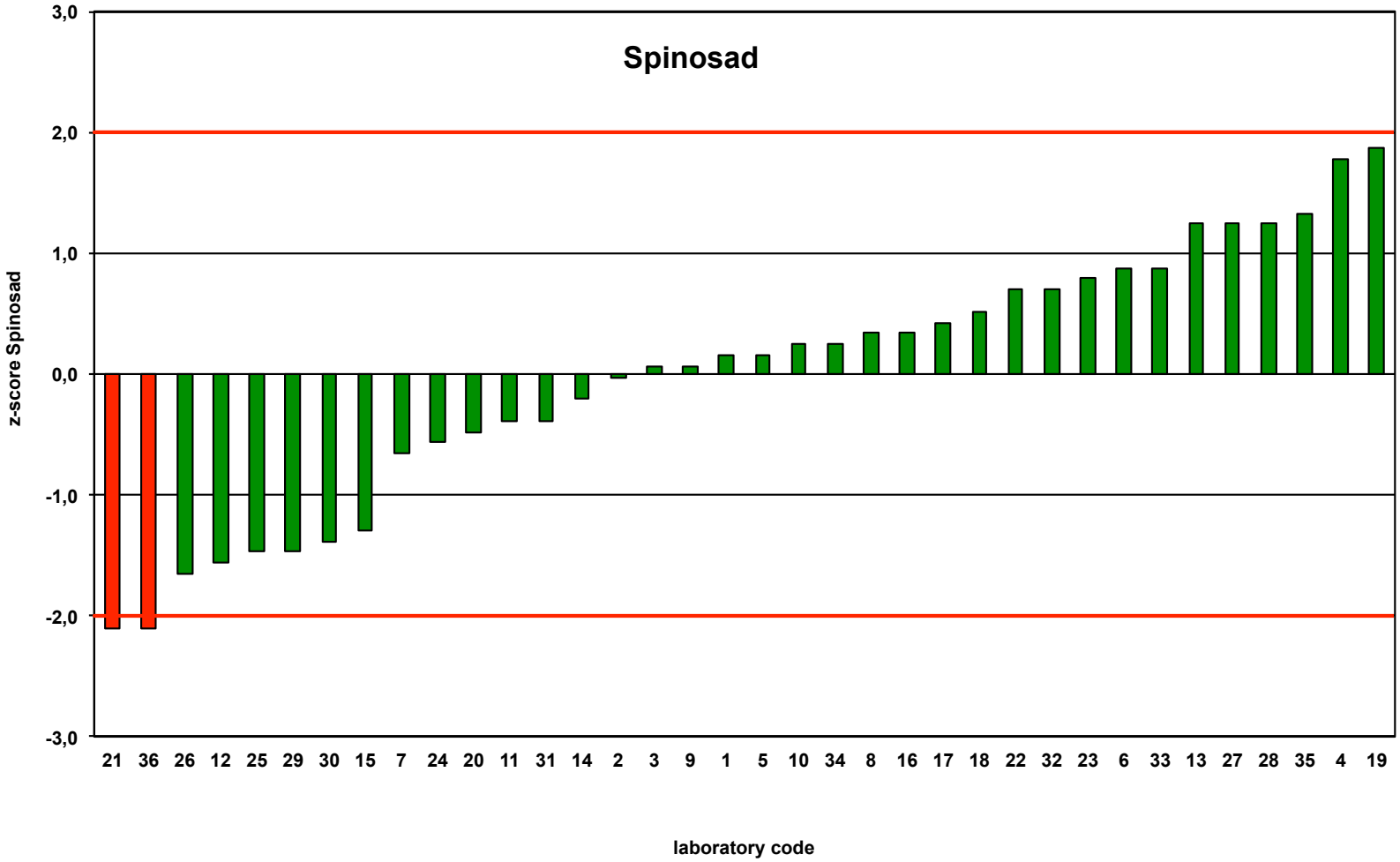
Green: satisfactory results, red: dissatisfactory results

Figure 8: Assessment of Pyraclostrobin (comparability)



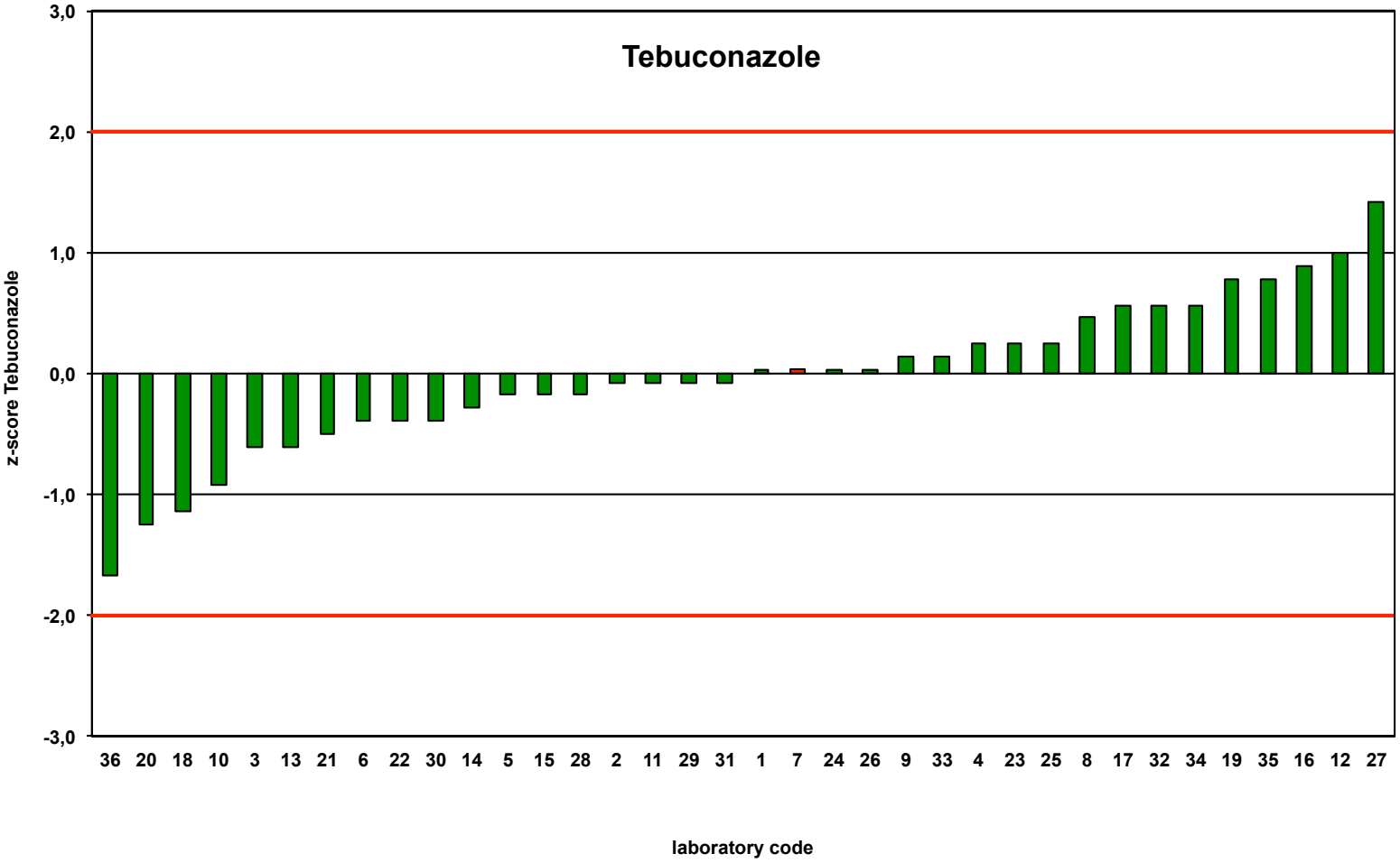
Green: satisfactory results, red: dissatisfactory results

Figure 9: Assessment of Spinosad (comparability)



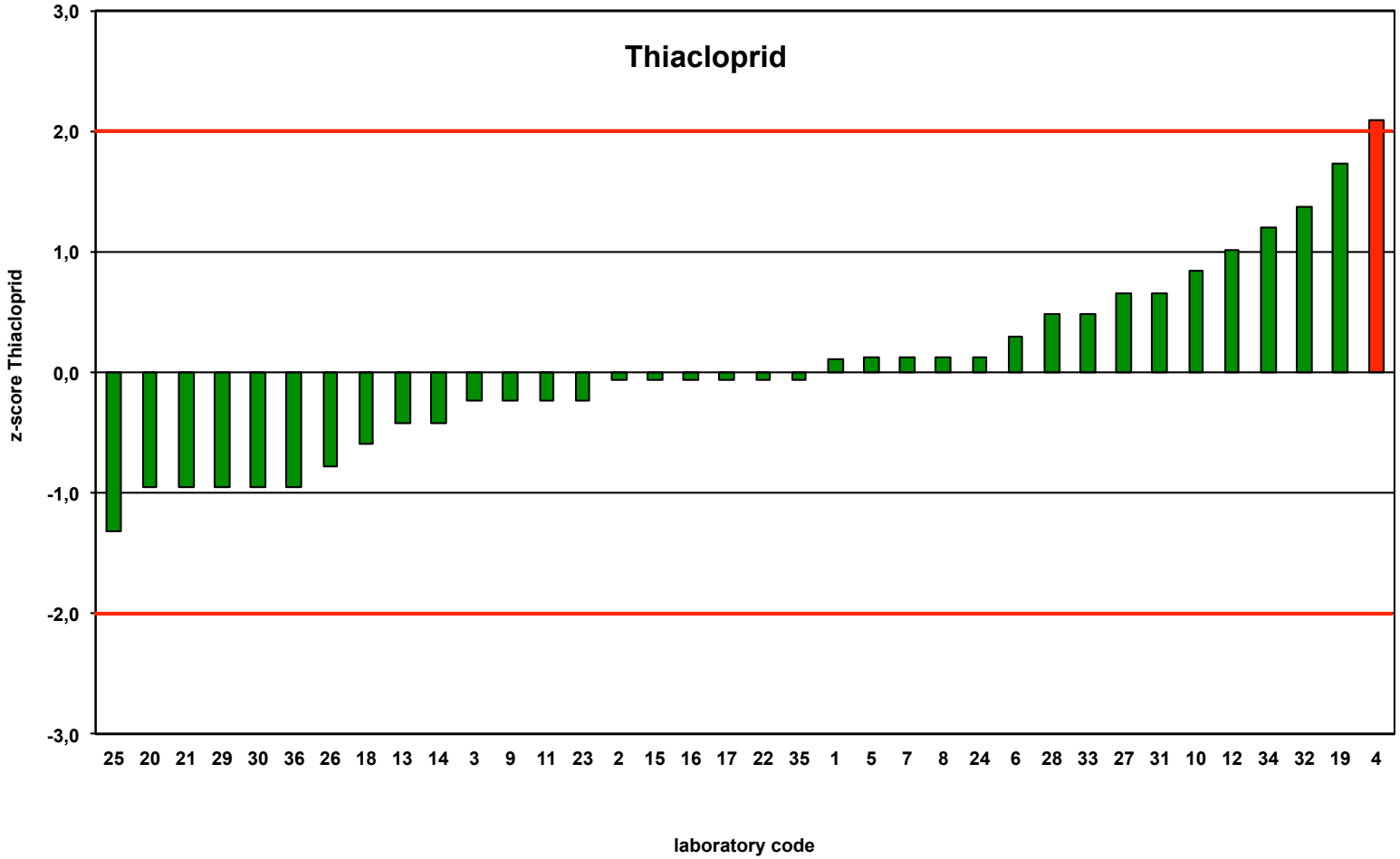
Green: satisfactory results, red: dissatisfactory results

Figure 10: Assessment of Tebuconazole (comparability)



Green: satisfactory results, red: dissatisfactory results

Figure 11: Assessment of Thiacloprid (comparability)



Green: satisfactory results, red: dissatisfactory results

5. Homogeneity and stability testing

Ten randomly chosen test samples were used for representative testing. Each sample was analysed in duplicate. The results confirm the homogeneous distribution of the pesticides in the test samples. After the closure of transmission of results one fridge-stored test sample was analysed twice to confirm the stability of the pesticides over the period of the test. The mean of the results is compared to the mean result of the homogeneity testing. The results confirm the stability of all analytes throughout the test.

Table 15. Results of the homogeneity and stability testing

(Detailed results available on request)

Pesticide	Homogeneity			Stability	
	mean samples 1-10	SD samples 1-10	CV samples 1-10	sample 11	stability versus homogeneity
	[mg/kg]	[mg/kg]	%	[mg/kg]	%
Acetamiprid	0,031	0,0026	8,4	0,037	119
Boscalid	0,073	0,0050	6,8	0,061	84
Cyantraniliprole	0,031	0,0019	6,3	0,031	100
Fenpyroximate	0,039	0,0031	8,1	0,046	118
Fluopyram	0,047	0,0047	10,0	0,063	134
Pyraclostrobin	0,014	0,0017	12,4	0,014	100
Spinosad	0,043	0,0034	7,9	0,051	119
Thiacloprid	0,020	0,0015	7,8	0,025	126
Dodine	0,146	0,0041	2,8	0,139	96
Myclobutanil	0,004	0,0006	14,7	0,003	75
Tebuconazole	0,031	0,0033	10,7	0,035	113

SD = standard deviation
CV = coeficient of variation