Evaluation of the three main multiresidue methods for the validation of new substances of SANCO/12745/2013 and those with low analytical coverage

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1. Aim and scope

This document describes the validation data for 33 pesticides included in the Working document SANCO/12745/2013 using three multiresidue extraction methods by LC-QqQ-MS/MS and GC-QqQ-MS/MS in zucchini, orange and avocado.

2. Short description

Homogenous samples were extracted using three different methods (QuEChERS, ethyl acetate and Dutch mini-Luke) with and without clean-up, as well as using the Acidified-QuEChERS method. The obtained extracts were then analyzed by LC-QqQ-MS/MS and GC-QqQ-MS/MS.

3. Experimental

3.1. Extraction procedures

3.1.1. QuEChERS

3.1.1.1. Citrate-buffered QuEChERS without clean-up

1. Weigh 10 g ± 0.1 g of sample in 50 mL PTFE centrifuge tube.
2. Add 10 mL of acetonitrile and 10 µL of 10 mg/L carbendazim-d3, dichlorvos-d6 and malathion-d10 (procedure internal standards).
3. Shake the sample using an automatic axial shaker for 4 min.
4. Add 4 g of anhydrous magnesium sulfate, 1 g of sodium chloride, 1 g of trisodium citrate dihydrate and 0.5 g of disodium hydrogenocitrate sesquihydrate.
5. Shake the samples again in the automatic shaker for 4 min.
6. Centrifuge the tubes at 3700 rpm for 5 min.
7. Injection vials preparation:
   a. for LC analysis, dilute 100 mL extract with 400 mL of water containing dimethoate-d6 at 0.0625 mg/L (Injection Internal Standard) and ascorbic acid at 600 mg/L.
   b. for GC analysis, evaporate 50 µL extract and reconstitute with 50 µL of ethyl acetate. Additionally, 2 µL of lindane-d6 (Injection Internal Standard) were added to the final vials.

3.1.1.2. Citrate-buffered QuEChERS with clean-up

1. Transfer 5 mL of the supernatant obtained in step 6 of section 3.1.1.1. to a 15 mL PTFE tube containing:
   a. 750 mg anhydrous magnesium sulfate and 125 mg PSA for matrices with high water content.
   b. 750 mg anhydrous magnesium sulfate and 125 mg Z-Sep for matrices with high fat content.
2. Vortex the tube for 30 sec.
3. Centrifuge the tubes at 3700 rpm for 5 min.
4. Add 40 µL (10 µL/mL) of formic acid 5% in acetonitrile to option a in step 1.
5. Injection vials preparation: follow step 7 of section 3.1.1.1.

3.1.1.3. Acidified-QuEChERS

1. Weigh 10 g ± 0.1 g of sample in 50 mL PTFE centrifuge tube.
2. Add 10 mL of acetonitrile containing 1% formic acid, and 10 µL of 10 mg/L carbendazim-d3, dichlorvos-d6 and malathion-d10 (procedure internal standards).
3. Shake the sample using an automatic axial shaker for 4 min.
4. Add 4 g of anhydrous magnesium sulfate and 1 g of sodium chloride.
5. Shake the samples again in the automatic shaker for 4 min.
6. Centrifuge the tubes at 3700 rpm for 5 min.
7. Injection vials preparation: follow step 7.a of section 3.1.1.1.

With this treatments, 1 mL of sample extract represents 0.2 g of sample in LC and 1 g of sample in GC.

3.1.2. Ethyl acetate method

3.1.2.1. Without clean-up

1. Weigh 10 g ± 0.1 g of sample in a 50 mL PTFE centrifuge tube.
2. Add 10 mL of ethyl acetate and 10 µL of 10 mg/L carbendazim-d3, dichlorvos-d6 and malathion-d10 (procedure internal standards).
3. Shake with the automatic axial extractor during 15 min.
4. Add 1.5 g of sodium chloride and 8 g of anhydrous magnesium sulfate.
5. Shake with the automatic axial extractor during 15 min.
6. Centrifuge for 5 min at 3500 rpm.
7. Injection vials preparation:
   a. for LC analysis, evaporate 100 µL of the extract and reconstitute with 100 of acetonitrile and 400 mL of water containing dimethoate-d6 at 0.0625 mg/L (Injection Internal Standard) and ascorbic acid at 600 mg/L.
   b. for GC analysis 2 µL of lindane-d6 (Injection Internal Standard) at 1.5 mg/L were added to 50 µL of ethyl acetate.

3.1.2.2. With clean-up

1. Transfer 5 mL of the supernatant obtained in step 6 of section 3.1.2.1. to a 15 mL PTFE tube containing:
   a. 750 mg anhydrous magnesium sulfate and 125 mg PSA for matrices with high water content.
   b. 750 mg anhydrous magnesium sulfate and 125 mg Z-Sep for matrices with high fat content.
2. Vortex the tube for 30 sec.
3. Centrifuge the tubes at 3700 rpm for 5 min.
4. Add 40 µL of formic acid 5% in acetonitrile to option a in step 1.
5. Injection vials preparation: follow step 7 of section 3.1.2.1.

With this treatments, 1 mL of sample extract represents 0.2 g of sample in LC and 1 g of sample in GC.

3.1.3. Dutch mini-Luke method

3.1.2.1. Without clean-up

1. Weigh 7.5 g ± 0.1 g of subsample in a 50 mL PTFE centrifuge tube.
2. Add 10 mL of acetone and 3 g of sodium chloride.
3. Add 7.5 µL of 10 mg/L carbendazim-d3, dichlorvos-d6 and malathion-d10 (procedure internal standards).
4. Blend the sample with Polytron homogenizer at 1500 rpm for 30 sec.
5. Add 10 mL of petroleum ether and 5 mL of dichlorometane.
6. Blend again the sample with Polytron homogenizer at 1500 rpm for 30 sec.
7. Centrifuge for 5 min at 3500 rpm.
8. Injection vials preparation:
   a. for LC analysis, evaporate 167 µL extract and reconstitute with 50 µL of acetonitrile and 200 mL of water containing dimethoate-d6 at 0.0625 mg/L (Injection Internal Standard) and ascorbic acid at 600 mg/L.
   c. for GC analysis, evaporate 167 µL extract and reconstitute with 50 µL of ethyl acetate. Additionally, 2 µL of lindane-d6 (Injection Internal Standard) were added to the final vials.

3.1.2.2. With clean-up

1. Transfer 5 mL of the supernatant obtained in step 7 of section 3.1.3.1. to a 15 mL PTFE tube containing:
   a. 750 mg anhydrous magnesium sulfate and 125 mg PSA for matrices with high water content.
   b. 750 mg anhydrous magnesium sulfate and 125 mg of Z-Sep for matrices with high fat content.
2. Vortex the tube for 30 sec.
3. Centrifuge the tubes at 3700 rpm for 5 min.
4. Add 40 µL of formic acid 5% in acetonitrile to option a in step 1.
5. Injection vials preparation: follow step 8 of section 3.1.3.1.

With this treatments, 1 mL of sample extract represents 0.2 g of sample in LC; in GC, the final matrix concentration is 1 g/mL.

3.2. Instrumentation and analytical conditions for the LC- MS/MS system

All samples were analyzed by a 1200 UHPLC Instrument coupled to a 6490A LC/MS Triple Quad (Agilent Technologies). The analytical parameters are detailed below.

3.2.1. 1290 UHPLC (Agilent)

- Column: Zorbax Eclipse Plus C8 2.1 x 100 mm and 1.8 µm particle size (Agilent).
- Mobile phase A: Water (0.1% formic acid, 5mM ammonium formate, 2% MeOH).
- Mobile phase B: Methanol (0.1% formic acid, 5mM ammonium formate, 2% H2O).
- Column temperature: 35ºC

- Flow rate: 0.3 mL/min
- Injection volume: 5 µL.
- Mobile phase gradient:

Time (min)	Mobile phase A (%)	Mobile phase B (%)
0	100	0
2	80	20
15	0	100
18	0	100

- Re-equilibration with initial mobile phase: 2.5 minutes.

3.2.2. 6490 triple quadrupole system (Agilent)

- Ionization mode: Positive and negative mode.
- Capillary (positive and negative): 3000 V.
- Nebulizer and collision gas: Nitrogen.
- Nebulizer: 45 psi.
- Nozzle: 400 V.
- Drying gas flow: 15 L/min.
- Drying gas temperature: 120ºC.
- Sheath gas flow: 10 L/min.
- Sheath gas temperature: 375ºC.
- High Pressure RF (positive): 150 V.
- High Pressure RF (negative): 110 V.
- Low Pressure RF (positive): 60 V.
- Low Pressure RF (negative): 60 V.

3.3. Instrumentation and analytical conditions for the GC- MS/MS system

All samples were analyzed by an Intuvo 9000 GC Instrument coupled to a 7410 GC/MS Triple Quad (Agilent Technologies). The analytical parameters are detailed below. The mass transitions used are presented in Appendix I (Table 1 for LC-MS/MS and Table 2 for GC-MS/MS parameters).

3.3.1. Intuvo 9000 GC system (Agilent)

- Column: 2 Planar columns HP-5MS UI (15 m long × 0.25 mm i.d. × 0.25 µm film thickness) (Agilent).
- Injection mode: splitless, 1 µL.
- Ultra-inert inlet liner with glass wool frit (Agilent).
- Injector temperature: 80 °C (0.1 min), then up to 300 °C at 600 °C/min (hold for 5 min) and finally down to 250 °C at 100 °C/min.
- Carrier gas: Helium (purity 99.999%) at constant flow = 1.611 mL/min.
- Carrier gas purity: 99.999%.
- Oven temperature: 60 °C for 0.5 min, up to 170 °C (40 °C/min) and up to 310 °C (10 °C/min).

3.3.2. 7410 triple quadrupole system (Agilent)

- Ionization mode: electron impact ionization.
- Temperature of the transfer line: 280 °C.
- Temperature of ion source: 280 °C.
- Collision gas: Nitrogen.
- Collision gas purity: 99.999%.
- Solvent delay: 2.6 minutes.

4. Results and discussion

The performance of the three main multiresidue methods for pesticide analysis (QuEChERS, ethyl acetate and Dutch mini-Luke), with and without clean-up, as well as the acidified-QuEChERS method were evaluated in zucchini, orange and avocado. Acidified-QuEChERS extracts were assessed only for LC-amenable compounds. In the case of avocado matrix, ethyl acetate and Ducth mini-Luke extracts were not injected in the LC system due to the presence of flocs in the injection vials (**Figure 1**). For the same reason, Dutch mini-Luke avocado extracts without clean-up, were not injected in the GC system.

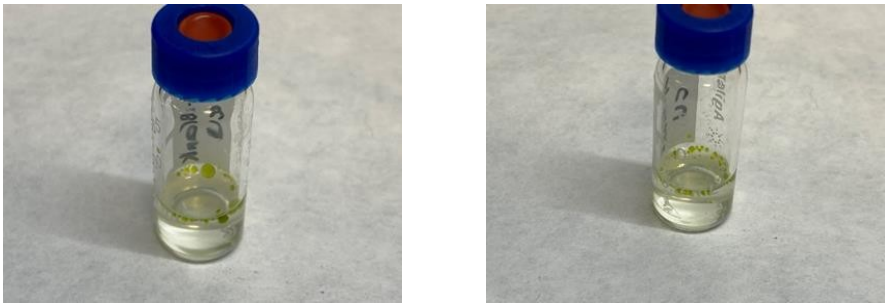

Figure 1. Presence of flocs in avocado LC injection vials.

4.1. Linearity

Linearity of the MS/MS system was evaluated by assessing the signal responses of the target analytes from matrix-matched calibration solutions prepared by spiking blank extracts at seven concentration levels, from 0.002 to 0.200 mg/L. In most cases, coefficient of determination (R^2) was higher than 0.99 and back-calculated concentrations were within ± 20%. The exceptions were the LC-amenable pesticides diafenthiuron, maleic hydrazide, metaflumizone and trinexapac (free acid). Therefore, these compounds were not included in the validation study.

Table 1 and **Table 2** of **Appendix I** show the detection and chromatographic parameters for the selected compounds analyzed by LC-MS/MS and GC-MS/MS, respectively.

Linearity ranges for all pesticides are summarized in **Appendix II**:

A) **Tables 3-5**, for QuEChERS method.

B) **Tables 6-7**, for ethyl acetate method.

C) **Tables 8-9**, for Dutch mini-Luke method.

4.2. Matrix effects

Matrix effects were assessed by comparison of the slopes of seven-point matrix-matched calibration curves with the slopes of the calibration curves in solvent (LC) or in tomato (GC). For values (in absolute terms) between 0% and 20%, matrix effect was considered low; a moderate matrix effect would have values between 20% and 50%, and for compounds with a value above 50 %, matrix effect was considered strong. **Figure 2** represents matrix effects obtained for 29 LC-amenable and 9 GC-amenable pesticides evaluated in the three studied matrices.

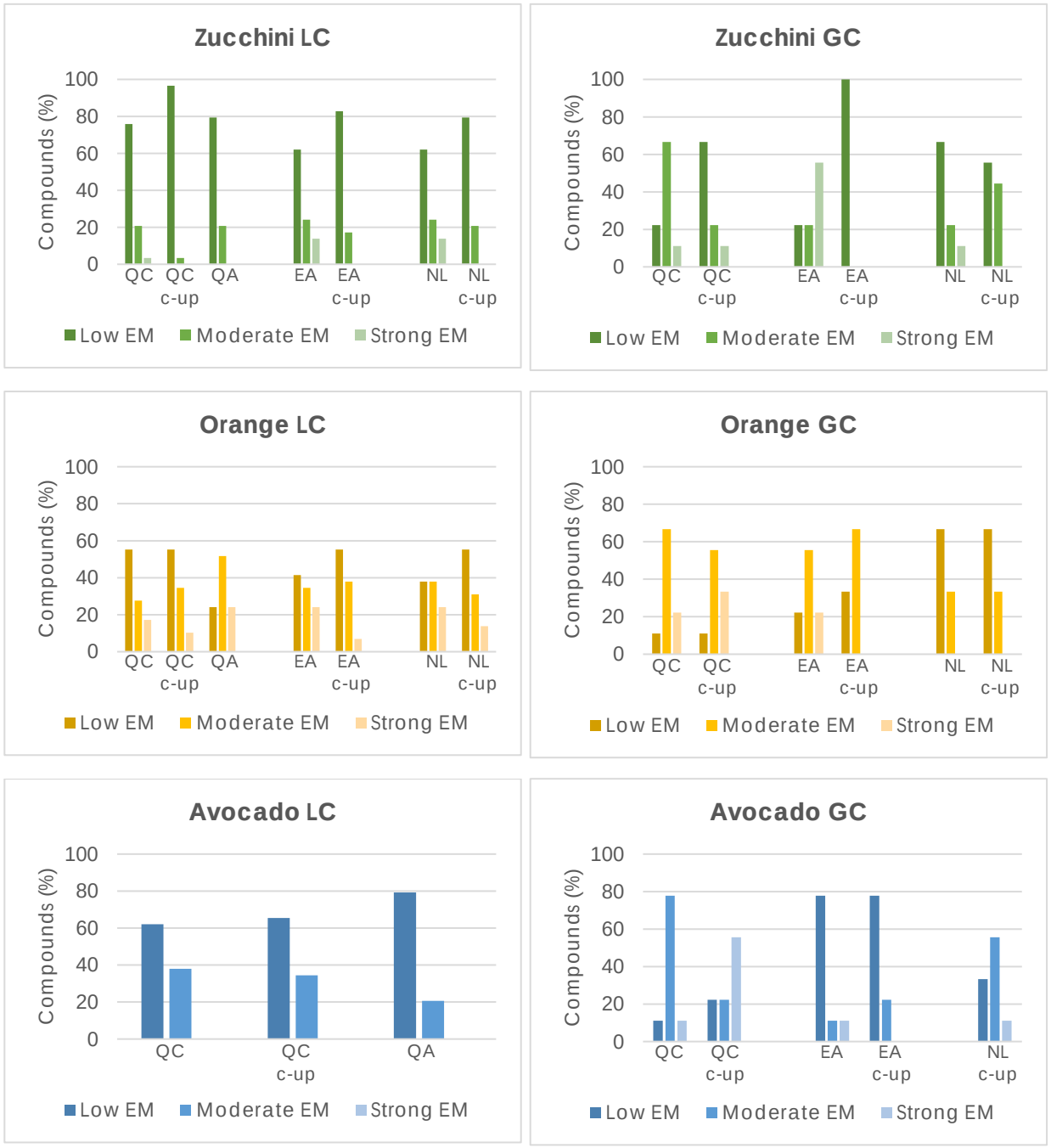

Figure 2. Matrix effects (QC: Citrate-buffered QuEChERS, QA: Acidified-QuEChERS, EA: Ethyl acetate, NL: Dutch mini-Luke, c-up: clean-up).

Values of matrix effects are summarized in **Appendix II**:

A) **Tables 3-5**, for QuEChERS method.

B) **Tables 6-7**, for ethyl acetate method.

C) **Tables 8-9**, for Dutch mini-Luke method.

4.3. Ion ratio and peak shape

The ion ratio was calculated between the qualitative peak area and the quantitative peak area. In all cases, the obtained values of ion ratio were within ± 30% of the average of calibration standards ion ratios from the same sequence.

Most of the studied pesticides showed acceptable peak shape, except matrine (pKa = 9.75), which exhibited peak splitting (**Figure 3** due to the high polarity of this compound.

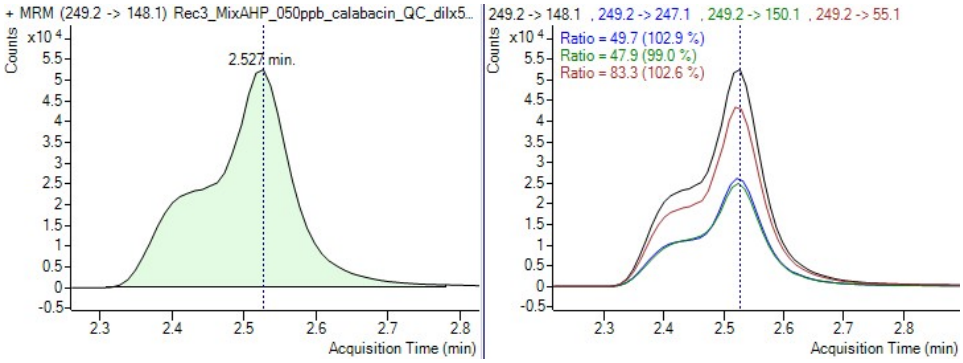

Figure 3. Extracted ion chromatograms of matrine in zucchini (spiked at 50 µg/kg) extracted with QuEChERS method without clean-up.

4.4. Recoveries and within-laboratory reproducibility

The mean recovery (n=5) and within-laboratory reproducibility in terms of relative standard deviation (RSDr) of 33 pesticides were evaluated at two spiking levels (0.005 and 0.050 mg/kg) in the three matrices included in the present study (zucchini, orange and avocado).

The results are summarized in **Appendix II**:

A) **Tables 10-12**, for QuEChERS method.

B) **Tables 13-14**, for ethyl acetate method.

C) **Tables 15-16**, for Dutch mini-Luke method.

Most recovery results were within the range of 70-120% (RSD ≤ 20%). **Figure 4** shows the obtained results.

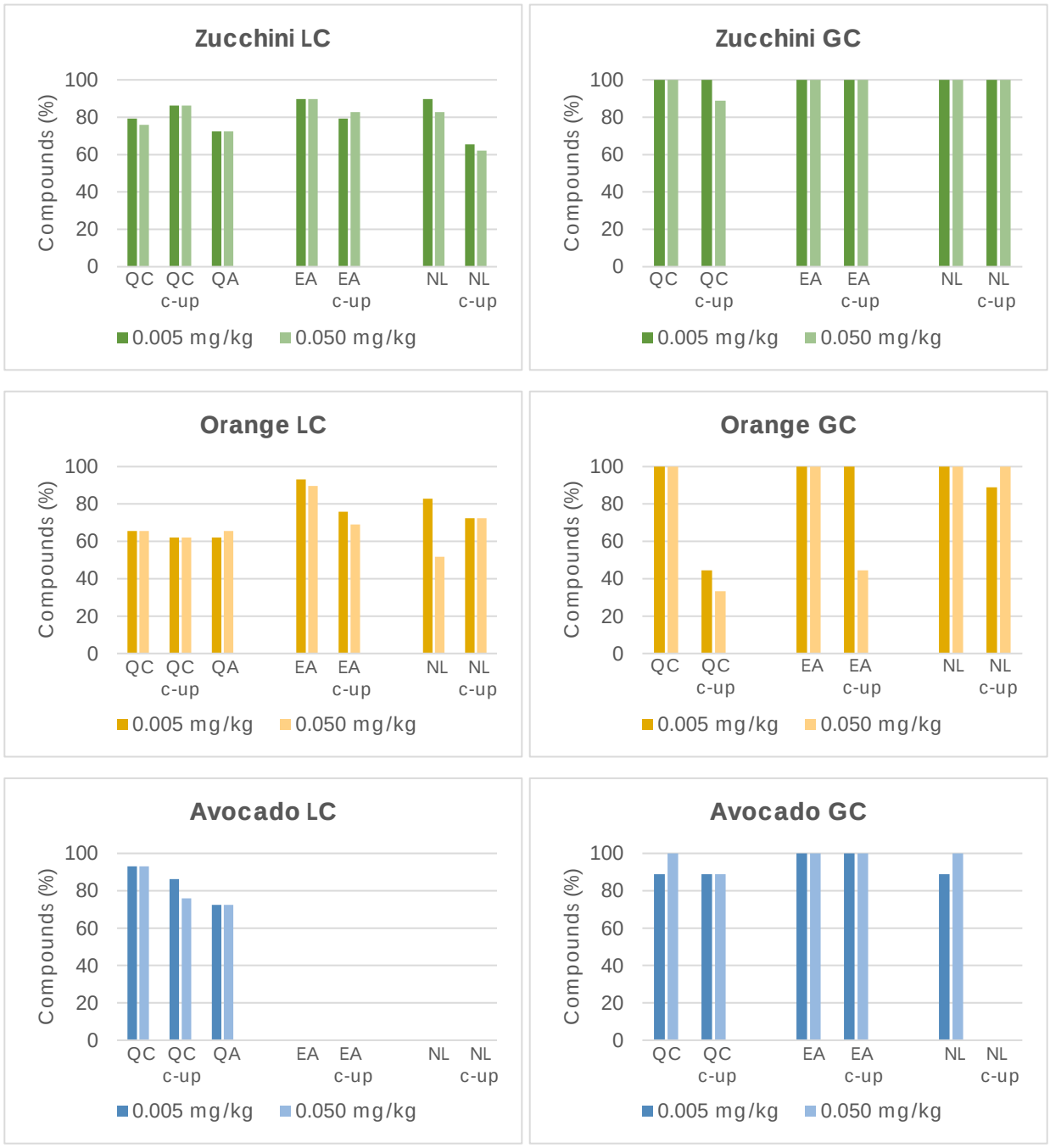

Figure 4. Percentage of compound with recoveries in the range of 70% -120% and RSD ≤ 20%.

5. References

Analytical quality control and method validation procedures for pesticide residues analysis in food and feed. Document SANTE/11312/2021.

Working document on pesticides to be considered for inclusion in the national control programmes to ensure compliance with maximum residue levels of pesticides residues in and on food of plant and animal origin. Document SANCO/12745/2013.

APPENDIX I: MASS TRANSITIONS

Table 1. Detection and chromatographic parameters for the selected compounds analyzed by LC-MS/MS.

	Name	t_R (min)	Precursor ion 1 (m/z)	Product ion 1 (m/z)	CE 1 (V)	Precursor ion 2 (m/z)	Product ion 2 (m/z)	CE 2 (V)
1	Benzovindiflupyr	12.48	398.0	342.0	15	398.0	377.0	10
2	Bifenazate	11.57	301.1	198.2	10	301.1	169.9	20
3	Chloridazon	5.98	222.1	104.1	20	222.1	92.0	20
4	Clomazone	10.54	240.1	124.9	20	240.1	127.8	10
5	Cyantraniliprole	9.26	474.9	285.8	25	474.9	444.0	15
6	Cyflumetofen	13.35	465.3	173.1	25	465.3	248.8	10
7	Dinotefuran	3.28	203.1	129.1	9	203.1	114.1	9
8	Diuron	10.09	233.0	72.1	20	233.0	46.1	16
9	Fenobucarb	10.88	208.2	95.1	20	208.2	151.9	5
10	Fenpicoxamid	13.35	615.3	238.9	25	615.3	515.0	13
11	Florpyrauxifen-benzyl	12.78	439.2	91.1	40	441.2	90.9	55
12	Flupyradifuron	6.13	289.2	126.0	20	289.2	72.9	75
13	Flutianil	12.52	427.1	192.1	35	427.1	410.9	30
14	Fluxapyroxad	11.3	381.9	362.0	10	381.9	342.0	15
15	Forchlorfenuron	9.95	248.0	128.9	20	248.0	93.0	30
16	Isofetamid	11.78	360.4	125.0	30	360.4	210.0	5
17	Matrine	2.47	249.2	148.1	37	249.2	55.1	37
18	Matrine-N-oxide	3.03	265.2	247.1	29	265.2	205.0	29
19	Mefentrifluconazole	12.68	397.8	70.0	25	397.8	181.9	30
20	Novaluron	13.29	490.8	470.7	5	490.8	305.1	15
21	Oxathiapipronil	11.22	540.2	500.0	29	540.2	522.0	29
22	Penflufen	12.37	318.1	234.0	10	318.1	141.0	20
23	Penthiopyrad	12.54	357.9	149.0	25	357.9	207.6	20
24	Pyriofenone	12.86	366.1	183.9	20	366.1	209.0	20
25	Rotenone	11.89	395.0	213.1	20	395.0	192.1	20
26	Tolfenpyrad	13.53	384.1	197.0	25	384.1	170.9	20
27	Triflumizole	13.23	346.1	277.8	5	346.1	72.9	15
28	Trinexapac-ethyl	10.16	253.1	68.9	20	253.1	41.1	45
29	Trinexapac-methyl	9.08	239.1	69.0	10	239.1	41.2	40

Table 2. Detection and chromatographic parameters for the selected compounds analyzed by GC-MS/MS.

	Name	t_R (min)	Precursor ion 1 (m/z)	Product ion 1 (m/z)	CE 1 (V)	Precursor ion 2 (m/z)	Product ion 2 (m/z)	CE 2 (V)
1	Aclonifen	7.85	264	194	15	212	182	10
2	Cyflumetofen	8.92	173	145	5	173	95	10
3	Flutianil	10.66	426	231	15	231	200	15
4	Isofetamid	9.35	182	125	10	177	135	10
5	Isopyrazam	9.41	359	303	8	159	139	10
6	Novaluron	3.43	335	168	35	168	139,9	10
7	Penthiopyrad	7.82	302	177	20	177	101	20
8	Pyriofenone	8.51	365	350	5	350	320	5
9	Quintozene	5.59	295	265	10	295	237	15

APPENDIX II: VALIDATION RESULTS

Table 3. Linearity ranges, coefficients of determination and matrix effects for selected matrices studied by using citrate-buffered QuEChERS method without clean-up. Negative values of matrix effects mean suppression of the signal, and positives values, enhancement.

No.	Compound	Linear Range (mg/kg)			R^2			Matrix effect (%)		
		Zucchini	Orange	Avocado	Zucchini	Orange	Avocado	Zucchini	Orange	Avocado
1	**Benzovindiflupyr**	0.002-0.200	0.002-0.200	0.002-0.100	> 0.99	> 0.99	> 0.99	-9	-9	-12
2	**Bifenazate**	0.002-0.200	0.002-0.200	0.002-0.200	> 0.99	> 0.99	> 0.99	-4	-29	-12
3	**Chloridazon**	0.002-0.200	0.002-0.200	0.002-0.200	> 0.99	> 0.99	> 0.99	-4	-55	-28
4	**Clomazone**	0.002-0.200	0.002-0.200	0.002-0.200	> 0.99	> 0.99	> 0.99	-4	-38	-5
5	**Cyantraniliprole**	0.002-0.200	0.002-0.200	0.002-0.200	> 0.99	> 0.99	> 0.99	-5	-29	-12
6	**Cyflumetofen**	0.002-0.050	0.002-0.200	0.002-0.050	> 0.99	> 0.99	> 0.99	-48	9	41
7	**Dinotefuran**	0.002-0.200	0.002-0.200	0.002-0.200	> 0.99	> 0.99	> 0.99	1	-3	-23
8	**Diuron**	0.002-0.200	0.002-0.200	0.002-0.200	> 0.99	> 0.99	> 0.99	-1	-86	-1
9	**Fenobucarb**	0.002-0.200	0.002-0.200	0.002-0.200	> 0.99	> 0.99	> 0.99	-6	-89	-7
10	**Fenpicoxamid**	0.002-0.200	0.002-0.200	0.002-0.050	> 0.99	> 0.99	> 0.99	-30	10	22
11	**Florpyrauxifen-benzyl**	0.002-0.200	0.002-0.200	0.002-0.050	> 0.99	> 0.99	> 0.99	-30	12	52
12	**Flupyradifuron**	0.002-0.200	0.002-0.200	0.002-0.200	> 0.99	> 0.99	> 0.99	-1	14	27
13	**Flutianil**	0.002-0.200	0.002-0.200	0.002-0.050	> 0.99	> 0.99	> 0.99	-25	9	19
14	**Fluxapyroxad**	0.002-0.200	0.002-0.200	0.002-0.200	> 0.99	> 0.99	> 0.99	3	-31	-2
15	**Forchlorfenuron**	0.002-0.200	0.002-0.200	0.002-0.200	> 0.99	> 0.99	> 0.99	0	-38	-5
16	**Isofetamid**	0.002-0.200	0.002-0.200	0.002-0.100	> 0.99	> 0.99	> 0.99	-4	-48	-9
17	**Matrine**	0.002-0.200	0.002-0.200	0.002-0.200	> 0.99	> 0.99	> 0.99	1	0	0
18	**Matrine-N-oxide**	0.002-0.200	0.002-0.200	0.002-0.200	> 0.99	> 0.99	> 0.99	-2	-6	-12
19	**Mefentrifluconazole**	0.002-0.200	0.002-0.200	0.002-0.200	> 0.99	> 0.99	> 0.99	-9	-12	-20
20	**Novaluron**	0.002-0.050	0.002-0.200	0.002-0.050	> 0.99	> 0.99	> 0.99	-48	21	63
21	**Oxathiapipronil**	0.002-0.200	0.002-0.200	0.002-0.200	> 0.99	> 0.99	> 0.99	9	-17	42
22	**Penflufen**	0.002-0.200	0.002-0.200	0.002-0.200	> 0.99	> 0.99	> 0.99	-5	-14	-9

No.	Compound	Linear Range (mg/kg)			R^2			Matrix effect (%)		
		Zucchini	Orange	Avocado	Zucchini	Orange	Avocado	Zucchini	Orange	Avocado
23	**Penthiopyrad**	0.002-0.200	0.002-0.200	0.002-0.200	> 0.99	> 0.99	> 0.99	23	20	28
24	**Pyriofenone**	0.002-0.200	0.002-0.200	0.002-0.200	> 0.99	> 0.99	> 0.99	-10	-10	-10
25	**Rotenone**	0.002-0.200	0.002-0.200	0.002-0.200	> 0.99	> 0.99	> 0.99	-10	11	-4
26	**Tolfenpyrad**	0.002-0.200	0.002-0.200	0.002-0.050	> 0.99	> 0.99	> 0.99	-51	8	32
27	**Triflumizole**	0.002-0.200	0.002-0.200	0.002-0.200	> 0.99	> 0.99	> 0.99	-8	-11	-30
28	**Trinexapac-ethyl**	0.002-0.200	0.002-0.200	0.002-0.200	> 0.99	> 0.99	> 0.99	-2	-97	0
29	**Trinexapac-methyl**	0.002-0.200	0.002-0.200	0.002-0.200	> 0.99	> 0.99	> 0.99	-3	-85	-7
30	*Aclonifen*	0.002-0.200	0.002-0.200	0.002-0.200	0.9997	0.9991	0.9992	37	65	38
31	*Cyflumetofen*	0.002-0.200	0.002-0.200	0.002-0.200	0.9989	0.9993	0.9991	30	44	36
32	*Flutianil*	0.002-0.200	0.002-0.200	0.002-0.200	0.9993	0.9994	0.9993	15	39	41
33	*Isofetamid*	0.002-0.200	0.002-0.200	0.002-0.200	0.9992	0.9993	0.9993	28	47	50
34	*Isopyrazam*	0.002-0.200	0.002-0.200	0.002-0.200	0.9991	0.9995	0.9996	30	47	43
35	*Novaluron*	0.002-0.200	0.002-0.200	0.002-0.200	0.9974	0.9995	0.9998	-27	-29	-37
36	*Penthiopyrad*	0.002-0.200	0.002-0.200	0.002-0.200	0.9993	0.9995	0.9995	55	60	57
37	*Pyriofenone*	0.002-0.200	0.002-0.200	0.002-0.200	0.9992	0.9997	0.9993	28	30	26
38	*Quintozene*	0.002-0.200	0.002-0.200	0.002-0.200	0.9998	0.9996	0.9991	-5	19	6

In bold, pesticides analysed by LC-MS/MS
In italic, pesticides analysed by GC-MS/MS

Table 4. Linearity ranges, coefficients of determination and matrix effects for selected matrices studied by using citrate-buffered QuEChERS method with clean-up. Negative values of matrix effects mean suppression of the signal, and positives values, enhancement.

No.	Compound	Linear Range (mg/kg)			R^2			Matrix effect (%)		
		Zucchini	Orange	Avocado	Zucchini	Orange	Avocado	Zucchini	Orange	Avocado
1	**Benzovindiflupyr**	0.002-0.200	0.002-0.200	0.002-0.200	> 0.99	> 0.99	> 0.99	-1	-13	-24
2	**Bifenazate**	0.002-0.200	0.002-0.200	0.002-0.200	> 0.99	> 0.99	> 0.99	1	-24	-21
3	**Chloridazon**	0.002-0.200	0.002-0.200	0.002-0.200	> 0.99	> 0.99	> 0.99	1	-18	-8
4	**Clomazone**	0.002-0.200	0.002-0.200	0.002-0.200	> 0.99	> 0.99	> 0.99	1	-28	-2
5	**Cyantraniliprole**	0.002-0.200	0.002-0.200	0.002-0.200	> 0.99	> 0.99	> 0.99	1	-12	-4
6	**Cyflumetofen**	0.002-0.200	-	0.002-0.050	> 0.99	≤ 0.99	> 0.99	-13	-50	-35
7	**Dinotefuran**	0.002-0.200	0.002-0.200	0.002-0.200	> 0.99	> 0.99	> 0.99	1	8	6
8	**Diuron**	0.002-0.200	0.002-0.200	0.002-0.200	> 0.99	> 0.99	> 0.99	3	-82	0
9	**Fenobucarb**	0.002-0.200	-	0.002-0.200	> 0.99	≤ 0.99	> 0.99	-1	-97	-6
10	**Fenpicoxamid**	0.002-0.200	0.002-0.100	0.002-0.050	> 0.99	> 0.99	> 0.99	-4	-13	-20
11	**Florpyrauxifen-benzyl**	0.002-0.200	0.002-0.200	0.002-0.050	> 0.99	> 0.99	> 0.99	4	-26	-19
12	**Flupyradifuron**	0.002-0.200	0.002-0.200	0.002-0.200	> 0.99	> 0.99	> 0.99	2	47	28
13	**Flutianil**	0.002-0.200	0.002-0.100	0.002-0.050	> 0.99	> 0.99	> 0.99	6	-10	-12
14	**Fluxapyroxad**	0.002-0.200	0.002-0.200	0.002-0.200	> 0.99	> 0.99	> 0.99	4	-24	4
15	**Forchlorfenuron**	0.002-0.200	0.002-0.200	0.002-0.200	> 0.99	> 0.99	> 0.99	5	-26	0
16	**Isofetamid**	0.002-0.200	0.002-0.200	0.002-0.200	> 0.99	> 0.99	> 0.99	3	-41	-8
17	**Matrine**	0.002-0.200	0.002-0.200	0.002-0.200	> 0.99	> 0.99	> 0.99	11	13	7
18	**Matrine-N-oxide**	0.002-0.200	0.002-0.200	0.002-0.200	> 0.99	> 0.99	> 0.99	6	7	4
19	**Mefentrifluconazole**	0.002-0.200	0.002-0.200	0.002-0.200	> 0.99	> 0.99	> 0.99	2	-12	-23
20	**Novaluron**	0.002-0.100	-	0.002-0.050	> 0.99	≤ 0.99	> 0.99	5	-47	-35
21	**Oxathiapipronil**	0.002-0.200	0.002-0.200	0.002-0.200	> 0.99	> 0.99	> 0.99	4	-18	35
22	**Penflufen**	0.002-0.200	0.002-0.200	0.002-0.200	> 0.99	> 0.99	> 0.99	0	-14	-11
23	**Penthiopyrad**	0.002-0.200	0.002-0.200	0.002-0.200	> 0.99	> 0.99	> 0.99	8	11	15
24	**Pyriofenone**	0.002-0.200	0.002-0.200	0.002-0.200	> 0.99	> 0.99	> 0.99	-2	-16	-12

No.	Compound	Linear Range (mg/kg)			R^2			Matrix effect (%)		
		Zucchini	Orange	Avocado	Zucchini	Orange	Avocado	Zucchini	Orange	Avocado
25	**Rotenone**	0.002-0.200	0.002-0.200	0.002-0.200	> 0.99	> 0.99	> 0.99	1	-6	-11
26	**Tolfenpyrad**	0.002-0.200	-	0.002-0.050	> 0.99	≤ 0.99	> 0.99	-27	-43	-36
27	**Triflumizole**	0.002-0.200	0.002-0.200	0.002-0.200	> 0.99	> 0.99	> 0.99	13	-15	-38
28	**Trinexapac-ethyl**	0.002-0.200	0.002-0.200	0.002-0.200	> 0.99	> 0.99	> 0.99	1	-88	-1
29	**Trinexapac-methyl**	0.002-0.200	0.002-0.200	0.002-0.200	> 0.99	> 0.99	> 0.99	4	-1	-2
30	*Aclonifen*	0.002-0.100	0.002-0.200	0.002-0.200	0.9925	0.9960	0.9997	-30	34	56
31	*Cyflumetofen*	0.002-0.200	0.002-0.200	0.002-0.200	0.9985	0.9952	0.9996	-77	-51	44
32	*Flutianil*	0.002-0.200	0.002-0.200	0.002-0.200	0.9956	0.9978	0.9999	-16	42	66
33	*Isofetamid*	0.002-0.200	0.002-0.200	0.002-0.200	0.9964	0.9983	0.9996	-10	47	79
34	*Isopyrazam*	0.002-0.200	0.002-0.200	0.002-0.200	0.9950	0.9983	0.9999	-8	51	73
35	*Novaluron*	0.002-0.200	0.002-0.200	0.002-0.200	0.9972	0.9996	0.9997	-19	-32	-17
36	*Penthiopyrad*	0.002-0.200	0.002-0.200	0.002-0.200	0.9929	0.9984	0.9998	-11	51	78
37	*Pyriofenone*	0.002-0.200	0.002-0.200	0.002-0.200	0.9962	0.9991	1.0000	0	33	45
38	*Quintozene*	0.002-0.200	0.002-0.200	0.002-0.200	0.9974	0.9986	0.9998	-20	17	14

In bold, pesticides analysed by LC-MS/MS
In italic, pesticides analysed by GC-MS/MS

Table 5. Linearity ranges, coefficients of determination and matrix effects for selected matrices studied by using Acidified-QuEChERS method. Negative values of matrix effects mean suppression of the signal, and positives values, enhancement.

No.	Compound	Linear Range (mg/kg)			R^2			Matrix effect (%)		
		Zucchini	Orange	Avocado	Zucchini	Orange	Avocado	Zucchini	Orange	Avocado
1	**Benzovindiflupyr**	0.002-0.200	0.002-0.200	0.002-0.200	> 0.99	> 0.99	> 0.99	-7	-14	-7
2	**Bifenazate**	0.002-0.200	0.002-0.200	0.002-0.200	> 0.99	> 0.99	> 0.99	-1	-33	-1
3	**Chloridazon**	0.002-0.200	0.002-0.200	0.002-0.200	> 0.99	> 0.99	> 0.99	-7	-60	-7
4	**Clomazone**	0.002-0.200	0.002-0.200	0.002-0.200	> 0.99	> 0.99	> 0.99	-4	-38	-4
5	**Cyantraniliprole**	0.002-0.200	0.002-0.200	0.002-0.200	> 0.99	> 0.99	> 0.99	0	-34	0
6	**Cyflumetofen**	0.002-0.200	-	-	> 0.99	≤ 0.99	≤ 0.99	-28	-52	-28
7	**Dinotefuran**	0.002-0.200	0.002-0.200	0.002-0.200	> 0.99	> 0.99	> 0.99	-7	-18	-7
8	**Diuron**	0.002-0.200	0.002-0.200	0.002-0.200	> 0.99	> 0.99	> 0.99	0	-84	0
9	**Fenobucarb**	0.002-0.200	0.002-0.200	0.002-0.200	> 0.99	> 0.99	> 0.99	-9	-97	-9
10	**Fenpicoxamid**	0.002-0.200	0.002-0.200	0.002-0.200	> 0.99	> 0.99	> 0.99	-19	-26	-19
11	**Florpyrauxifen-benzyl**	0.002-0.200	-	-	> 0.99	≤ 0.99	≤ 0.99	-14	-35	-14
12	**Flupyradifuron**	0.002-0.200	0.002-0.200	0.002-0.200	> 0.99	> 0.99	> 0.99	1	5	1
13	**Flutianil**	0.002-0.200	0.002-0.200	-	> 0.99	> 0.99	≤ 0.99	-11	-22	-11
14	**Fluxapyroxad**	0.002-0.200	0.002-0.200	0.002-0.200	> 0.99	> 0.99	> 0.99	3	-34	3
15	**Forchlorfenuron**	0.002-0.200	0.002-0.200	0.002-0.200	> 0.99	> 0.99	> 0.99	2	-38	2
16	**Isofetamid**	0.002-0.200	0.002-0.200	0.002-0.200	> 0.99	> 0.99	> 0.99	-4	-49	-4
17	**Matrine**	0.002-0.200	0.002-0.100	0.002-0.200	> 0.99	> 0.99	> 0.99	32	32	32
18	**Matrine-N-oxide**	0.002-0.200	0.002-0.200	0.002-0.200	> 0.99	> 0.99	> 0.99	-10	-32	-10
19	**Mefentrifluconazole**	0.002-0.200	0.002-0.200	0.002-0.200	> 0.99	> 0.99	> 0.99	1	-16	1
20	**Novaluron**	0.002-0.100	-	-	> 0.99	≤ 0.99	≤ 0.99	-36	-62	-36
21	**Oxathiapipronil**	0.002-0.200	0.002-0.200	0.002-0.200	> 0.99	> 0.99	> 0.99	12	-24	12
22	**Penflufen**	0.002-0.200	0.002-0.200	0.002-0.200	> 0.99	> 0.99	> 0.99	-4	-16	-4
23	**Penthiopyrad**	0.002-0.200	0.002-0.200	0.002-0.200	> 0.99	> 0.99	> 0.99	24	-5	24
24	**Pyriofenone**	0.002-0.200	0.002-0.200	0.002-0.200	> 0.99	> 0.99	> 0.99	-6	-24	-6

No.	Compound	Linear Range (mg/kg)			R^2			Matrix effect (%)		
		Zucchini	Orange	Avocado	Zucchini	Orange	Avocado	Zucchini	Orange	Avocado
25	**Rotenone**	0.002-0.200	0.002-0.200	0.002-0.200	> 0.99	> 0.99	> 0.99	2	0	2
26	**Tolfenpyrad**	0.002-0.200	-	-	> 0.99	≤ 0.99	≤ 0.99	-32	-51	-32
27	**Triflumizole**	0.002-0.200	0.002-0.200	0.002-0.200	> 0.99	> 0.99	> 0.99	34	-20	34
28	**Trinexapac-ethyl**	0.002-0.200	-	0.002-0.200	> 0.99	≤ 0.99	> 0.99	-1	-97	-1
29	**Trinexapac-methyl**	0.002-0.200	0.002-0.200	0.002-0.200	> 0.99	> 0.99	> 0.99	0	-30	0

In bold, pesticides analysed by LC-MS/MS

Table 6. Linearity ranges, coefficients of determination and matrix effects for selected matrices studied by using ethyl acetate method without clean-up. Negative values of matrix effects mean suppression of the signal, and positives values, enhancement.

No.	Compound	Linear Range (mg/kg)			R^2			Matrix effect (%)		
		Zucchini	Orange	Avocado	Zucchini	Orange	Avocado	Zucchini	Orange	Avocado
1	**Benzovindiflupyr**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	-25	-16	n.e
2	**Bifenazate**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	-21	-26	n.e
3	**Chloridazon**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	-8	-22	n.e
4	**Clomazone**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	-7	-15	n.e
5	**Cyantraniliprole**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	-2	-8	n.e
6	**Cyflumetofen**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	-63	-53	n.e
7	**Dinotefuran**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	-3	-1	n.e
8	**Diuron**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	-6	-51	n.e
9	**Fenobucarb**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	-7	-80	n.e
10	**Fenpicoxamid**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	-38	-24	n.e
11	**Florpyrauxifen-benzyl**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	-53	-43	n.e
12	**Flupyradifuron**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	3	54	n.e
13	**Flutianil**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	-42	-31	n.e
14	**Fluxapyroxad**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	1	-32	n.e
15	**Forchlorfenuron**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	-4	-10	n.e
16	**Isofetamid**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	-14	-50	n.e
17	**Matrine**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	8	6	n.e
18	**Matrine-N-oxide**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	3	1	n.e
19	**Mefentrifluconazole**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	-25	-18	n.e
20	**Novaluron**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	-65	-59	n.e
21	**Oxathiapipronil**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	41	-37	n.e
22	**Penflufen**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	-12	-11	n.e
23	**Penthiopyrad**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	-4	0	n.e
24	**Pyriofenone**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	-22	-20	n.e

No.	Compound	Linear Range (mg/kg)			R^2			Matrix effect (%)		
		Zucchini	Orange	Avocado	Zucchini	Orange	Avocado	Zucchini	Orange	Avocado
25	**Rotenone**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	-18	-23	n.e
26	**Tolfenpyrad**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	-68	-62	n.e
27	**Triflumizole**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	-19	-1	n.e
28	**Trinexapac-ethyl**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	-2	-62	n.e
29	**Trinexapac-methyl**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	-1	1	n.e
30	*Aclonifen*	0.002-0.200	0.002-0.200	0.002-0.200	0.9968	0.9997	0.9989	64	69	-6
31	*Cyflumetofen*	0.002-0.200	0.002-0.200	0.002-0.200	0.9995	0.9991	0.9995	50	49	-4
32	*Flutianil*	0.002-0.200	0.002-0.200	0.002-0.200	0.9992	0.9994	0.9995	37	19	0
33	*Isofetamid*	0.002-0.200	0.002-0.200	0.002-0.200	0.9994	0.9994	0.9998	60	48	-9
34	*Isopyrazam*	0.002-0.200	0.002-0.200	0.002-0.200	0.9995	0.9997	0.9999	55	45	-17
35	*Novaluron*	0.002-0.200	0.002-0.200	0.002-0.200	0.9993	0.9989	0.9998	-7	-9	-59
36	*Penthiopyrad*	0.002-0.200	0.002-0.200	0.002-0.200	0.9995	0.9996	0.9993	74	60	32
37	*Pyriofenone*	0.002-0.200	0.002-0.200	0.002-0.200	0.9995	0.9997	0.9997	38	30	-6
38	*Quintozene*	0.002-0.200	0.002-0.200	0.002-0.200	0.9981	1.0000	0.9990	19	35	-6

In bold, pesticides analysed by LC-MS/MS
In italic, pesticides analysed by GC-MS/MS
n.e: not evaluated

Table 7. Linearity ranges, coefficients of determination and matrix effects for selected matrices studied by using ethyl acetate method with clean-up. Negative values of matrix effects mean suppression of the signal, and positives values, enhancement.

No.	Compound	Linear Range (mg/kg)			R^2			Matrix effect (%)		
		Zucchini	Orange	Avocado	Zucchini	Orange	Avocado	Zucchini	Orange	Avocado
1	**Benzovindiflupyr**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	-5	-10	n.e
2	**Bifenazate**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	-5	-24	n.e
3	**Chloridazon**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	-2	-6	n.e
4	**Clomazone**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	-3	-13	n.e
5	**Cyantraniliprole**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	-3	-13	n.e
6	**Cyflumetofen**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	-32	-29	n.e
7	**Dinotefuran**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	-3	-5	n.e
8	**Diuron**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	-1	-47	n.e
9	**Fenobucarb**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	-3	-79	n.e
10	**Fenpicoxamid**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	-11	-10	n.e
11	**Florpyrauxifen-benzyl**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	-26	-32	n.e
12	**Flupyradifuron**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	1	3	n.e
13	**Flutianil**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	-15	-19	n.e
14	**Fluxapyroxad**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	-3	-31	n.e
15	**Forchlorfenuron**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	-3	-15	n.e
16	**Isofetamid**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	-7	-46	n.e
17	**Matrine**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	10	8	n.e
18	**Matrine-N-oxide**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	4	1	n.e
19	**Mefentrifluconazole**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	-6	-13	n.e
20	**Novaluron**	0.002-0.100	0.002-0.050	n.e	> 0.99	> 0.99	n.e	-28	-28	n.e
21	**Oxathiapipronil**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	1	-35	n.e
22	**Penflufen**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	-3	-11	n.e
23	**Penthiopyrad**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	-2	-14	n.e
24	**Pyriofenone**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	-13	-13	n.e

No.	Compound	Linear Range (mg/kg)			R^2			Matrix effect (%)		
		Zucchini	Orange	Avocado	Zucchini	Orange	Avocado	Zucchini	Orange	Avocado
25	**Rotenone**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	-16	-21	n.e
26	**Tolfenpyrad**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	-39	-40	n.e
27	**Triflumizole**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	24	26	n.e
28	**Trinexapac-ethyl**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	0	-57	n.e
29	**Trinexapac-methyl**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	2	0	n.e
30	*Aclonifen*	0.002-0.200	0.002-0.200	0.002-0.200	0.9903	0.9976	0.9995	-2	13	2
31	*Cyflumetofen*	0.002-0.200	0.002-0.200	0.002-0.200	0.9983	0.9997	0.9998	6	34	2
32	*Flutianil*	0.002-0.200	0.002-0.200	0.002-0.200	0.9985	0.9999	0.9986	1	22	-3
33	*Isofetamid*	0.002-0.200	0.002-0.200	0.002-0.200	0.9978	0.9999	0.9995	7	42	-2
34	*Isopyrazam*	0.002-0.200	0.002-0.200	0.002-0.200	0.9972	0.9996	0.9994	10	40	-8
35	*Novaluron*	0.002-0.200	0.002-0.200	0.002-0.200	0.9989	0.9993	0.9985	-16	-4	-29
36	*Penthiopyrad*	0.002-0.200	0.002-0.200	0.002-0.200	0.9971	0.9993	0.9998	12	36	36
37	*Pyriofenone*	0.002-0.200	0.002-0.200	0.002-0.200	0.9988	1.0000	0.9999	14	35	4
38	*Quintozene*	0.002-0.200	0.002-0.200	0.002-0.200	0.9967	0.9994	0.9997	2	20	2

In bold, pesticides analysed by LC-MS/MS
In italic, pesticides analysed by GC-MS/MS
n.e: not evaluated

Table 8. Linearity ranges, coefficients of determination and matrix effects for selected matrices studied by using Dutch mini-Luke method without clean-up. Negative values of matrix effects mean suppression of the signal, and positives values, enhancement.

	Compound	Linear Range (mg/kg)		R^2		Matrix effect (%)	
		Zucchini	Orange	Zucchini	Orange	Zucchini	Orange
1	**Benzovindiflupyr**	0.002-0.200	0.002-0.200	> 0.99	> 0.99	-22	-22
2	**Bifenazate**	0.002-0.200	0.002-0.200	> 0.99	> 0.99	-15	-32
3	**Chloridazon**	0.002-0.200	0.002-0.200	> 0.99	> 0.99	-3	-17
4	**Clomazone**	0.002-0.200	0.002-0.200	> 0.99	> 0.99	-4	-17
5	**Cyantraniliprole**	0.002-0.200	0.002-0.200	> 0.99	> 0.99	-1	-4
6	**Cyflumetofen**	-	0.002-0.200	≤ 0.99	> 0.99	-67	-50
7	**Dinotefuran**	0.002-0.200	0.002-0.200	> 0.99	> 0.99	-1	-1
8	**Diuron**	0.002-0.200	0.002-0.200	> 0.99	> 0.99	-2	-53
9	**Fenobucarb**	0.002-0.200	0.002-0.200	> 0.99	> 0.99	-7	-82
10	**Fenpicoxamid**	-	0.002-0.200	≤ 0.99	> 0.99	-40	-40
11	**Florpyrauxifen-benzyl**	-	0.002-0.200	≤ 0.99	> 0.99	-55	-37
12	**Flupyradifuron**	0.002-0.200	0.002-0.200	> 0.99	> 0.99	2	47
13	**Flutianil**	0.002-0.200	0.002-0.200	> 0.99	> 0.99	-42	-30
14	**Fluxapyroxad**	0.002-0.200	0.002-0.200	> 0.99	> 0.99	-1	-37
15	**Forchlorfenuron**	0.002-0.200	0.002-0.200	> 0.99	> 0.99	-3	-7
16	**Isofetamid**	0.002-0.200	0.002-0.200	> 0.99	> 0.99	-10	-58
17	**Matrine**	0.002-0.200	0.002-0.200	> 0.99	> 0.99	2	1
18	**Matrine-N-oxide**	0.002-0.200	0.002-0.200	> 0.99	> 0.99	6	5
19	**Mefentrifluconazole**	0.002-0.200	0.002-0.200	> 0.99	> 0.99	-25	-28
20	**Novaluron**	-	0.002-0.200	≤ 0.99	> 0.99	-78	-59
21	**Oxathiapipronil**	0.002-0.200	0.002-0.200	> 0.99	> 0.99	49	-44
22	**Penflufen**	0.002-0.200	0.002-0.200	> 0.99	> 0.99	-9	-12
23	**Penthiopyrad**	0.002-0.200	0.002-0.200	> 0.99	> 0.99	8	-9
24	**Pyriofenone**	0.002-0.200	0.002-0.200	> 0.99	> 0.99	-18	-15

	Compound	Linear Range (mg/kg)		R^2		Matrix effect (%)	
		Zucchini	Orange	Zucchini	Orange	Zucchini	Orange
25	**Rotenone**	0.002-0.200	0.002-0.200	> 0.99	> 0.99	-24	-30
26	**Tolfenpyrad**	-	0.002-0.200	≤ 0.99	> 0.99	-66	-55
27	**Triflumizole**	-	0.002-0.200	≤ 0.99	> 0.99	-43	-44
28	**Trinexapac-ethyl**	0.002-0.200	0.002-0.200	> 0.99	> 0.99	-1	-63
29	**Trinexapac-methyl**	0.002-0.200	0.002-0.200	> 0.99	> 0.99	4	1
30	*Aclonifen*	0.002-0.200	0.002-0.200	0.9989	0.9987	53	47
31	*Cyflumetofen*	0.002-0.200	0.002-0.200	0.9984	0.9998	10	11
32	*Flutianil*	0.002-0.200	0.002-0.200	0.9979	0.9995	13	5
33	*Isofetamid*	0.002-0.200	0.002-0.200	0.9985	0.9998	20	13
34	*Isopyrazam*	0.002-0.200	0.002-0.200	0.9989	0.9995	15	10
35	*Novaluron*	0.002-0.200	0.002-0.200	0.9978	0.9990	-4	-22
36	*Penthiopyrad*	0.002-0.200	0.002-0.200	0.9992	0.9999	23	17
37	*Pyriofenone*	0.002-0.200	0.002-0.200	0.9993	0.9998	12	10
38	*Quintozene*	0.002-0.200	0.002-0.200	0.9994	0.9982	25	30

In bold, pesticides analysed by LC-MS/MS
In italic, pesticides analysed by GC-MS/MS

Table 9. Linearity ranges, coefficients of determination and matrix effects for selected matrices studied by using Dutch mini-Luke method with clean-up. Negative values of matrix effects mean suppression of the signal, and positives values, enhancement.

No.	Compound	Linear Range (mg/kg)			R^2			Matrix effect (%)		
		Zucchini	Orange	Avocado	Zucchini	Orange	Avocado	Zucchini	Orange	Avocado
1	**Benzovindiflupyr**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	-12	-13	n.e
2	**Bifenazate**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	-9	-28	n.e
3	**Chloridazon**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	-5	-6	n.e
4	**Clomazone**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	-5	-15	n.e
5	**Cyantraniliprole**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	-4	-9	n.e
6	**Cyflumetofen**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	-38	-41	n.e
7	**Dinotefuran**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	-7	-7	n.e
8	**Diuron**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	-4	-55	n.e
9	**Fenobucarb**	0.002-0.200	0.002-0.100	n.e	> 0.99	> 0.99	n.e	-17	-84	n.e
10	**Fenpicoxamid**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	-17	-18	n.e
11	**Florpyrauxifen-benzyl**	0.002-0.200	0.002-0.100	n.e	> 0.99	> 0.99	n.e	-29	-32	n.e
12	**Flupyradifuron**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	-9	-5	n.e
13	**Flutianil**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	-24	-15	n.e
14	**Fluxapyroxad**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	-5	-37	n.e
15	**Forchlorfenuron**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	-6	-21	n.e
16	**Isofetamid**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	-7	-56	n.e
17	**Matrine**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	-1	-2	n.e
18	**Matrine-N-oxide**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	-5	-4	n.e
19	**Mefentrifluconazole**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	-2	-7	n.e
20	**Novaluron**	0.002-0.100	0.002-0.200	n.e	> 0.99	> 0.99	n.e	-39	-35	n.e
21	**Oxathiapipronil**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	-1	-42	n.e
22	**Penflufen**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	-7	-11	n.e
23	**Penthiopyrad**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	7	6	n.e
24	**Pyriofenone**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	-12	-14	n.e

No.	Compound	Linear Range (mg/kg)			R^2			Matrix effect (%)		
		Zucchini	Orange	Avocado	Zucchini	Orange	Avocado	Zucchini	Orange	Avocado
25	**Rotenone**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	-36	-46	n.e
26	**Tolfenpyrad**	0.002-0.200	0.002-0.100	n.e	> 0.99	> 0.99	n.e	-41	-50	n.e
27	**Triflumizole**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	-4	-12	n.e
28	**Trinexapac-ethyl**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	-1	-61	n.e
29	**Trinexapac-methyl**	0.002-0.200	0.002-0.200	n.e	> 0.99	> 0.99	n.e	-2	-3	n.e
30	*Aclonifen*	0.002-0.100	0.002-0.200	0.002-0.200	0.9984	0.9974	0.9983	-43	-25	-7
31	*Cyflumetofen*	0.002-0.200	0.002-0.200	0.002-0.200	0.9982	0.9999	0.9974	-28	-22	-30
32	*Flutianil*	0.002-0.200	0.002-0.200	0.002-0.200	0.9976	0.9999	0.9999	-13	-3	-29
33	*Isofetamid*	0.002-0.200	0.002-0.200	0.002-0.200	0.9978	0.9997	0.9999	-15	-2	-38
34	*Isopyrazam*	0.002-0.200	0.002-0.200	0.002-0.200	0.9966	0.9997	0.9998	-16	-4	-41
35	*Novaluron*	0.002-0.200	0.002-0.200	0.002-0.200	0.9995	0.9994	0.9996	-23	-20	-65
36	*Penthiopyrad*	0.002-0.200	0.002-0.200	0.002-0.200	0.9968	0.9998	0.9993	-15	-5	-6
37	*Pyriofenone*	0.002-0.200	0.002-0.200	0.002-0.200	0.9990	0.9999	0.9999	-2	3	-26
38	*Quintozene*	0.002-0.200	0.002-0.200	0.002-0.200	0.9930	0.9991	0.9991	-26	-11	-7

In bold, pesticides analysed by LC-MS/MS
In italic, pesticides analysed by GC-MS/MS
n.e: not evaluated

Table 10. Accuracy data (as % recovery) and precision data (as reproducibility RSDr, n=5) at 0.005 and 0.050 mg/kg for zucchini, orange and avocado by using citrate-buffered QuEChERS method without clean-up.

No.	Compound	Zucchini				Orange				Avocado			
		0.005 mg/kg		0.050 mg/kg		0.005 mg/kg		0.050 mg/kg		0.005 mg/kg		0.050 mg/kg	
		Recov (%)	RSD (%)	Recov (%)	RSD (%)	Recov (%)	RSD (%)	Recov (%)	RSD (%)	Recov (%)	RSD (%)	Recov (%)	RSD (%)
1	**Benzovindiflupyr**	97	4	106	0	75	7	78	13	97	4	107	6
2	**Bifenazate**	78	1	85	2	88	5	89	7	94	2	101	3
3	**Chloridazon**	89	1	94	1	89	2	92	2	94	2	91	4
4	**Clomazone**	91	1	93	1	94	2	95	5	97	2	94	3
5	**Cyantraniliprole**	91	1	95	0	99	0	98	4	100	1	98	1
6	**Cyflumetofen**	171	5	225	8	32	27	25	45	103	3	89	11
7	**Dinotefuran**	84	1	91	2	83	1	89	3	83	2	84	1
8	**Diuron**	91	1	95	1	103	1	104	2	98	1	93	2
9	**Fenobucarb**	92	1	94	1	103	1	107	6	97	3	99	2
10	**Fenpicoxamid**	92	0	112	6	50	11	46	24	101	3	91	11
11	**Florpyrauxifen-benzyl**	149	4	176	9	39	30	36	32	97	9	85	12
12	**Flupyradifuron**	88	2	93	2	91	2	93	3	92	2	90	1
13	**Flutianil**	126	2	133	8	49	21	43	25	100	6	88	12
14	**Fluxapyroxad**	90	1	94	1	95	4	97	6	104	3	103	2
15	**Forchlorfenuron**	89	0	92	1	95	2	98	4	98	2	95	2
16	**Isofetamid**	93	1	96	2	90	5	93	7	95	2	100	2
17	**Matrine**	65	1	57	6	47	1	47	4	34	17	36	15
18	**Matrine-N-oxide**	70	0	61	6	50	1	46	4	36	13	33	14
19	**Mefentrifluconazole**	99	1	105	3	82	5	88	7	103	3	110	4
20	**Novaluron**	188	2	293	9	35	32	28	44	100	9	87	12
21	**Oxathiapipronil**	92	1	99	0	92	4	98	5	101	2	106	3
22	**Penflufen**	91	1	101	0	82	3	88	7	97	2	102	4

No.	Compound	Zucchini				Orange				Avocado			
		0.005 mg/kg		0.050 mg/kg		0.005 mg/kg		0.050 mg/kg		0.005 mg/kg		0.050 mg/kg	
		Recov (%)	RSD (%)	Recov (%)	RSD (%)	Recov (%)	RSD (%)	Recov (%)	RSD (%)	Recov (%)	RSD (%)	Recov (%)	RSD (%)
23	**Penthiopyrad**	93	2	104	2	71	9	87	7	98	3	107	3
24	**Pyriofenone**	98	2	104	1	58	7	44	19	91	5	102	1
25	**Rotenone**	92	3	102	1	68	7	68	13	93	10	103	6
26	**Tolfenpyrad**	163	3	214	10	31	26	24	43	92	7	85	10
27	**Triflumizole**	111	1	119	0	71	9	74	13	98	1	108	5
28	**Trinexapac-ethyl**	97	1	96	0	114	6	101	3	102	2	94	2
29	**Trinexapac-methyl**	97	1	93	1	100	3	99	3	101	2	92	2
30	*Aclonifen*	81	8	82	4	93	6	91	2	79	7	84	3
31	*Cyflumetofen*	80	7	84	8	93	6	96	4	86	7	96	3
32	*Flutianil*	80	6	83	8	90	6	92	2	87	6	94	3
33	*Isofetamid*	79	7	84	7	89	6	92	3	86	7	93	3
34	*Isopyrazam*	78	3	85	8	90	5	92	2	84	5	93	3
35	*Novaluron*	81	5	87	6	89	3	100	1	91	8	96	2
36	*Penthiopyrad*	79	5	84	7	89	6	92	3	85	6	95	3
37	*Pyriofenone*	81	7	85	5	89	4	93	3	75	8	87	2
38	*Quintozene*	76	5	78	6	87	6	85	5	58	8	64	1

In bold, pesticides analysed by LC-MS/MS
In italic, pesticides analysed by GC-MS/MS

Table 11. Accuracy data (as % recovery) and precision data (as reproducibility RSDr, n=5) at 0.005 and 0.050 mg/kg for zucchini, orange and avocado by using citrate-buffered QuEChERS method with clean-up.

No.	Compound	Zucchini				Orange				Avocado			
		0.005 mg/kg		0.050 mg/kg		0.005 mg/kg		0.050 mg/kg		0.005 mg/kg		0.050 mg/kg	
		Recov (%)	RSD (%)	Recov (%)	RSD (%)	Recov (%)	RSD (%)	Recov (%)	RSD (%)	Recov (%)	RSD (%)	Recov (%)	RSD (%)
1	**Benzovindiflupyr**	88	3	99	3	79	2	81	2	99	3	112	4
2	**Bifenazate**	74	0	82	1	86	1	88	2	100	4	111	1
3	**Chloridazon**	92	1	97	1	90	1	82	14	90	3	93	2
4	**Clomazone**	93	1	96	1	93	2	95	6	95	2	98	0
5	**Cyantraniliprole**	92	1	97	1	96	1	95	1	95	1	102	1
6	**Cyflumetofen**	94	7	86	14	53	2	20	8	105	8	85	22
7	**Dinotefuran**	89	1	93	1	86	2	89	1	80	7	83	8
8	**Diuron**	91	0	95	2	104	2	100	3	97	3	98	1
9	**Fenobucarb**	95	1	98	1	98	11	103	5	100	2	103	1
10	**Fenpicoxamid**	70	5	73	10	56	5	50	10	100	6	97	7
11	**Florpyrauxifen-benzyl**	93	13	88	16	48	6	40	14	96	8	80	18
12	**Flupyradifuron**	91	0	98	0	94	3	95	2	96	2	102	2
13	**Flutianil**	93	7	91	10	50	5	44	11	96	7	86	11
14	**Fluxapyroxad**	92	0	99	1	95	2	99	3	99	2	109	1
15	**Forchlorfenuron**	91	2	95	2	95	2	92	3	98	2	97	2
16	**Isofetamid**	93	1	96	1	86	3	88	3	92	4	104	1
17	**Matrine**	65	0	62	1	51	2	37	30	15	4	20	65
18	**Matrine-N-oxide**	61	1	58	2	40	1	28	29	14	5	9	70
19	**Mefentrifluconazole**	91	1	98	1	88	3	92	2	96	3	110	3
20	**Novaluron**	87	12	86	17	38	6	28	11	109	6	90	23
21	**Oxathiapipronil**	92	2	98	1	97	1	101	4	99	5	109	4
22	**Penflufen**	91	2	99	2	82	3	89	4	93	2	104	1

No.	Compound	Zucchini				Orange				Avocado			
		0.005 mg/kg		0.050 mg/kg		0.005 mg/kg		0.050 mg/kg		0.005 mg/kg		0.050 mg/kg	
		Recov (%)	RSD (%)	Recov (%)	RSD (%)	Recov (%)	RSD (%)	Recov (%)	RSD (%)	Recov (%)	RSD (%)	Recov (%)	RSD (%)
23	**Penthiopyrad**	90	3	105	3	83	5	91	2	98	8	103	3
24	**Pyriofenone**	94	2	100	3	45	3	39	8	95	4	98	3
25	**Rotenone**	93	3	96	1	70	3	75	5	96	3	106	2
26	**Tolfenpyrad**	93	10	91	13	36	1	18	10	103	7	84	23
27	**Triflumizole**	90	1	90	1	73	4	75	3	96	5	103	5
28	**Trinexapac-ethyl**	43	2	37	2	10	147	62	18	40	10	38	19
29	**Trinexapac-methyl**	44	3	33	1	62	6	55	17	38	9	35	22
30	*Aclonifen*	99	6	84	7	66	9	65	19	85	9	89	11
31	*Cyflumetofen*	75	2	79	20	70	16	90	46	94	4	101	11
32	*Flutianil*	84	3	82	5	59	9	59	16	92	3	100	4
33	*Isofetamid*	83	2	84	6	61	9	62	15	89	5	101	4
34	*Isopyrazam*	81	4	82	4	64	9	64	14	91	2	100	3
35	*Novaluron*	82	1	86	2	74	6	94	16	91	3	104	2
36	*Penthiopyrad*	84	4	83	6	57	10	59	17	92	2	99	7
37	*Pyriofenone*	82	2	85	3	74	7	73	10	81	2	92	5
38	*Quintozene*	75	3	71	4	80	4	75	9	62	1	68	8

In bold, pesticides analysed by LC-MS/MS
In italic, pesticides analysed by GC-MS/MS

Table 12. Accuracy data (as % recovery) and precision data (as reproducibility RSDr, n=5) at 0.005 and 0.050 mg/kg for zucchini, orange and avocado by using Acidified-QuEChERS method.

No.	Compound	Zucchini				Orange				Avocado			
		0.005 mg/kg		0.050 mg/kg		0.005 mg/kg		0.050 mg/kg		0.005 mg/kg		0.050 mg/kg	
		Recov (%)	RSD (%)	Recov (%)	RSD (%)	Recov (%)	RSD (%)	Recov (%)	RSD (%)	Recov (%)	RSD (%)	Recov (%)	RSD (%)
1	**Benzovindiflupyr**	70	1	78	8	69	4	72	5	70	1	78	8
2	**Bifenazate**	68	2	71	5	82	5	81	2	68	2	71	5
3	**Chloridazon**	89	2	90	3	97	6	94	1	89	2	90	3
4	**Clomazone**	88	1	88	3	93	4	89	1	88	1	88	3
5	**Cyantraniliprole**	86	1	87	4	106	6	96	1	86	1	87	4
6	**Cyflumetofen**	53	2	49	19	38	22	15	4	53	2	49	19
7	**Dinotefuran**	85	1	86	4	88	5	88	1	85	1	86	4
8	**Diuron**	85	1	88	4	97	0	93	2	85	1	88	4
9	**Fenobucarb**	90	1	89	3	81	2	90	2	90	1	89	3
10	**Fenpicoxamid**	57	1	51	11	42	3	57	7	57	1	51	11
11	**Florpyrauxifen-benzyl**	57	1	57	16	76	35	37	6	57	1	57	16
12	**Flupyradifuron**	86	0	88	4	100	6	96	2	86	0	88	4
13	**Flutianil**	65	4	65	14	49	12	43	7	65	4	65	14
14	**Fluxapyroxad**	83	1	91	5	93	4	92	2	83	1	91	5
15	**Forchlorfenuron**	85	2	88	3	101	8	92	1	85	2	88	3
16	**Isofetamid**	80	0	83	5	78	2	77	2	80	0	83	5
17	**Matrine**	58	3	54	3	47	3	45	4	58	3	54	3
18	**Matrine-N-oxide**	71	3	66	3	55	4	53	2	71	3	66	3
19	**Mefentrifluconazole**	71	2	78	5	81	1	87	3	71	2	78	5
20	**Novaluron**	17	17	47	25	34	23	28	4	17	17	47	25
21	**Oxathiapipronil**	75	1	79	7	90	4	92	2	75	1	79	7
22	**Penflufen**	80	1	90	3	80	3	82	3	80	1	90	3

No.	Compound	Zucchini				Orange				Avocado			
		0.005 mg/kg		0.050 mg/kg		0.005 mg/kg		0.050 mg/kg		0.005 mg/kg		0.050 mg/kg	
		Recov (%)	RSD (%)	Recov (%)	RSD (%)	Recov (%)	RSD (%)	Recov (%)	RSD (%)	Recov (%)	RSD (%)	Recov (%)	RSD (%)
23	**Penthiopyrad**	73	2	82	4	75	3	85	4	73	2	82	4
24	**Pyriofenone**	75	1	79	5	37	4	36	3	75	1	79	5
25	**Rotenone**	74	2	78	6	61	4	65	4	74	2	78	6
26	**Tolfenpyrad**	57	4	49	18	35	37	17	2	57	4	49	18
27	**Triflumizole**	94	2	91	4	89	17	76	3	94	2	91	4
28	**Trinexapac-ethyl**	89	1	82	3	104	9	95	2	89	1	82	3
29	**Trinexapac-methyl**	88	2	80	2	107	3	96	2	88	2	80	2

In bold, pesticides analysed by LC-MS/MS

Table 13. Accuracy data (as % recovery) and precision data (as reproducibility RSDr, n=5) at 0.005 and 0.050 mg/kg for zucchini, orange and avocado by using ethyl acetate method without clean-up.

1	**Benzovindiflupyr**	101	5	102	4	82	2	80	6	n.e	-	n.e	-
2	**Bifenazate**	53	5	51	1	81	2	73	5	n.e	-	n.e	-
3	**Chloridazon**	108	2	105	1	103	1	101	1	n.e	-	n.e	-
4	**Clomazone**	107	1	101	1	94	1	85	2	n.e	-	n.e	-
5	**Cyantraniliprole**	105	1	103	2	95	1	91	1	n.e	-	n.e	-
6	**Cyflumetofen**	108	16	102	6	81	8	75	24	n.e	-	n.e	-
7	**Dinotefuran**	84	0	79	1	74	1	71	2	n.e	-	n.e	-
8	**Diuron**	109	1	102	2	99	1	89	3	n.e	-	n.e	-
9	**Fenobucarb**	107	1	104	1	85	4	88	3	n.e	-	n.e	-
10	**Fenpicoxamid**	108	3	103	4	90	4	78	17	n.e	-	n.e	-
11	**Florpyrauxifen-benzyl**	105	9	101	9	86	8	80	12	n.e	-	n.e	-
12	**Flupyradifuron**	108	1	105	0	104	1	103	1	n.e	-	n.e	-
13	**Flutianil**	110	7	102	5	88	5	82	13	n.e	-	n.e	-
14	**Fluxapyroxad**	102	0	102	1	84	1	78	1	n.e	-	n.e	-
15	**Forchlorfenuron**	103	3	98	2	92	2	86	1	n.e	-	n.e	-
16	**Isofetamid**	101	1	96	0	84	4	78	6	n.e	-	n.e	-
17	**Matrine**	15	6	6	5	9	1	1	1	n.e	-	n.e	-
18	**Matrine-N-oxide**	12	2	2	4	10	2	1	1	n.e	-	n.e	-
19	**Mefentrifluconazole**	104	2	97	3	80	2	78	2	n.e	-	n.e	-
20	**Novaluron**	99	16	99	7	78	14	82	15	n.e	-	n.e	-
21	**Oxathiapipronil**	98	1	97	3	84	2	80	3	n.e	-	n.e	-

22	**Penflufen**	105	0	105	1	85	3	82	5	n.e	-	n.e	-
23	**Penthiopyrad**	100	4	103	3	79	8	78	2	n.e	-	n.e	-
24	**Pyriofenone**	101	2	96	1	81	4	73	20	n.e	-	n.e	-
25	**Rotenone**	98	1	97	2	90	3	77	7	n.e	-	n.e	-
26	**Tolfenpyrad**	105	15	96	6	81	8	74	20	n.e	-	n.e	-
27	**Triflumizole**	106	6	97	2	84	0	72	12	n.e	-	n.e	-
28	**Trinexapac-ethyl**	104	0	90	1	106	2	93	2	n.e	-	n.e	-
29	**Trinexapac-methyl**	86	5	70	2	109	1	97	1	n.e	-	n.e	-
30	*Aclonifen*	84	7	85	1	79	5	77	2	103	1	103	1
31	*Cyflumetofen*	91	5	91	2	91	2	88	0	92	4	99	1
32	*Flutianil*	88	5	87	2	84	4	82	2	96	4	99	1
33	*Isofetamid*	88	5	87	2	76	3	76	2	86	4	87	2
34	*Isopyrazam*	84	4	86	1	78	2	77	2	92	2	92	2
35	*Novaluron*	90	6	90	3	92	6	89	1	93	6	99	2
36	*Penthiopyrad*	84	5	86	2	74	4	73	2	93	2	91	1
37	*Pyriofenone*	88	5	87	2	78	2	81	1	93	1	93	0
38	*Quintozene*	85	6	86	2	87	4	83	1	102	3	103	1

In bold, pesticides analysed by LC-MS/MS
In italic, pesticides analysed by GC-MS/MS
n.e: not evaluated

Table 14. Accuracy data (as % recovery) and precision data (as reproducibility RSDr, n=5) at 0.005 and 0.050 mg/kg for zucchini, orange and avocado by using ethyl acetate method with clean-up.

No.	Compound	Zucchini				Orange				Avocado			
		0.005 mg/kg		0.050 mg/kg		0.005 mg/kg		0.050 mg/kg		0.005 mg/kg		0.050 mg/kg	
		Recov (%)	RSD (%)	Recov (%)	RSD (%)	Recov (%)	RSD (%)	Recov (%)	RSD (%)	Recov (%)	RSD (%)	Recov (%)	RSD (%)
1	**Benzovindiflupyr**	91	6	89	1	83	4	76	4	n.e	-	n.e	-
2	**Bifenazate**	51	1	45	2	83	2	75	2	n.e	-	n.e	-
3	**Chloridazon**	99	1	96	1	99	2	98	1	n.e	-	n.e	-
4	**Clomazone**	102	3	96	1	94	2	86	1	n.e	-	n.e	-
5	**Cyantraniliprole**	77	3	71	2	77	2	73	1	n.e	-	n.e	-
6	**Cyflumetofen**	70	17	73	8	64	12	59	19	n.e	-	n.e	-
7	**Dinotefuran**	72	2	70	0	68	3	66	2	n.e	-	n.e	-
8	**Diuron**	100	2	94	1	94	1	90	3	n.e	-	n.e	-
9	**Fenobucarb**	99	3	98	0	82	4	87	3	n.e	-	n.e	-
10	**Fenpicoxamid**	91	10	86	5	89	5	74	13	n.e	-	n.e	-
11	**Florpyrauxifen-benzyl**	77	16	79	10	70	9	72	15	n.e	-	n.e	-
12	**Flupyradifuron**	101	2	99	1	102	3	96	2	n.e	-	n.e	-
13	**Flutianil**	88	13	87	8	87	9	74	12	n.e	-	n.e	-
14	**Fluxapyroxad**	95	2	94	1	80	1	79	1	n.e	-	n.e	-
15	**Forchlorfenuron**	77	4	72	2	73	1	63	2	n.e	-	n.e	-
16	**Isofetamid**	95	2	91	1	84	3	78	3	n.e	-	n.e	-
17	**Matrine**	14	6	5	7	8	2	1	1	n.e	-	n.e	-
18	**Matrine-N-oxide**	13	0	2	3	9	2	1	1	n.e	-	n.e	-
19	**Mefentrifluconazole**	92	2	91	4	82	3	72	3	n.e	-	n.e	-
20	**Novaluron**	72	26	89	11	56	11	65	12	n.e	-	n.e	-
21	**Oxathiapipronil**	95	2	90	3	83	1	82	4	n.e	-	n.e	-

No.	Compound	Zucchini				Orange				Avocado			
		0.005 mg/kg		0.050 mg/kg		0.005 mg/kg		0.050 mg/kg		0.005 mg/kg		0.050 mg/kg	
		Recov (%)	RSD (%)	Recov (%)	RSD (%)	Recov (%)	RSD (%)	Recov (%)	RSD (%)	Recov (%)	RSD (%)	Recov (%)	RSD (%)
22	**Penflufen**	94	2	100	2	84	2	80	3	n.e	-	n.e	-
23	**Penthiopyrad**	90	4	98	1	82	4	78	5	n.e	-	n.e	-
24	**Pyriofenone**	90	2	90	3	86	9	70	10	n.e	-	n.e	-
25	**Rotenone**	95	2	91	3	87	1	78	5	n.e	-	n.e	-
26	**Tolfenpyrad**	75	14	81	7	72	10	64	17	n.e	-	n.e	-
27	**Triflumizole**	92	1	88	1	90	6	80	4	n.e	-	n.e	-
28	**Trinexapac-ethyl**	37	4	24	5	48	7	32	3	n.e	-	n.e	-
29	**Trinexapac-methyl**	32	5	16	5	46	0	31	5	n.e	-	n.e	-
30	*Aclonifen*	87	3	76	3	83	3	63	2	102	5	95	2
31	*Cyflumetofen*	81	4	71	3	79	3	66	2	97	1	96	1
32	*Flutianil*	87	2	79	1	84	1	73	2	94	4	93	2
33	*Isofetamid*	87	3	78	2	76	1	67	2	86	3	84	2
34	*Isopyrazam*	84	3	74	2	77	1	67	2	88	2	87	2
35	*Novaluron*	92	5	81	2	87	2	80	1	100	5	89	2
36	*Penthiopyrad*	83	6	73	1	72	1	60	3	92	3	88	2
37	*Pyriofenone*	85	4	79	2	79	2	73	1	96	1	93	1
38	*Quintozene*	93	6	82	1	89	1	75	1	104	6	101	0

In bold, pesticides analysed by LC-MS/MS
In italic, pesticides analysed by GC-MS/MS
n.e: not evaluated

Table 15. Accuracy data (as % recovery) and precision data (as reproducibility RSDr, n=5) at 0.005 and 0.050 mg/kg for zucchini, orange and avocado by using Dutch mini-Luke method without clean-up.

No.	Compound	Zucchini				Orange			
		0.005 mg/kg		0.050 mg/kg		0.005 mg/kg		0.050 mg/kg	
		Recov (%)	RSD (%)	Recov (%)	RSD (%)	Recov (%)	RSD (%)	Recov (%)	RSD (%)
1	**Benzovindiflupyr**	88	7	83	10	76	7	68	8
2	**Bifenazate**	54	9	56	6	77	6	70	6
3	**Chloridazon**	77	14	81	5	88	5	76	5
4	**Clomazone**	78	12	78	4	86	5	73	6
5	**Cyantraniliprole**	76	14	78	4	84	6	72	7
6	**Cyflumetofen**	99	6	84	21	71	24	60	10
7	**Dinotefuran**	72	12	76	7	77	6	67	6
8	**Diuron**	78	14	78	5	91	1	81	3
9	**Fenobucarb**	77	12	80	4	91	1	86	2
10	**Fenpicoxamid**	91	7	84	15	73	14	68	6
11	**Florpyrauxifen-benzyl**	93	10	85	19	75	18	65	10
12	**Flupyradifuron**	77	13	78	6	78	8	69	8
13	**Flutianil**	98	9	88	13	73	16	68	8
14	**Fluxapyroxad**	76	11	85	6	86	7	77	5
15	**Forchlorfenuron**	78	15	80	4	86	5	75	6
16	**Isofetamid**	77	11	79	5	87	2	79	2
17	**Matrine**	53	16	54	15	9	1	1	4
18	**Matrine-N-oxide**	12	16	7	32	9	1	1	1
19	**Mefentrifluconazole**	87	10	86	10	78	8	69	2
20	**Novaluron**	105	10	89	26	62	43	57	12
21	**Oxathiapipronil**	81	11	80	7	84	5	76	3
22	**Penflufen**	77	11	81	3	79	6	73	7

No.	Compound	Zucchini				Orange			
		0.005 mg/kg		0.050 mg/kg		0.005 mg/kg		0.050 mg/kg	
		Recov (%)	RSD (%)	Recov (%)	RSD (%)	Recov (%)	RSD (%)	Recov (%)	RSD (%)
23	**Penthiopyrad**	79	14	84	5	75	11	71	2
24	**Pyriofenone**	84	9	80	5	75	10	66	4
25	**Rotenone**	82	9	79	6	81	7	71	4
26	**Tolfenpyrad**	87	5	75	20	65	33	61	8
27	**Triflumizole**	86	4	78	8	71	10	63	1
28	**Trinexapac-ethyl**	82	12	80	3	98	4	84	2
29	**Trinexapac-methyl**	78	12	75	3	90	5	76	6
30	*Aclonifen*	85	6	87	1	83	4	85	1
31	*Cyflumetofen*	86	5	88	0	80	4	89	2
32	*Flutianil*	84	5	87	1	84	6	89	4
33	*Isofetamid*	88	4	89	1	83	5	90	3
34	*Isopyrazam*	85	4	87	0	84	7	89	2
35	*Novaluron*	89	4	89	1	81	6	90	8
36	*Penthiopyrad*	86	6	89	0	82	6	89	2
37	*Pyriofenone*	83	4	89	1	79	6	89	2
38	*Quintozene*	87	3	85	1	106	3	84	1

In bold, pesticides analysed by LC-MS/MS
In italic, pesticides analysed by GC-MS/MS

Table 16. Accuracy data (as % recovery) and precision data (as reproducibility RSDr, n=5) at 0.005 and 0.050 mg/kg for zucchini, orange and avocado by using Dutch mini-Luke method with clean-up.

No.	Compound	Zucchini				Orange				Avocado			
		0.005 mg/kg		0.050 mg/kg		0.005 mg/kg		0.050 mg/kg		0.005 mg/kg		0.050 mg/kg	
		Recov (%)	RSD (%)	Recov (%)	RSD (%)	Recov (%)	RSD (%)	Recov (%)	RSD (%)	Recov (%)	RSD (%)	Recov (%)	RSD (%)
1	**Benzovindiflupyr**	76	1	82	11	81	3	78	5	n.e	-	n.e	-
2	**Bifenazate**	54	4	56	8	83	3	81	3	n.e	-	n.e	-
3	**Chloridazon**	74	4	81	6	83	5	82	4	n.e	-	n.e	-
4	**Clomazone**	79	3	78	6	87	3	81	4	n.e	-	n.e	-
5	**Cyantraniliprole**	59	11	61	6	71	5	66	4	n.e	-	n.e	-
6	**Cyflumetofen**	63	3	56	19	59	12	68	5	n.e	-	n.e	-
7	**Dinotefuran**	72	4	76	6	80	4	77	4	n.e	-	n.e	-
8	**Diuron**	79	3	79	7	91	3	92	3	n.e	-	n.e	-
9	**Fenobucarb**	79	2	82	6	84	3	98	3	n.e	-	n.e	-
10	**Fenpicoxamid**	79	3	82	8	78	6	86	5	n.e	-	n.e	-
11	**Florpyrauxifen-benzyl**	70	5	72	21	67	12	82	8	n.e	-	n.e	-
12	**Flupyradifuron**	76	1	82	6	85	4	83	4	n.e	-	n.e	-
13	**Flutianil**	80	3	84	15	79	8	80	7	n.e	-	n.e	-
14	**Fluxapyroxad**	78	2	82	7	87	3	87	3	n.e	-	n.e	-
15	**Forchlorfenuron**	57	14	59	7	71	5	63	3	n.e	-	n.e	-
16	**Isofetamid**	78	2	79	6	92	3	89	1	n.e	-	n.e	-
17	**Matrine**	61	12	60	12	12	3	1	5	n.e	-	n.e	-
18	**Matrine-N-oxide**	15	11	8	22	13	0	1	1	n.e	-	n.e	-
19	**Mefentrifluconazole**	79	4	78	8	81	7	84	5	n.e	-	n.e	-
20	**Novaluron**	54	9	53	22	55	25	59	6	n.e	-	n.e	-
21	**Oxathiapipronil**	79	2	81	6	91	3	87	2	n.e	-	n.e	-

No.	Compound	Zucchini				Orange				Avocado			
		0.005 mg/kg		0.050 mg/kg		0.005 mg/kg		0.050 mg/kg		0.005 mg/kg		0.050 mg/kg	
		Recov (%)	RSD (%)	Recov (%)	RSD (%)	Recov (%)	RSD (%)	Recov (%)	RSD (%)	Recov (%)	RSD (%)	Recov (%)	RSD (%)
22	**Penflufen**	77	2	84	6	83	6	84	6	n.e	-	n.e	-
23	**Penthiopyrad**	82	6	82	7	87	5	87	4	n.e	-	n.e	-
24	**Pyriofenone**	76	4	78	8	80	8	81	6	n.e	-	n.e	-
25	**Rotenone**	83	3	78	6	86	5	81	4	n.e	-	n.e	-
26	**Tolfenpyrad**	67	5	56	19	55	9	73	5	n.e	-	n.e	-
27	**Triflumizole**	74	6	74	6	79	4	77	3	n.e	-	n.e	-
28	**Trinexapac-ethyl**	28	14	22	12	48	2	34	1	n.e	-	n.e	-
29	**Trinexapac-methyl**	26	12	17	11	39	1	26	1	n.e	-	n.e	-
30	*Aclonifen*	90	9	88	8	85	4	73	3	95	24	77	5
31	*Cyflumetofen*	85	3	84	3	75	5	77	4	105	5	86	6
32	*Flutianil*	88	2	84	4	78	4	78	1	80	5	85	6
33	*Isofetamid*	88	1	87	3	78	5	79	2	79	9	86	7
34	*Isopyrazam*	88	3	84	4	79	4	77	1	78	10	84	7
35	*Novaluron*	85	3	82	4	73	5	72	13	80	10	85	6
36	*Penthiopyrad*	86	1	84	3	78	5	77	2	82	8	87	5
37	*Pyriofenone*	92	4	87	3	81	3	79	1	77	4	81	6
38	*Quintozene*	85	1	77	4	75	6	69	4	71	7	71	2

In bold, pesticides analysed by LC-MS/MS
In italic, pesticides analysed by GC-MS/MS
n.e: not evaluated