

Determination of pesticide residues in avocado and almond by liquid and gas chromatography tandem mass spectrometry

CONTENTS

1. Aim and scope	3
2. Short description.....	3
3. Apparatus and consumables	3
4. Chemicals.....	3
5. Procedure	4
5.1. Sample preparation.....	4
5.2. Recovery experiments for method validation	4
5.3. Extraction	4
5.3.1. Avocado.....	4
5.3.2. Almond.....	5
5.4. Measurement.....	6
5.5. Instrumentation and analytical conditions for the LC- MS/MS system.....	6
5.5.1. Agilent 1200 HPLC	6
5.5.2. Agilent 6490 QqQ MS/MS.....	7
5.6. Instrumentation and analytical conditions for the GC- MS/MS system	7
5.6.1. Agilent 7890.....	7
5.6.2. Agilent 7000 QqQ MS/MS.....	8
6. Validation of the method	8
6.1. Recoveries and within-laboratory reproducibility	8
6.2. Limits of quantitation.....	8
6.3. Linearity	8
6.4. Matrix effects.....	9
7. References	9
 APPENDIX I: MASS TRANSITIONS	 10
APPENDIX II: VALIDATION RESULTS	17

1. Aim and scope

This report describes a validation data of 279 pesticides using a multiresidue method by LC-MS/MS and GC-MS/MS in avocado and almond.

2. Short description

An homogenous sample is extracted with acetonitrile according to modified QuEChERS protocol. The obtained extract is analysed by GC-MS/MS and LC-MS/MS.

3. Apparatus and consumables

- Automatic pipettes, suitable for handling volumes of 4 μ L to 500 μ L and 1 mL to 5 mL.
- 50 ml PTFE centrifuge tubes with screw caps
- 15 ml PTFE centrifuge tubes with screw caps
- Vortex
- Automatic axial extractor
- Centrifuge, suitable for the centrifuge tubes employed in the procedure and capable to achieve at least 3700 rpm
- Concentration workstation
- Syringes, e.g. 2 mL disposable syringes
- Syringe filters, 0.45 μ m pore size
- Injection vials, 2 ml, suitable for LC and GC auto-sampler
- Volumetric flasks
- Z-Sep[®] sorbent (Supelco)

4. Chemicals

- Acetonitrile ultra gradient grade
- Formic acid
- Trisodium citrate dihydrate
- Sodium chloride
- Disodium hydrogencitrate sesquihydrate
- Anhydrous magnesium sulphate
- Ultra pure water
- Ethyl acetate HPLC grade
- Pesticides standards

5. Procedure

5.1. Sample preparation

To obtain representative subsamples, samples should be frozen over night and after that minced. Before freezing, the stones of avocado should be eliminated.

5.2. Recovery experiments for method validation

The samples employed in the validation studies did not contain any of the analysed pesticides.

Individual pesticide stock solutions (1000–2000 mg/L) were prepared in acetonitrile and ethyl acetate and were stored in amber screw-capped glass vials in the dark at -20 °C.

For spiking,

- 70 g representative portions of previously homogenised avocado were weighed and transferred to a beaker, where they were fortified homogeneously with 700 µL of the appropriate working standard solution and then the mixture was blended for 30 min.
- 40 g representative portions of previously homogenised almond were weighed and transferred to a crystallizer, where they were spiked with 20 mL of the working standard solution in methanol. Following this, the sample was blended thoroughly for 30 min under a nitrogen stream until dryness.

The validation method was performed at two fortification levels (0.010 mg/kg and 0.050 mg/kg). Five replicates were analysed at each level.

5.3. Extraction

5.3.1. Avocado

1. Weigh 10 g ± 0.1 g of sample in 50 mL PTFE centrifuge tube.
2. Add 10 mL of acetonitrile and 50 µL of 10 mg/L mix of surrogate standards (triphenyl phosphate, dichlorvos-d₆ and malathion-d₁₀)
3. Shake in automatic axial extractor for 4 minutes.
4. Add 4 g of magnesium sulphate, 1 g of sodium chloride, 1 g of trisodiumcitrate dehydrate and 0.5 g of disodium hydrogencitrate sesquihydrate.
5. Shake in automatic axial extractor for 4 minutes.

6. Centrifuge for 5 min at 3700 rpm.
7. Transfer 5 mL of supernatant into 15 mL PTFE centrifuge tube containing 175 mg of Z-Sep and 750 mg of MgSO₄ and shake in a vortex 30 s.
8. Centrifuge for 5 min at 3700 rpm.
9. Evaporate an aliquot under gentle stream of nitrogen:
 - a. for LC analysis 250 µL of extract. To dry vial add 150 µL of acetonitrile and vortex. Subsequently add 350 µL of water and vortex again. Filter the sample thorough 0.45 µm PTFE filter. Add 10 µL of dimethoate-d₆ 2.5 µg/L (injection control standard).
 - b. for GC analysis 100 µL of extract. Reconstitute with 100 µL of ethyl acetate. Add 4 µL of lindane-d₆ 1.25 µg/L (injection control standard).

With this treatment 1 mL of final sample for LC analysis represents 0.5 g of avocado and 1 mL of final sample for GC analysis represents 1 g of avocado.

5.3.2. Almond

1. Weigh 5 g ± 0.1 g of sample in 50 mL PTFE centrifuge tube, add 5 mL water and left for 30 minutes.
2. Add 10 mL of acetonitrile and 50 µL of 10 mg/L mix of surrogate standards (triphenyl phosphate, dichlorvos-d₆ and malathion-d₁₀)
3. Shake in automatic axial extractor for 4 minutes.
4. Add 4 g of magnesium sulphate, 1 g of sodium chloride, 1 g of trisodiumcitrate dehydrate and 0.5 g of disodium hydrogencitrate sesquihydrate.
5. Shake in automatic axial extractor for 4 minutes.
6. Centrifuge for 5 min at 3700 rpm.
7. Transfer 5 mL of supernatant into 15 mL PTFE centrifuge tube containing 175 mg of Z-Sep and 750 mg of MgSO₄ and shake in a vortex 30 s.
8. Centrifuge for 5 min at 3700 rpm.
9. Evaporate an aliquot under gentle stream of nitrogen:
 - a. for LC analysis, 250 µL of extract. To dry vial add 200 µL of acetonitrile and vortex. Subsequently add 300 µL of water and vortex again. Filter the sample thorough 0.45 µm PTFE filter. Add 10 µL of dimethoate-d₆ 2.5 µg/L (injection control standard).

b. for GC analysis, 100 µL of extract. Reconstitute with 50 µL of ethyl acetate. Add 2 µL of lindane-d₆ 1.25 µg/L (injection control standard).

With this treatment, 1 mL of final sample for LC analysis represents 0.25 g of almond and 1 mL of final sample for GC analysis represents 1 g of almond.

5.4. Measurement

Both LC and GC systems were operated in multiple reaction monitoring mode (MRM). Selected reaction monitoring (SRM) experiments were carried out to obtain the maximum sensitivity for the detection of the target molecules. For confirmation of the studied compounds, two SRM transitions and a correct ratio between the abundances of the two optimised SRM transitions (SRM2/SRM1) were used, along with retention time matching. The mass transitions used are presented in Appendix I.

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

5.5.1. Agilent 1200 HPLC

- Column: Agilent Zorbax SB, C8, 4.6 mm x 150 mm x 5 µm
- Mobile phase A: acetonitrile
- Mobile phase B: 0.1% formic acid in ultra pure water
- Flow rate: 0.6 mL/min
- Injection volume: 10 µL

Mobile phase gradient for pesticides analyse in positive mode

Time [min]	Mobile phase A	Mobile phase B
0	20%	80%
3	20%	80%
30	100%	0%
33	100%	0%

Re-equilibration with initial mobile phase: 5 minutes.

5.5.2. Agilent 6490 QqQ MS/MS

- ESI source gas temperature: 120 °C
- Gas flow: 15 L/min
- Nebuliser gas and collision gas: nitrogen
- Nebuliser gas pressure: 35 psi
- Sheath gas flow: 12 L/min
- Sheath gas temperature: 375 °C
- Ionisation mode: positive
- Capillary voltage: 3500 V
- Nozzle voltage 300 V
- iFunnel parameters: high pressure RF 150 V and low pressure RF 60 V

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

5.6.1. Agilent 7890

- Column: HP-5MS UI 15 m × 0.25 mm × 0.25 µm
- Retention Time Locking compound: trifluralin (retention time 5.81 min)
- Injection mode: splitless
- Ultra inert inlet liner, with a glass wool frit from Agilent
- Injection volume: 2 µl
- Injector temperature:

Time [min]	Temperature	
0	80 °C	solvent evaporation
0.1	80 °C	
0.6	300 °C	
20	300 °C	

- Carrier gas: helium
- Carrier gas purity: 99.999%
- Carrier gas pressure: constant, 13.172 psi
- Quenching gas: helium
- Oven temperature: 70°C for 1 min, programmed to 150°C at 50°C/min, then to 200°C at 6°C/min and finally to 280°C at 16°C/min (4.07 min). The total run time was 20 minutes with 3 additional minutes for backflushing at 280°C.

5.6.2. Agilent 7000 QqQ MS/MS

- Ionisation mode: electron impact ionisation
- Temperature of the transfer line: 280 °C
- Temperature of ion source: 280 °C
- Temperature of quadrupole 1 and 2: 150 °C
- Collision gas: nitrogen
- Collision gas purity: 99.999%
- Solvent delay: 2 minutes

6. Validation of the method

6.1. Recoveries and within-laboratory reproducibility

The results corresponding to the mean recovery (n=5) and within-laboratory reproducibility in terms of relative standard deviation (RSD) at both fortification levels are summarized in Appendix II.

6.2. Limits of quantitation

SANCO/12571/2013 defines limit of quantitation as the lowest validated spike level meeting the method performance acceptability criteria.

Due to the high fat content in almond and low polarity of some of GC analysed pesticides and considering the good repeatability of the method, we accepted recoveries in the range 60–120%. In other cases accepted recoveries are in the range 70-120%.

LOQs are summarized in Appendix II.

6.3. Linearity

Linearity of the (QqQ)MS systems 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 corresponding to concentrations from 1 to 500 µg/kg in the sample. Linearity ranges for all pesticides in all matrices are summarized in Appendix II.

6.4. 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. Values of matrix effects are summarized in Appendix II.

This report aims to provide information to laboratories that analyse pesticide residues in avocado and almond or are interested in it.

7. References

- **Determination of pesticide residues in high oil vegetal commodities by using various multi-residue methods and clean-ups followed by liquid chromatography tandem mass spectrometry.** Łukasz Rajski, Ana Lozano, Ana Uclés, Carmen Ferrer, Amadeo R. Fernández-Alba.
Journal of Chromatography A, 1304 (2013) 109– 120
- **Evaluation of zirconium dioxide-based sorbents to decrease the matrix effect in avocado and almond multiresidue pesticide analysis followed by gas chromatography tandem mass spectrometry.** Ana Lozano, Łukasz Rajski, Samanta Uclés, Noelia Belmonte-Valles, Milagros Mezcua, Amadeo R. Fernández-Alba.
Talanta. 118 (2014) 68-83
- **Guidance document on analytical quality control and validation procedures for pesticide residues analysis in food and feed.** (SANCO/12571/2013)
- <http://www.eurl-pesticides.eu>

APPENDIX I: MASS TRANSITIONS

Table 1a. Acquisition parameters for the pesticides analysed by LC-MS/MS.

No.	Compound	t _R (min)	SRM1	CE1 (V)	SRM2	CE2 (V)
1	Acephate	3,11	184 / 143	5	184 / 125	15
2	Acetamiprid	10,99	223 / 126	20	223 / 56	15
3	Aldicarb	13,58	213 / 89	15	213 / 116	10
4	Azinphos-methyl	20,17	318 / 132	8	318 / 261	0
5	Azoxystrobin	20,80	404 / 372	10	404 / 344	20
6	Bitertanol	21,81	338 / 269	5	338 / 99	10
7	Boscalid	21,06	343 / 307	16	343 / 272	32
8	Bromuconazole	20,26 ; 21, 28	378 / 159	20	378 / 70	20
9	Bupirimate	19,25	317 / 166	20	317 / 272	20
10	Buprofezin	24,59	306 / 201	10	306 / 116	15
11	Carbaryl	16,90	202 / 145	10	202 / 127	20
12	Carbendazim	3,31	192 / 160	15	192 / 132	20
13	Chlorantraniliprole	18,76	484 / 286	8	484 / 453	16
14	Chlorpyrifos	28,07	350 / 198	20	350 / 97	20
15	Chlorpyrifos-methyl	27,47	322 / 125	16	322 / 290	14
16	Clofentezine	24,66	303 / 138	12	303 / 102	40
17	Cymoxanil	12,47	199 / 128	4	199 / 111	12
18	Cyproconazole	19,85	292 / 70	16	292 / 125	32
19	Cyprodinil	18,71	226 / 93	40	226 / 77	40
20	Cyromazine	2,28	167 / 85	20	167 / 125	15
21	Diazinon	25,03	305 / 169	15	305 / 153	20
22	Dicrotophos	5,53	238 / 112	8	238 / 72	28
23	Diethofencarb	20,31	268 / 226	5	268 / 180	15
24	Difenoconazole	23,45	406 / 251	20	406 / 337	15
25	Dimethoate	10,89	230 / 199	5	230 / 171	10
26	Dimethoate-d6	10,88	236 / 205	4	236 / 131	16
27	Dimethomorph	18,56 ; 18,99	388 / 301	20	388 / 165	20
28	Diniconazole	22,74	326 / 70	28	326 / 159	28
29	Diphenylamine	22,95	170 / 93	32	170 / 65	36
30	Dodine	17,91	228 / 57	20	228 / 60	20
31	Ethion	28,33	385 / 199	5	385 / 171	10
32	Ethirimol	6,62	210 / 140	20	210 / 43	52
33	Ethoprophos	21,57	243 / 131	15	243 / 97	30
34	Fenamidone	21,18	312 / 92	28	312 / 65	56
35	Fenamiphos	20,59	304 / 217	20	304 / 234	12
36	Fenarimol	20,25	331 / 268	20	331 / 259	20
37	Fenazaquin	27,47	307 / 161	15	307 / 147	15
38	Fenbuconazole	21,81	337 / 70	33	337 / 125	40

39	Fenoxycarb	22,37	302 / 88	20	302 / 116	5
40	Fenpropathrin	28,07	350 / 97	32	350 / 125	10
41	Fenpropimorph	15,84	304 / 147	30	304 / 130	25
42	Fenpyroximate	27,91	422 / 366	12	422 / 107	64
43	Fenthion	24,36	279 / 247	8	279 / 169	12
44	Fluazifop	20,09	328 / 282	15	328 / 254	20
45	Flufenoxuron	27,28	489 / 158	20	489 / 141	56
46	Fluquinconazole	21,22	376 / 307	24	376 / 108	56
47	Flusilazole	21,76	316 / 247	12	316 / 165	24
48	Flutriafol	16,72	302 / 70	16	302 / 95	56
49	Formetanate	2,97	222 / 65	52	222 / 165	8
50	Haloxifop	22,18	362 / 316	12	362 / 288	24
51	Hexythiazox	28,04	353 / 228	10	353 / 168	20
52	Imazalil	13,69	297 / 159	20	297 / 255	15
53	Imidacloprid	9,98	256 / 209	15	256 / 175	15
54	Indoxacarb	25,94	528 / 203	45	528 / 150	20
55	Iprovalicarb	20,79	321 / 119	16	321 / 203	0
56	Isofenphos-Methyl	25,14	231 / 121	15	231 / 199	15
57	Isoprocab	18,45	194 / 95	15	194 / 152	5
58	Kresoxim-methyl	23,91	314 / 267	0	314 / 222	10
59	Linuron	20,35	249 / 160	20	249 / 133	36
60	Malathion	22,74	331 / 127	10	331 / 99	20
61	Malathion-d10	22,76	341 / 132	12	341 / 100	24
62	Mandipropamid	21,13	412 / 328	8	412 / 356	4
63	Metalaxyl	17,25	280 / 220	5	280 / 192	10
64	Metconazole	22,13	320 / 70	24	320 / 125	48
65	Methamidophos	3,07	142 / 94	10	142 / 125	10
66	Methidathion	20,39	303 / 145	0	303 / 85	15
67	Methiocarb	19,99	226 / 169	5	226 / 121	12
68	Methoxyfenozide	22,11	369 / 149	15	369 / 133	20
69	Metobromuron	18,26	259 / 170	15	259 / 148	10
70	Monocrotophos	4,66	224 / 193	5	224 / 127	10
71	Myclobutanil	20,93	289 / 70	15	289 / 125	20
72	Nitenpyram	4,38	271 / 225	10	271 / 99	10
73	Oxamyl	4,87	237 / 72	10	237 / 90	5
74	Oxydemeton-methyl	3,97	247 / 109	24	247 / 169	8
75	Paclobutrazole	19,42	294 / 70	16	294 / 125	36
76	Pencycuron	25,15	329 / 125	24	329 / 89	60
77	Pendimethalin	27,98	282 / 212	4	282 / 194	16
78	Phenthoate	24,73	321 / 247	4	321 / 79	44
79	Phosalone	25,47	368 / 182	8	368 / 111	44
80	Phosmet	20,74	318 / 160	8	318 / 133	26
81	Phoxim	25,59	299 / 129	4	299 / 77	24
82	Pirimicarb	6,61	239 / 72	20	239 / 182	15
83	Pirimiphos-methyl	25,04	306 / 164	20	306 / 108	20

84	Prochloraz	19,29	376 / 308	10	376 / 266	15
85	Profenofos	25,95	375 / 305	15	375 / 347	5
86	Propamocarb	3,07	189 / 102	15	189 / 144	10
87	Propiconazole	22,81	342 / 159	32	342 / 69	16
88	Propoxur	16,06	210 / 168	0	210 / 153	0
89	Propyzamide	21,65	256 / 190	10	256 / 173	20
90	Pymetrozine	2,36	218 / 105	20	218 / 51	60
91	Pyraclostrobin	24,47	388 / 194	8	388 / 163	20
92	Pyrethrins	29,14	329 / 161	5	329 / 143	20
93	Pyridaben	29,34	365 / 309	10	365 / 147	20
94	Pyrimethanil	15,33	200 / 107	20	200 / 183	20
95	Pyriproxyfen	27,13	322 / 96	10	322 / 185	20
96	Quinoxifen	25,64	308 / 197	35	308 / 272	25
97	Rotenone	22,30	395 / 213	20	395 / 192	20
98	Spinosyn A	17,36	732 / 142	20	732 / 98	20
99	Spinosyn D	18,16	746 / 142	20	746 / 98	20
100	Spirodiclofen	30,19	411 / 71	15	411 / 313	5
101	Spiromesifen	30,08	371 / 273	5	371 / 255	20
102	Tebuconazole	21,41	308 / 70	20	308 / 125	20
103	Tebufenozide	23,49	353 / 133	15	353 / 297	5
104	Tebufenpyrad	26,03	344 / 145	20	344 / 171	20
105	Tetraconazole	21,58	372 / 159	36	372 / 70	20
106	Trichlorfon	8,30	257/221	4	257/109	12
107	Thiabendazole	3,50	202 / 175	30	202 / 131	40
108	Thiacloprid	12,97	253 / 126	20	253 / 186	10
109	Thiamethoxam	7,12	292 / 211	10	292 / 181	20
110	Thiophanate-methyl	15,30	343 / 151	20	343 / 93	56
111	TPP	24,35	327 / 77	35	327 / 152	30
112	Triadimefon	21,35	294 / 197	10	294 / 225	10
113	Triazophos	22,57	314 / 162	20	314 / 286	10
114	Triflumuron	23,82	359 / 156	8	359 / 139	32
115	Triticonazole	19,55	318 / 70	33	318 / 125	41
116	Zoxamide	24,65	336 / 187	16	336 / 159	44

Table 1b. Acquisition parameters for the pesticides analysed by GC-MS/MS.

No.	Compound	t _R (min)	SRM1	CE1 (V)	SRM2	CE2 (V)	Time segment
1	2,4-DDE	12,2	235>165	20	235>199	15	23
2	2,4-DDT	11,3	246>176	30	246>211	20	25
3	4,4-DDD	12,9	235>165	20	235>199	15	27
4	4,4-DDE	12,1	246>176	30	246>211	20	26
5	4,4-DDT	12,9	235>165	20	235>199	20	29
6	Acrinathrin	15,4	208>181	5	209>141	20	35
7	Alachlor	8,6	188>160	10	188>130	40	11

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8	Ametryn	8,7	227>185	5	227>212	8	13
9	Azoxystrobin	18,5	344>329	10	344>156	40	39
10	Benalaxyl	13,5	148>105	20	204>176	2	28
11	Bifenox	14,7	311>279	14	311>216	25	31
12	Bifenthrin	14,4	181>166	10	181>115	50	32
13	Bixafen	16,9	159>139	15	413>159	12	37
14	Boscalid	16,5	140>112	10	140>76	25	37
15	Bromopropylate	14,4	341>185	20	341>155	20	32
16	Bupirimate	12,6	273>193	5	273>108	15	27
17	Buprofezin	12,3	305>172	5	305>140	10	26
18	Butralin	10,2	266>174	20	266>190	12	15
19	Butylate	3,8	156>57	5	174>146	3	1
20	Cadusafos	5,9	159>97	10	213>73	10	6
21	Carbophenothion	13,4	199>143	10	342>157	10	28
22	Carbosulfan	3,2	164>149	12	164>122	12	1
23	Chinomethionat	11,2	234>206	10	206>148	15	23
24	Chlorbromuron	3,7	233>124	25	233>205	12	1
25	Chlorfenapyr	12,7	247>227	15	247>200	25	27
26	Chlorfenvinphos	10,9	267>159	20	267>81	40	22
27	Chlorobenzilate	12,8	139>111	15	139>75	30	27
28	Chlorothalonil	8,4	266>231	20	266>133	40	8
29	Chlorpropham	5,6	213>171	5	213>127	5	4
30	Chlorpyrifos	9,6	313>258	15	313>286	5	15
31	Chlorpyrifos-methyl	8,3	288>93	26	286>271	16	10
32	Chlorthal-dimethyl	9,7	330>299	12	330>221	35	14
33	Chlozolate	10,7	259>188	10	331>216	5	18
34	Cyfluthrin	16,3	163>127	5	226>206	10	36
35	Cypermethrin	16.5 - 16.6	163>127	5	209>141	20	37
36	Cyproconazole	12,6	139>111	14	222>125	18	27
37	Cyprodinil	10,4	224>208	20	224>197	21	18
38	Deltamethrin	18,1	253>93	20	253>172	5	39
39	Diazinon	7,2	304>179	15	304>137	30	8
40	Dichlorvos	3,0	185>93	15	185>109	15	1
41	Dichlorvos-d ₆	2,9	191>99	15	191>115	20	1
42	Diclobutrazol	12,3	270>159	15	270>201	8	27
43	Dicloran	6,5	206>176	5	206>148	20	7
44	Dimethenamid	8,0	230>154	10	154>111	10	8
45	Diphenylamine	5,3	169>77	35	168>140	40	4
46	Endosulfan alpha	11,3	239>204	15	241>206	25	24
47	Endosulfan beta	12,7	241>206	14	239>204	15	27
48	Endosulfan sulfate	13,4	387>289	5	387>206	40	29
49	EPN	14,4	157>77	25	157>110	15	32
50	Epoxiconazole	13.4 - 14.1	192>138	10	192>111	35	29
51	Ethion	13,1	231>129	25	231>175	5	27
52	Ethofenprox	16,6	163>107	15	163>135	5	37

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53	Ethofumesate	9,2	207>161	5	207>137	10	13
54	Ethoprophos	5,4	158>97	15	158>114	5	4
55	Etrimfos	7,6	292>181	5	292>153	20	8
56	Fenamidone	14,6	268>180	20	238>103	20	32
57	Fenarimol	15,3	139>111	15	219>107	10	34
58	Fenazaquin	14,6	160>145	5	160>117	20	31
59	Fenbuconazole	16,2	198>129	5	129>102	15	36
60	Fenchlorphos	8,7	285>270	18	285>240	30	13
61	Fenhexamid	13,6	177>78	20	177>113	10	29
62	Fenitrothion	9,1	277>260	5	277>109	20	13
63	Fenpropathrin	14,5	181>152	26	265>210	10	32
64	Fenpropimorph	9,6	128>70	12	128>110	10	14
65	Fenthion	9,6	278>109	20	278>169	20	15
66	Fenvalerate/Esfenvalerate RR/SS	17,5	167>125	12	125>89	22	38
67	Fenvalerate/Esfenvalerate RS/SR	17,3	167>125	12	125>89	22	38
68	Flamprop-isopropyl	12,9	276>105	5	304>105	12	27
69	Flamprop-methyl	12,4	276>105	8	230>170	15	25
70	Flonicamid	5,52	174>146	15	174>126	25	4
71	Fluacrypyrim	13,4	145>102	30	145>115	15	28
72	Fluazifop-P-butyl	12,7	282>91	15	282>238	20	26
73	Flucythrinate	16.6 - 16.8	199>157	5	157>107	15	37
74	Fludioxonil	12,4	248>127	30	248>154	25	26
75	Fluquinconazole	15,9	340>298	20	340>286	30	35
76	Flusilazole	12,5	233>165	20	233>152	20	27
77	Flutolanil	12,1	323>173	13	323>281	4	25
78	Flutriafol	11,9	219>123	12	219>95	20	25
79	Fluvalinate-tau	17,5	250>55	18	250>200	22	38
80	Fonofos	6,9	137>109	5	246>137	5	8
81	Formothion	7,9	170>93	5	224>125	20	7
82	Fosthiazate	10,2	195>103	5	195>139	5	18
83	Heptachlor	8,4	272>237	10	272>143	40	10
84	Heptenophos	4,9	124>89	15	215>200	10	3
85	Hexaconazole	11,8	214>159	22	214>172	22	25
86	Indoxacarb	18,1	203>134	10	264>148	28	39
87	Iprodione	14,4	314>245	10	314>56	20	32
88	Iprovalicarb	12,4	158>116	5	158>98	10	27
89	Isazofos	7,5	161>119	5	257>162	5	8
90	Isocarbophos	9,9	136>108	14	230>212	8	16
91	Isofenphos-ethyl	10,9	213>121	15	213>185	3	18
92	Isofenphos-methyl	10,4	199>121	10	199>167	10	18
93	Kresoxim-methyl	12,5	206>116	5	206>131	10	27
94	Lambda-cyhalothrin	15,2	197>141	10	197>161	5	34
95	Lindane	6,8	219>183	5	181>145	12	7
96	Lindane-d ₆	6,7	224>187	5	224>150	20	7
97	Malathion	9,4	173>99	15	158>125	8	14

98	Malathion-d ₁₀	9,3	183>132	5	183>151	3	13
99	Mecarbam	10,9	159>131	5	329>160	3	21
100	Merphos	12,1	169>57	8	169>113	3	26
101	Metalaxyl	8,7	206>132	20	266>162	8	13
102	Metazachlor	10,5	209>133	10	133>117	25	19
103	Metconazole	14,8	125>89	20	125>99	20	32
104	Methamidophos	3,1	141>95	6	141>79	18	1
105	Methidathion	11,3	145>85	5	145>58	15	24
106	Methiocarb	9,2	168>153	10	153>109	10	13
107	Methoxychlor	13,9	227>169	25	227>115	40	30
108	Metolachlor	9,5	238>162	8	162>133	12	15
109	Mevinphos	3,8	127>109	10	127>95	15	2
110	Myclobutanyl	12,4	179>125	10	179>152	5	27
111	Napropamide	11,8	128>72	3	271>128	3	24
112	Nuarimol	13,8	203>107	10	235>139	12	28
113	Ofurace	13,4	232>158	20	232>186	5	28
114	o-Phenylphenol	4,5	170>141	30	170>115	40	3
115	Oxadixyl	13,1	163>132	15	163>117	25	27
116	Paclobutrazol	11,4	236>125	10	236>167	20	24
117	Parathion-ethyl	9,7	291>109	10	291>81	10	16
118	Parathion-methyl	8,4	263>109	10	233>124	10	10
119	Pebulate	4,0	128>57	5	161>128	3	1
120	Penconazole	10,6	248>157	25	248>192	15	19
121	Pendimethalin	10,5	252>162	10	252>191	10	20
122	Permethrin	15.7 - 15.9	163>127	5	183>153	15	35
123	Phenothrin	14.7 - 14.8	123>81	8	183>153	15	32
124	Phenthoate	10,9	274>121	10	274>246	5	21
125	Phorate	6,0	231>129	20	231>175	20	6
126	Phosmet	14,4	160>77	30	160>133	15	32
127	Picolinafen	14,8	238>145	25	376>238	25	31
128	Picoxystrobin	11,9	335>173	10	303>157	15	24
129	Pirimicarb	7,8	238>166	10	166>96	20	9
130	Pirimiphos-methyl	9,1	290>151	15	305>180	5	12
131	Procymidone	11,0	283>96	8	283>255	8	20
132	Profenofos	12,0	337>267	16	337>309	6	25
133	Prometon	6,6	225>183	3	225>168	10	6
134	Prometryn	8,7	241>184	12	241>226	8	12
135	Propaphos	11,4	220>140	12	220>125	25	24
136	Propazine	6,8	214>172	8	229>187	3	6
137	Propiconazole	13.5 - 13.7	259>173	10	259>191	8	29
138	Propyzamide	7,0	173>145	16	173>109	32	8
139	Prosulfocarb	8,7	128>86	3	251>128	5	12
140	Prothiofos	11,9	309>239	15	309>221	25	25
141	Pyrazophos	15,4	221>193	10	221>149	15	35
142	Pyridaben	15,8	147>117	20	147>132	10	35

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143	Pyrimethanil	7,1	198>118	25	198>156	25	8
144	Pyriproxyfen	15,0	136>78	18	136>96	8	34
145	Quinalphos	10,9	146>91	30	157>129	15	22
146	Quinoxifen	13,5	307>272	5	307>237	25	29
147	Quintozene	6,9	295>237	15	295>265	10	7
148	Spirodiclofen	15,7	312>259	10	312>109	20	35
149	Spiroxamine I	8,2	100>58	10	100>72	10	9
150	Spiroxamine II	8,9	100>72	10	100>58	10	13
151	Sulprofos	13,2	156>141	15	322>156	10	28
152	Tebuconazole	13,8	250>125	20	250>153	12	29
153	Tebufenpyrad	14,6	333>171	20	333>276	5	31
154	Tecnazene	5,2	215>179	12	203>143	20	3
155	Tefluthrin	7,5	177>127	15	177>137	15	9
156	Terbufos	6,9	231>129	25	231>175	10	8
157	Terbumeton	6,8	169>154	5	225>169	3	6
158	Terbutryn	9,1	241>185	3	241>170	10	13
159	Tetrachlorvinphos	11,5	329>109	25	329>79	35	24
160	Tetraconazole	10,1	336>204	30	336>218	30	18
161	Tetradifon	14,8	356>159	10	356>229	10	33
162	Tetramethrin	14,4	164>77	30	164>107	15	32
163	Tolclofos-methyl	8,5	265>250	15	265>220	25	11
164	Tolyfluanid	10,7	137>91	20	238>137	10	20
165	TPP	13,9	326>233	10	326>169	35	30
166	Triadimefon	9,7	208>181	5	208>127	15	15
167	Triazophos	13,3	161>134	5	161>106	10	28
168	Trifloxystrobin	13,7	222>190	3	222>130	15	29
169	Trifluralin	5,8	306>264	10	264>160	15	4
170	Vinclozolin	8,3	212>172	15	212>109	40	10

APPENDIX II: VALIDATION RESULTS

Table 2a. Recoveries % (RSD) at 10 and 50 µg/kg (n=5). LC analysed pesticides.

No.	Compound	Avocado				Almonds			
		10 µg/Kg		50 µg/Kg		10 µg/Kg		50 µg/Kg	
		Rec, %	RSD, %	Rec, %	RSD, %	Rec, %	RSD, %	Rec, %	RSD, %
1	Acephate	79	7	76	7	73	7	78	4
2	Acetamiprid	107	2	101	1	93	1	99	1
3	Aldicarb	103	3	94	2	88	1	95	4
4	Azinphos-methyl	114	3	99	4	83	2	92	3
5	Azoxystrobin	95	3	92	4	79	5	102	2
6	Bitertanol	92	3	89	2	82	2	97	1
7	Boscalid	104	5	89	4	83	3	91	1
8	Bromuconazole	98	5	87	2	76	4	94	1
9	Bupirimate	97	1	86	4	74	3	87	2
10	Buprofezin	91	1	94	3	48	3	61	3
11	Carbaryl	102	2	90	2	74	3	94	1
12	Carbendazim	93	4	91	6	83	1	87	4
13	Chlorantraniliprole	98	1	92	3	95	2	102	2
14	Chlorpyrifos	107	5	72	4	58	8	55	7
15	Chlorpyrifos-methyl	97	3	75	3	74	8	72	4
16	Clofentezine	88	15	86	5	71	4	73	3
17	Cymoxanil	104	3	100	1	88	1	104	2
18	Cyproconazole	98	3	91	2	79	3	92	3
19	Cyprodinil	80	5	75	2	47	3	60	1
20	Cyromazine	48	1	44	10	69	1	71	14
21	Diazinon	93	4	87	3	83	1	81	2
22	Dicrotophos	97	1	88	2	78	3	94	2
23	Diethofencarb	106	4	92	2	81	1	98	3
24	Difenoconazole	90	4	86	1	70	1	88	1
25	Dimethoate	107	2	99	1	70	2	99	1
26	Dimethomorph	94	2	92	1	83	5	103	3
27	Diniconazole	95	2	81	3	70	2	86	1
28	Diphenylamine	87	2	74	3	70	1	70	2
29	Dodine	112	4	106	8	72	3	85	4
30	Ethion	119	5	84	2	56	5	67	6
31	Ethirimol	54	6	55	3	75	1	71	4
32	Ethoprophos	95	3	84	2	77	3	87	2
33	Fenamidone	105	4	92	1	82	2	98	2
34	Fenamiphos	95	2	80	3	83	2	98	2
35	Fenarimol	95	3	84	2	72	7	86	3
36	Fenazaquin	70	4	72	1	26	2	42	4
37	Fenbuconazole	98	5	92	3	87	2	104	1
38	Fenoxycarb	105	5	102	2	80	1	93	4
39	Fenpropathrin	100	4	76	3	53	8	60	4
40	Fenpropimorph	94	5	86	2	59	5	57	8
41	Fenpyroximate	87	4	77	3	50	1	67	4

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42	Fenthion	109	2	106	8	75	2	80	3
43	Fluazifop	89	3	83	2	36	2	38	5
44	Flufenoxuron	103	5	98	12	61	7	71	4
45	Fluquinconazole	115	1	91	4	74	7	91	1
46	Flusilazole	98	3	92	2	77	5	100	1
47	Flutriafol	102	1	94	2	82	1	99	2
48	Formetanate	92	2	86	3	82	2	80	2
49	Haloxifop	85	4	85	5	37	4	40	3
50	Hexythiazox	95	3	89	6	41	5	49	5
51	Imazalil	78	2	78	2	88	3	84	3
52	Imidacloprid	98	1	101	1	80	1	100	2
53	Indoxacarb	99	6	92	2	77	2	95	2
54	Iprovalicarb	73	4	91	2	82	2	104	1
55	Isofenphos-Methyl	105	1	98	4	76	2	88	2
56	Isoprocab	92	2	91	1	87	1	98	1
57	Kresoxim-methyl	99	1	91	3	79	2	97	3
58	Linuron	94	3	90	2	82	7	91	2
59	Malathion	96	3	93	2	88	2	99	3
60	Mandipropamid	107	3	94	2	96	8	110	2
61	Metalaxyl	98	2	95	1	92	2	104	2
62	Metconazole	95	4	88	2	79	2	92	1
63	Methamidophos	78	3	72	6	46	1	63	1
64	Methidathion	78	3	95	1	86	3	94	2
65	Methiocarb	106	2	92	2	85	3	90	2
66	Methoxyfenozide	99	2	99	2	97	4	104	4
67	Metobromuron	94	3	92	2	89	1	94	2
68	Monocrotophos	91	1	91	2	83	1	96	1
69	Myclobutanil	101	4	93	1	91	2	100	2
70	Nitenpyram	34	1	33	8	61	6	57	9
71	Oxamyl	81	13	94	5	84	8	100	2
72	Oxydemeton-methyl	91	2	89	2	87	2	88	1
73	Paclobutrazole	96	3	94	1	90	1	98	1
74	Pencycuron	96	1	95	3	75	2	80	4
75	Pendimethalin	105	4	73	7	47	2	53	6
76	Phenthoate	92	2	94	6	80	4	90	2
77	Phosalone	106	11	105	7	83	1	81	2
78	Phosmet	103	4	93	2	84	1	89	3
79	Phoxim	99	4	101	3	82	9	87	4
80	Pirimicarb	84	4	88	3	86	2	94	1
81	Pirimiphos-methyl	95	3	83	2	77	2	76	2
82	Prochloraz	85	2	80	3	77	1	91	4
83	Profenofos	90	1	85	4	76	3	75	1
84	Propamocarb	79	3	78	2	71	1	76	1
85	Propiconazole	95	3	87	3	82	1	89	2
86	Propoxur	93	2	96	3	90	2	101	1
87	Propyzamide	93	2	93	3	84	1	91	3
88	Pymetrozine	39	6	46	7	37	1	67	4
89	Pyraclostrobin	103	1	82	2	78	1	88	4
90	Pyrethrins	99	7	96	4	48	14	61	8
91	Pyridaben	81	4	79	10	38	3	48	7
92	Pyrimethanil	90	3	85	2	71	2	73	1
93	Pyriproxyfen	91	1	88	4	55	4	58	6
94	Quinoxifen	68	4	46	1	41	2	45	3

95	Rotenone	93	3	92	4	81	3	96	3
96	Spinosyn A	96	3	98	1	78	1	95	2
97	Spinosyn D	94	3	100	1	75	5	92	2
98	Spirodiclofen	104	6	115	1	71	1	74	2
99	Spiromesifen	116	6	97	5	72	6	76	3
100	Tebuconazole	96	3	93	1	82	3	93	2
101	Tebufenozide	98	4	102	1	89	1	101	2
102	Tebufenpyrad	87	3	82	2	75	4	70	2
103	Tetraconazole	93	3	95	4	97	1	111	2
104	Thiabendazole	79	2	77	2	94	9	85	7
105	Thiacloprid	108	2	107	1	85	2	101	2
106	Thiamethoxam	113	2	109	1	79	2	98	1
107	Thiophanate-methyl	11	28	21	3	107	5	94	4
108	Triadimefon	99	3	94	2	92	4	96	2
109	Triazophos	95	3	94	1	89	2	98	2
110	Trichlorfon	99	2	100	2	91	1	95	2
111	Triflumuron	101	6	86	4	77	8	91	2
112	Triticonazole	96	2	91	1	86	2	98	1
113	Zoxamide	95	4	96	3	81	3	89	1

Table 2b. Recoveries % (RSD) at 10 and 50 µg/kg (n=5). GC analysed pesticides.

No.	Compound	Avocado				Almond			
		10 µg/Kg		50 µg/Kg		10 µg/Kg		50 µg/Kg	
		Rec, %	RSD, %	Rec, %	RSD, %	Rec, %	RSD, %	Rec, %	RSD, %
1	2,4-DDE	66	6	67	4	34	2	32	6
2	2,4-DDT	62	3	61	7	34	7	31	9
3	4,4-DDD	71	5	67	3	42	2	40	2
4	4,4-DDE	65	3	60	4	-	-	28	5
5	4,4-DDT	71	5	67	3	42	2	40	2
6	Acrinathrin	93	8	91	3	63	14	62	6
7	Alachlor	86	2	84	2	77	10	75	2
8	Ametryn	93	3	91	1	72	5	75	2
9	Azoxystrobin	89	7	93	2	-	-	88	4
10	Benalaxyl	90	4	83	7	-	-	86	2
11	Bifenox	92	8	83	6	78	5	72	3
12	Bifenthrin	72	5	72	3	46	2	41	6
13	Bixafen	92	7	90	2	99	4	86	3
14	Boscalid	89	4	93	3	92	3	79	3
15	Bromopropylate	73	9	76	4	59	3	54	3
16	Bupirimate	91	10	84	3	81	9	79	6
17	Buprofezin	83	18	80	12	-	-	57	4
18	Butralin	81	16	78	6	53	26	45	7
19	Butylate	75	8	72	3	60	4	42	20
20	Cadusafos	87	3	84	3	72	4	67	3
21	Carbophenothion	83	15	86	4	55	8	51	2
22	Carbosulfan	-	-	107	6	-	-	71	6
23	Chinomethionat	70	5	96	3	30	2	37	7
24	Chlorbromuron	112	5	107	3	84	18	79	2
25	Chlorfenapyr	-	-	81	10	-	-	55	18


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26	Chlorfenvinphos	90	7	88	1	73	4	74	4
27	Chlorobenzilate	85	5	82	6	72	1	70	2
28	Chlorpropham	86	6	82	4	67	3	79	8
29	Chlorpyrifos	79	6	77	6	54	4	60	5
30	Chlorpyrifos-methyl	95	6	77	3	69	4	60	2
31	Chlorothalonil	85	17	85	5	-	-	25	27
32	Chlozolinate	82	9	86	4	-	-	74	3
33	Cyfluthrin	90	3	92	4	64	3	62	4
34	Cypermethrin	-	-	81	4	62	3	50	2
35	Chlorthal-dimethyl	79	3	83	7	71	10	65	5
36	Cyproconazole	85	10	87	4	73	2	70	4
37	Cyprodinil	87	1	76	2	-	-	52	3
38	Deltamethrin	82	10	82	2	75	22	55	4
39	Diazinon	82	6	84	4	-	-	67	1
40	Dichlorvos	81	13	83	3	73	7	77	4
41	Diclobutrazol	88	8	87	2	80	1	77	6
42	Dicloran	87	10	81	6	-	-	76	8
43	Dimethenamid	93	6	86	4	79	3	78	2
44	Diphenylamine	97	7	76	5	56	2	57	3
45	Endosulfan alpha	-	-	65	8	-	-	39	3
46	Endosulfan beta	-	-	83	4	-	-	55	3
47	Endosulfan sulfate	-	-	90	6	-	-	75	5
48	EPN	84	6	90	3	64	8	70	4
49	Epoxiconazole	89	5	91	3	84	1	82	6
50	Ethion	83	4	83	6	67	4	62	5
51	Ethofenprox	85	4	74	3	50	4	44	6
52	Ethofumesate	91	9	97	4	86	3	82	6
53	Ethoprophos	88	6	85	2	75	2	76	3
54	Etrimfos	93	5	85	4	66	3	67	5
55	Fenvalerate/Esfenvalerate RR/SS	77	5	81	4	71	5	52	7
56	Fenvalerate/Esfenvalerate RS/SR	76	6	83	5	66	6	53	6
57	Fenamidone	86	11	84	5	96	5	84	3
58	Fenarimol	94	6	101	2	83	5	74	1
59	Fenazaquin	70	8	72	3	44	5	44	3
60	Fenbuconazole	91	2	91	3	90	5	86	2
61	Fenchlorphos	77	7	74	4	54	6	48	2
62	Fenhexamid	91	5	88	2	70	6	79	2
63	Fenitrothion	86	14	85	3	81	12	66	1
64	Fenpropathrin	101	18	84	5	61	11	61	6
65	Fenpropimorph	109	3	104	5	64	12	61	5
66	Fenthion	78	7	82	5	73	4	79	5
67	Flamprop-isopropyl	90	1	90	3	89	7	83	2
68	Flamprop-methyl	94	5	92	6	84	6	79	4
69	Fonicamid	86	2	95	2	84	4	86	11
70	Fluacrypyrim	-	-	89	6	95	5	81	2
71	Fluazifop-P-butyl	83	8	90	4	91	7	72	6
72	Flucythrinate	79	8	92	5	86	4	69	6
73	Fludioxonil	86	9	91	7	-	-	83	6
74	Fluquinconazole	90	4	85	1	78	3	76	2
75	Flusilazole	88	7	87	3	78	5	83	3
76	Flutolanil	96	5	90	3	83	1	80	1
77	Flutriafol	-	-	94	4	-	-	91	5


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78	Fluvalinate-tau	86	2	82	3	59	11	54	3
79	Fonofos	88	6	85	1	70	8	62	7
80	Formothion	82	13	86	6	-	-	51	12
81	Fosthiazate	91	4	86	2	83	15	88	9
82	Heptachlor	60	2	61	5	-	-	36	7
83	Heptenophos	89	7	87	1	83	12	87	4
84	Hexaconazole	83	4	86	3	-	-	88	10
85	Indoxacarb	89	2	91	3	80	9	85	4
86	Iprodione	93	2	88	6	76	5	80	5
87	Iprovalicarb	89	12	80	7	77	15	94	1
88	Isazofos	85	3	87	5	99	3	80	4
89	Isocarbophos	102	8	109	2	83	11	84	5
90	Isofenphos-ethyl	86	5	98	4	74	2	78	3
91	Isofenphos-methyl	93	6	94	3	79	2	75	3
92	Kresoxim-methyl	94	9	91	3	79	5	85	4
93	Lambda-cyhalothrin	84	12	87	2	62	4	61	8
94	Lindane	76	11	77	5	60	6	53	4
95	Malathion	83	7	86	4	89	8	88	3
96	Mecarbam	-	-	86	5	-	-	119	3
97	Merphos	73	5	71	1	-	-	-	-
98	Metalaxyl	84	13	87	2	91	9	95	5
99	Methamidophos	78	7	77	5	-	-	74	9
100	Metazachlor	83	12	87	3	95	9	82	3
101	Metconazole	93	9	89	3	81	8	74	5
102	Methidathion	85	7	85	2	75	7	82	6
103	Methiocarb	111	17	115	5	78	13	74	9
104	Metolachlor	97	2	91	3	77	3	75	1
105	Methoxychlor	82	10	81	7	73	6	61	1
106	Mevinphos	74	14	77	2	57	12	67	12
107	Myclobutanyl	100	4	90	3	81	8	81	2
108	Napropamide	79	7	96	4	86	1	84	6
109	Nuarimol	84	4	84	3	84	9	81	1
110	o-Phenylphenol	79	7	83	4	82	2	77	4
111	Ofurace	91	9	96	3	88	4	80	6
112	Oxadixyl	102	9	91	5	88	8	90	3
113	Paclobutrazol	91	6	92	2	-	-	83	8
114	Parathion-ethyl	88	5	87	3	-	-	72	1
115	Parathion-methyl	97	6	90	4	-	-	77	9
116	Pebulate	71	5	76	3	67	5	48	13
117	Penconazole	85	10	82	3	73	2	73	4
118	Pendimethalin	84	12	85	4	-	-	48	2
119	Permethrin	80	5	73	3	60	7	47	4
120	Phenothrin	78	8	73	5	-	-	53	9
121	Phenthoate	87	2	85	2	73	6	75	2
122	Phorate	73	7	85	4	-	-	72	8
123	Phosmet	82	10	86	5	78	8	82	3
124	Picolinafen	82	4	83	1	71	4	65	6
125	Picoxystrobin	-	-	91	5	103	8	78	10
126	Pyrimethanil	71	14	75	5	-	-	61	3
127	Pirimicarb	83	7	81	2	78	3	78	5
128	Pirimiphos-methyl	83	9	85	3	70	9	66	2
129	Procymidone	86	8	79	4	77	2	77	1
130	Profenofos	84	5	78	7	-	-	55	10

131	Prometon	89	5	85	3	91	3	77	2
132	Prometryn	90	6	93	2	-	-	68	2
133	Propaphos	105	9	108	2	117	3	97	3
134	Propazine	79	3	90	5	80	6	76	4
135	Propiconazole	79	6	85	2	77	6	76	5
136	Propyzamide	94	7	88	1	71	1	82	5
137	Prosulfocarb	72	8	77	9	69	8	62	4
138	Prothiofos	75	4	72	3	38	14	37	6
139	Pyrazophos	92	7	87	4	81	10	76	2
140	Pyridaben	73	10	77	4	52	2	46	5
141	Pyriproxyfen	90	6	85	6	58	5	53	1
142	Quinalphos	-	-	87	2	-	-	63	2
143	Quinoxifen	66	9	66	4	45	3	40	5
144	Quintozene	66	18	63	5	-	-	33	2
145	Spirodiclofen	78	11	75	6	64	8	54	2
146	Spiroxamine I	-	-	105	5	154	12	159	5
147	Spiroxamine II	-	-	78	3	89	9	116	3
148	Sulprofos	82	2	84	3	75	6	63	4
149	Tebuconazole	95	4	88	4	76	5	85	1
150	Tebufenpyrad	79	9	78	3	66	6	62	5
151	Tecnazene	61	5	71	7	49	6	41	6
152	Tefluthrin	78	7	76	4	57	5	51	1
153	Terbufos	93	8	89	5	72	8	71	7
154	Terbumeton	84	13	87	7	91	3	75	2
155	Terbutryn	94	7	89	3	77	10	67	2
156	Tetrachlorvinphos	86	2	84	7	75	16	81	6
157	Tetraconazole	82	1	98	1	78	16	80	4
158	Tetradifon	73	9	76	2	43	7	45	4
159	Tetramethrin	74	11	80	3	82	3	70	3
160	Tolclofos-methyl	92	1	90	4	67	5	62	4
161	Tolyfluanid	84	17	100	7	-	-	16	6
162	Triadimefon	91	10	86	6	86	1	79	6
163	Triazophos	85	4	88	6	75	1	87	2
164	Trifloxystrobin	86	1	91	3	81	10	80	2
165	Trifluralin	80	6	77	1	57	6	56	5
166	Vinclozolin	85	11	87	5	65	5	69	5

Table 3a. Limits of quantitation, coefficients of determination (r^2) concentration ranges and matrix effects for LC analysed pesticides. Negative values of matrix effects mean suppression of the signal, and positives values, enhancement.

No.	Compound	LOQ ($\mu\text{g}/\text{kg}$)		R^2		Instrumental concentration range ($\mu\text{g}/\text{L}$)		ME(%) = ((slope matrix/slope solvent)-1) \times 100	
		Avocado	Almond	Avocado	Almond	Avocado	Almond	Avocado	Almond
1	Acephate	10	10	0.9971	0.9973	10 - 500	10 - 500	-26	-29
2	Acetamiprid	10	10	0.9979	0.9943	1 - 500	1 - 500	-17	-13
3	Aldicarb	10	10	0.9966	0.9909	1 - 500	1 - 500	-60	-48
4	Azinphos-methyl	10	10	0.9988	0.9995	2 - 500	1 - 500	-20	-3
5	Azoxystrobin	10	10	0.9997	0.9973	1 - 500	1 - 500	-2	-6
6	Bitertanol	10	10	0.9980	0.9984	1 - 500	1 - 500	-12	-3

7	Boscalid	10	10	0.9970	0.9971	1 – 500	1 - 500	-40	-4
8	Bromuconazole	10	10	0.9979	0.9997	2 – 500	1 - 500	-4	2
9	Bupirimate	10	10	0.9909	0.9929	1 – 500	1 - 500	-1	-1
10	Buprofezin	10	-	0.9970	0.9966	1 - 500	1 - 500	-59	-2
11	Carbaryl	10	10	0.9927	0.9993	2 - 500	2 - 500	-19	-14
12	Carbendazim	10	10	0.9923	0.9970	1 - 500	1 - 500	-43	-48
13	Chlorantraniliprole	10	10	0.9983	0.9994	1 – 500	1 - 500	-7	-2
14	Chlorpyrifos	10	-	0.9996	0.9997	2 – 500	1 - 500	-80	-3
15	Chlorpyrifos-methyl	10	10	0.9993	0.9994	2 – 500	1 - 500	-48	-7
16	Clofentezine	10	10	0.9990	0.9997	2 – 500	1 - 500	-43	-1
17	Cymoxanil	10	10	0.9997	0.9997	2 – 500	1 - 500	-4	-4
18	Cyproconazole	10	10	0.9982	0.9951	1 – 500	1 - 500	-15	-8
19	Cyprodinil	10	-	0.9944	0.9956	1 – 500	1 - 500	-20	-6
20	Cyromazine	-	50	0.9950	0.9914	2 – 500	1 - 500	-74	-49
21	Diazinon	10	10	0.9967	0.9978	1 – 500	1 - 500	-30	0
22	Dicrotophos	10	10	0.9937	0.9987	1 – 500	1 - 500	-11	-14
23	Diethofencarb	10	10	0.9964	0.9999	1 – 500	1 - 500	-16	-1
24	Difenoconazole	10	10	0.9946	0.9995	1 – 500	1 - 500	-23	1
25	Dimethoate	10	10	0.9960	0.9964	1 – 500	1 - 500	-11	-19
26	Dimethomorph	10	10	0.9975	0.9995	1 – 500	1 - 500	-5	-9
27	Diniconazole	10	10	0.9909	0.9979	1 – 500	1 - 500	-9	-2
28	Diphenylamine	10	10	0.9921	0.9967	1 – 500	1 - 500	-13	-1
29	Dodine	10	10	0.9968	0.9994	10 - 500	1 - 500	-34	-14
30	Ethion	10	-	0.9986	0.9954	1 – 500	1 - 500	-76	-8
31	Ethirimol	-	10	0.9964	0.9981	1 – 500	1 - 500	-15	-16
32	Ethoprophos	10	10	0.9904	0.9943	2 – 500	1 - 500	-30	-6
33	Fenamidone	10	10	0.9918	0.9938	2 – 500	1 - 500	-37	0
34	Fenamiphos	10	10	0.9908	0.9965	2 – 500	1 - 500	-7	2
35	Fenarimol	10	10	0.9992	1.0000	1 – 500	1 - 500	-8	-1
36	Fenazaquin	10	-	0.9947	0.9938	1 – 500	1 - 500	-57	1
37	Fenbuconazole	10	10	0.9983	0.9964	1 – 500	1 - 500	-10	1
38	Fenoxycarb	10	10	0.9980	0.9985	1 – 500	1 - 500	-30	2
39	Fenpropathrin	10	-	0.9991	0.9997	1 – 500	1 - 500	-79	2
40	Fenpropimorph	10	-	0.9964	0.9910	1 – 500	1 - 500	-20	-5
41	Fenpyroximate	10	-	0.9992	0.9904	1 – 200	1 - 500	-28	-32
42	Fenthion	10	10	0.9967	0.9999	1 – 500	1 - 500	-52	-5
43	Fluazifop	10	-	0.9991	0.9976	1 – 500	1 - 500	-19	1
44	Flufenoxuron	10	50	0.9949	0.9985	1 – 500	1 - 500	-72	1
45	Fluquinconazole	10	10	0.9984	0.9993	1 – 500	1 - 500	-23	-1
46	Flusilazole	10	10	0.9975	0.9916	1 – 500	1 - 500	-9	-1
47	Flutriafol	10	10	0.9978	0.9959	1 – 500	1 - 500	-3	0
48	Formetanate	10	10	0.9984	0.9907	1 – 200	1 - 500	-9	-34
49	Haloxifop	10	-	0.9953	0.9966	1 – 500	1 - 500	-15	-4
50	Hexythiazox	10	-	0.9957	0.9956	2 – 500	1 - 500	-66	-10
51	Imazalil	10	10	0.9998	0.9994	2 – 500	2 - 500	-23	-11
52	Imidacloprid	10	10	0.9997	0.9995	1 – 500	1 - 500	-13	-9
53	Indoxacarb	10	10	0.9990	0.9990	1 – 500	1 - 500	-44	-2
54	Iprovalicarb	10	10	0.9956	0.9995	2 – 500	1 - 500	1	17
55	Isofenphos-Methyl	10	10	0.9994	0.9960	1 – 500	1 - 500	3	2
56	Isoprocarb	10	10	0.9971	0.9989	1 – 500	1 - 500	-7	-6
57	Kresoxim-methyl	10	10	0.9994	0.9993	1 – 500	1 - 500	-27	-5
58	Linuron	10	10	0.9991	0.9998	1 – 500	1 - 500	-18	-2
59	Malathion	10	10	0.9969	0.9992	1 – 500	1 - 500	-13	-6
60	Mandipropamid	10	10	0.9937	0.9976	1 – 500	1 - 500	-34	3
61	Metalaxyl	10	10	0.9998	0.9969	1 – 200	1 - 500	4	-1
62	Metconazole	10	10	0.9938	0.9999	1 – 500	1 - 500	-19	27
63	Methamidophos	10	-	0.9986	1.0000	2 – 500	1 - 500	-17	-10
64	Methidathion	10	10	0.9985	0.9995	1 – 500	1 - 500	-22	0
65	Methiocarb	10	10	0.9999	0.9991	1 – 500	1 - 500	-32	-4
66	Methoxyfenozide	10	10	0.9959	0.9950	2 – 500	1 - 500	-7	-1

67	Metobromuron	10	10	0.9995	0.9997	2 – 500	1 - 500	-6	-4
68	Monocrotophos	10	10	0.9901	0.9960	2 – 500	1 - 500	-6	-15
69	Myclobutanil	10	10	0.9907	0.9966	2 – 500	1 - 500	-10	-4
70	Nitenpyram	-	-	0.9928	0.9959	2 – 500	1 - 500	-30	2
71	Oxamyl	10	10	0.9945	0.9998	10 - 500	10 - 500	-17	-49
72	Oxydemeton-methyl	10	10	0.9974	0.9990	1 – 500	1 - 500	-6	-6
73	Paclobutrazole	10	10	0.9972	0.9958	1 – 500	1 - 500	-6	-1
74	Pencycuron	10	10	0.9915	0.9973	1 – 200	1 - 500	-49	-4
75	Pendimethalin	10	-	0.9981	0.9975	2 – 500	1 - 500	-65	-7
76	Phenthoate	10	10	0.9981	0.9985	10 - 500	1 - 500	-26	-8
77	Phosalone	10	10	0.9927	0.9992	2 – 500	1 - 500	-58	-5
78	Phosmet	10	10	0.9999	0.9978	1 – 500	1 - 500	-46	-7
79	Phoxim	10	10	0.9996	0.9999	2 – 500	2 - 500	-41	-2
80	Pirimicarb	10	10	0.9902	0.9976	1 – 500	1 - 500	-4	-8
81	Pirimiphos-methyl	10	10	0.9998	0.9952	1 – 500	1 - 500	-39	-2
82	Prochloraz	10	10	0.9902	0.9986	1 – 500	1 - 500	-13	-6
83	Profenofos	10	10	0.9964	0.9996	1 – 500	1 - 500	-34	-2
84	Propamocarb	10	10	0.9985	0.9922	1 – 200	1 - 500	-11	-18
85	Propiconazole	10	10	0.9988	1.0000	1 – 500	2 - 500	-14	0
86	Propoxur	10	10	0.9947	0.9976	1 – 500	1 - 500	-16	-13
87	Propyzamide	10	10	0.9984	0.9987	1 – 200	1 - 500	-15	-2
88	Pymetrozine	-	-	0.9993	0.9986	1 – 50	1 - 200	-49	-57
89	Pyraclostrobin	10	10	0.9969	0.9921	1 – 200	1 - 500	-22	-3
90	Pyrethrins	10	-	0.9976	0.9998	10 - 500	2 - 500	-71	-16
91	Pyridaben	10	-	0.9910	0.9990	1 – 200	1 - 500	-79	-5
92	Pyrimethanil	10	10	0.9941	0.9983	1 – 500	1 - 500	-35	-7
93	Pyriproxyfen	10	-	0.9966	0.9996	1 – 500	1 - 500	-66	1
94	Quinoxifen	-	-	0.9944	0.9922	1 – 500	1 - 500	-30	-1
95	Rotenone	10	10	0.9981	0.9986	1 – 500	1 - 500	-24	-7
96	Spinosyn A	10	10	0.9974	0.9903	1 – 200	1 - 500	-19	-35
97	Spinosyn D	10	10	0.9993	0.9981	1 – 500	1 - 500	-28	-20
98	Spirodiclofen	10	10	0.9980	0.9909	10 - 500	1 - 500	-84	-12
99	Spiromesifen	10	10	0.9995	0.9940	2 – 500	1 - 500	-84	-28
100	Tebuconazole	10	10	0.9968	0.9928	1 – 500	1 - 500	-15	-23
101	Tebufenozide	10	10	0.9954	0.9944	1 – 500	1 - 500	-8	-1
102	Tebufenpyrad	10	10	0.9966	0.9951	1 – 500	1 - 500	-37	-3
103	Tetraconazole	10	10	0.9968	0.9934	1 – 500	1 - 500	-11	-2
104	Thiabendazole	10	10	0.9990	0.9925	1 – 500	1 - 500	-26	-28
105	Thiacloprid	10	10	0.9981	0.9936	1 – 500	1 - 500	-43	-12
106	Thiamethoxam	10	10	0.9983	0.9902	1 – 500	1 - 500	-17	-13
107	Thiophanate-methyl	-	10	0.9939	0.9941	2 – 500	1 - 500	-40	-6
108	Triadimefon	10	10	0.9925	0.9975	1 – 500	1 - 500	-9	-2
109	Triazophos	10	10	0.9999	0.9988	1 – 500	1 - 500	-9	1
110	Trichlorfon	10	10	0.9999	0.9997	1 – 500	1 - 500	3	19
111	Triflumuron	10	10	0.9997	0.9976	2 – 500	1 - 500	-68	-4
112	Triticonazole	10	10	0.9986	0.9952	1 – 500	1 - 500	-7	-2
113	Zoxamide	10	10	0.9951	0.9987	2 – 500	1 - 500	-23	-3

Table 3b. Limits of quantification, coefficients of determination concentration ranges and matrix effects for GC analysed pesticides. Negative values of matrix effects mean suppression of the signal, and positives values, enhancement.

No.	Compound	LOQ (µg/kg)		R ²		Instrumental concentration range (µg/L)		ME(%) = ((slope matrix/slope solvent)-1) × 100	
		Avocado	Almond	Avocado	Almond	Avocado	Almond	Avocado	Almond
1	2,4-DDE	10	-	0,997	1,000	10 - 500	10 - 500	25	3
2	2,4-DDT	10	-	1,000	0,999	10 - 500	10 - 500	76	27
3	4,4-DDD	10	-	0,996	0,999	1 - 500	10 - 500	58	36
4	4,4-DDE	10	-	0,996	1,000	10 - 500	10 - 500	36	8
5	4,4-DDT	10	-	0,996	0,999	1 - 500	10 - 500	57	36
6	Acrinathrin	10	10	0,994	0,992	10 - 500	10 - 500	300<	139
7	Alachlor	10	10	0,996	0,996	10 - 500	10 - 500	49	31
8	Ametryn	10	10	0,996	0,998	10 - 500	10 - 500	76	51
9	Azoxystrobin	10	50	0,994	0,998	10 - 500	10 - 500	300<	169
10	Benalaxyl	10	50	0,995	0,999	20 - 500	10 - 500	61	38
11	Bifenox	10	10	0,990	0,991	10 - 500	10 - 500	35	37
12	Bifenthrin	10	-	0,996	0,998	10 - 500	10 - 500	64	35
13	Bixafen	10	10	0,996	0,999	1 - 500	10 - 500	300<	99
14	Boscalid	10	10	0,996	0,998	1 - 500	10 - 500	227	69
15	Bromopropylate	10	-	0,997	0,999	2 - 500	10 - 500	164	118
16	Bupirimate	10	10	0,998	0,997	2 - 500	10 - 500	46	44
17	Buprofezin	10	-	0,991	1,000	10 - 500	50 - 500	41	28
18	Butralin	10	-	0,995	0,992	10 - 500	10 - 500	121	59
19	Butylate	10	-	0,997	0,999	1 - 500	10 - 500	39	25
20	Cadusafos	10	10	0,995	0,999	10 - 500	10 - 500	91	58
21	Carbophenothion	10	-	0,994	0,999	10 - 500	10 - 500	172	67
22	Carbosulfan	50	50	0,999	0,990	50 - 500	50 - 500	-65	-57
23	Chinomethionat	10	-	0,994	0,999	2 - 500	10 - 500	71	42
24	Chlorbromuron	10	10	0,997	0,999	2 - 500	10 - 500	19	-13
25	Chlorfenapyr	50	-	0,996	0,996	50 - 500	50 - 500	61	25
26	Chlorfenvinphos	10	10	0,997	0,998	10 - 500	10 - 500	156	42
27	Chlorobenzilate	10	10	0,997	0,999	10 - 500	10 - 500	69	48
28	Chlorpropham	10	10	0,996	0,999	1 - 500	10 - 500	154	41
29	Chlorpyrifos	10	50	0,996	0,999	2 - 500	10 - 500	42	29
30	Chlorpyrifos-methyl	10	10	0,996	0,996	2 - 500	10 - 500	104	55
31	Chlorothalonil	10	-	0,993	0,996	2 - 500	10 - 500	223	77
32	Chlozolinate	10	50	0,997	0,998	10 - 500	10 - 500	41	25
33	Cyfluthrin	10	10	0,995	0,996	10 - 500	10 - 500	297	76
34	Cypermethrin	50	-	0,997	0,997	20 - 500	10 - 500	205	63
35	Chlorthal-dimethyl	10	10	0,996	0,999	10 - 500	10 - 500	14	34
36	Cyproconazole	10	10	0,996	0,993	10 - 500	10 - 500	63	84
37	Cyprodinil	10	-	0,996	0,999	1 - 500	10 - 500	60	22
38	Deltamethrin	10	-	0,998	0,998	2 - 500	10 - 500	300<	123
39	Diazinon	10	50	0,996	0,999	10 - 500	50 - 500	-	-
40	Dichlorvos	10	10	0,997	0,999	1 - 500	10 - 500	62	65
41	Diclobutrazol	10	10	0,996	0,999	10 - 500	10 - 500	198	148
42	Dicloran	10	50	0,992	0,993	2 - 500	10 - 500	117	30
43	Dimethenamid	10	10	0,996	0,998	2 - 500	10 - 500	73	28
44	Diphenylamine	10	-	0,996	0,999	10 - 500	10 - 500	39	14
45	Endosulfan alpha	50	-	0,994	0,999	20 - 500	50 - 500	23	11
46	Endosulfan beta	50	-	0,997	0,998	20 - 500	50 - 500	24	4
47	Endosulfan sulfate	50	50	0,995	1,000	20 - 500	50 - 500	-	-
48	EPN	10	10	0,993	0,992	10 - 500	10 - 500	253	70
49	Epoxiconazole	10	10	0,997	0,997	2 - 500	10 - 500	176	79

50	Ethion	10	10	0,995	0,998	2 - 500	10 - 500	132	62
51	Ethofenprox	10	-	0,996	0,999	10 - 500	10 - 500	151	44
52	Ethofumesate	10	10	0,998	0,998	10 - 500	10 - 500	40	50
53	Ethoprophos	10	10	0,995	0,998	1 - 500	10 - 500	166	70
54	Etrimfos	10	10	0,995	0,998	10 - 500	10 - 500	79	52
55	Fenvalerate/Esfenvalerate RR/SS	10	-	0,993	0,994	1 - 500	10 - 500	300<	84
56	Fenvalerate/Esfenvalerate RS/SR	10	-	0,994	0,994	1 - 500	10 - 500	300<	93
57	Fenamidone	10	10	0,997	0,999	2 - 500	10 - 500	74	26
58	Fenarimol	10	10	0,997	0,999	10 - 500	10 - 500	98	54
59	Fenazaquin	10	-	0,997	0,999	10 - 500	10 - 500	80	37
60	Fenbuconazole	10	10	0,995	0,999	10 - 500	10 - 500	262	58
61	Fenchlorphos	10	-	0,995	0,999	2 - 500	10 - 500	77	61
62	Fenhexamid	10	10	0,996	1,000	10 - 500	10 - 500	300<	248
63	Fenitrothion	10	10	0,992	0,988	10 - 500	10 - 500	243	131
64	Fenpropathrin	10	10	0,996	0,999	10 - 500	10 - 500	63	46
65	Fenpropimorph	10	10	0,996	0,998	2 - 500	10 - 500	56	53
66	Fenthion	10	10	0,995	0,998	10 - 500	10 - 500	203	300<
67	Flamprop-isopropyl	10	10	0,997	0,999	10 - 500	10 - 500	55	43
68	Flamprop-methyl	10	10	0,997	1,000	10 - 500	10 - 500	33	24
69	Flonicamid	10	10	0,997	1,000	2 - 500	10 - 500	185	3
70	Fluacrypyrim	50	10	0,996	0,999	20 - 500	10 - 500	58	35
71	Fluazifop-P-butyl	10	10	0,996	0,999	10 - 500	10 - 500	97	52
72	Flucythrinate	10	10	0,994	0,992	10 - 500	10 - 500	300<	145
73	Fludioxonil	10	50	0,997	0,999	10 - 500	50 - 500	100	53
74	Fluquinconazole	10	10	0,996	0,998	1 - 500	10 - 500	108	54
75	Flusilazole	10	10	0,995	0,999	10 - 500	10 - 500	48	37
76	Flutolanil	10	10	0,993	0,999	10 - 500	10 - 500	98	61
77	Flutriafol	50	50	0,995	0,999	20 - 500	10 - 500	106	79
78	Fluvalinate-tau	10	-	0,990	0,990	2 - 500	10 - 500	300<	149
79	Fonofos	10	10	0,996	0,998	10 - 500	10 - 500	77	77
80	Formothion	10	-	0,994	0,994	10 - 500	50 - 500	-	-
81	Fosthiazate	10	10	0,994	0,994	10 - 500	10 - 500	-	-
82	Heptachlor	10	-	0,993	0,997	10 - 500	50 - 500	62	23
83	Heptenophos	10	10	0,996	1,000	10 - 500	10 - 500	300<	97
84	Hexaconazole	10	50	0,997	0,998	10 - 500	10 - 500	74	55
85	Indoxacarb	10	10	0,997	1,000	2 - 500	10 - 500	115	43
86	Iprodione	10	10	0,996	0,998	2 - 500	10 - 500	300<	135
87	Iprovalicarb	10	10	0,997	0,999	10 - 500	10 - 500	242	115
88	Isazofos	10	10	0,995	0,997	10 - 500	10 - 500	65	45
89	Isocarbophos	10	10	0,997	0,995	10 - 500	10 - 500	178	106
90	Isfenphos-ethyl	10	10	0,997	0,997	1 - 500	10 - 500	68	44
91	Isfenphos-methyl	10	10	0,995	0,998	2 - 500	10 - 500	75	43
92	Kresoxim-methyl	10	10	0,996	1,000	10 - 500	10 - 500	49	35
93	Lambda-cyhalothrin	10	10	0,996	0,996	10 - 500	10 - 500	220	71
94	Lindane	10	-	0,996	0,999	2 - 500	10 - 500	37	28
95	Malathion	10	10	0,994	0,998	2 - 500	10 - 500	131	66
96	Mecarbam	50	50	0,997	0,999	20 - 500	50 - 500	59	31
97	Merphos	10	-	0,997	0,999	10 - 500	10 - 500	65	45
98	Metalaxyl	10	10	0,996	0,999	10 - 500	10 - 500	37	30
99	Methamidophos	10	50	0,997	0,998	10 - 500	50 - 500	300<	44
100	Metazachlor	10	10	0,995	0,996	10 - 500	10 - 500	94	49
101	Metconazole	10	10	0,996	0,999	10 - 500	10 - 500	83	50
102	Methidathion	10	10	0,994	0,995	2 - 500	10 - 500	300<	66
103	Methiocarb	10	10	0,996	0,993	10 - 500	10 - 500	300<	159
104	Metolachlor	10	10	0,996	0,999	10 - 500	10 - 500	62	38
105	Methoxychlor	10	10	0,999	0,997	10 - 500	10 - 500	181	5
106	Mevinphos	10	50	0,995	0,999	1 - 500	10 - 500	300<	173
107	Myclobutanyl	10	10	0,997	0,998	2 - 500	10 - 500	58	30
108	Napropamide	10	10	0,996	1,000	10 - 500	10 - 500	76	67

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109	Nuarimol	10	10	0,997	0,999	10 - 500	10 - 500	79	42
110	o-Phenylphenol	10	10	0,997	1,000	1 - 500	10 - 500	166	61
111	Ofurace	10	10	0,995	1,000	2 - 500	10 - 500	133	53
112	Oxadixyl	10	10	0,997	1,000	10 - 500	10 - 500	71	29
113	Paclobutrazol	10	50	0,996	0,998	10 - 500	50 - 500	-	-
114	Parathion-ethyl	10	50	0,990	0,992	10 - 500	50 - 500	-	-
115	Parathion-methyl	10	50	0,998	0,990	10 - 500	10 - 500	300<	135
116	Pebulate	10	-	0,997	1,000	2 - 500	10 - 500	50	28
117	Penconazole	10	10	0,996	0,996	10 - 500	10 - 500	60	42
118	Pendimethalin	10	-	0,989	0,997	2 - 500	10 - 500	102	44
119	Permethrin	10	-	0,996	0,999	2 - 500	10 - 500	138	52
120	Phenothrin	10	-	0,995	0,999	10 - 500	10 - 500	149	43
121	Phenthoate	10	10	0,994	0,993	10 - 500	10 - 500	108	48
122	Phorate	10	50	0,994	0,997	10 - 500	50 - 500	300<	300<
123	Phosmet	10	10	0,993	0,996	2 - 500	10 - 500	300<	201
124	Picolinafen	10	10	0,997	1,000	2 - 500	10 - 500	94	43
125	Picoxystrobin	50	10	0,996	0,999	10 - 500	10 - 500	55	52
126	Pyrimethanil	10	50	0,996	0,997	10 - 500	10 - 500	83	50
127	Pirimicarb	10	10	0,995	0,997	2 - 500	10 - 500	57	34
128	Pirimiphos-methyl	10	10	0,997	0,998	10 - 500	10 - 500	51	41
129	Procymidone	10	10	0,997	0,999	10 - 500	10 - 500	29	22
130	Profenofos	10	-	0,996	1,000	10 - 500	50 - 500	164	85
131	Prometon	10	10	0,996	0,999	10 - 500	10 - 500	74	35
132	Prometryn	10	50	0,995	0,998	10 - 500	10 - 500	44	36
133	Propaphos	10	10	0,994	0,997	2 - 500	10 - 500	300<	300<
134	Propazine	10	10	0,997	0,998	2 - 500	10 - 500	66	51
135	Propiconazole	10	10	0,997	1,000	2 - 500	10 - 500	80	51
136	Propyzamide	10	10	0,995	0,999	2 - 500	10 - 500	72	39
137	Prosulfocarb	10	10	0,996	0,999	10 - 500	10 - 500	49	47
138	Prothiofos	10	-	0,997	0,999	10 - 500	10 - 500	61	50
139	Pyrazophos	10	10	0,995	0,996	10 - 500	10 - 500	300<	117
140	Pyridaben	10	-	0,996	0,997	10 - 500	10 - 500	170	61
141	Pyriproxyfen	10	-	0,997	0,999	10 - 500	10 - 500	128	44
142	Quinalphos	50	50	0,996	0,998	20 - 500	10 - 500	70	23
143	Quinoxyfen	10	-	0,997	0,999	1 - 500	10 - 500	52	38
144	Quintozene	10	-	0,993	0,993	10 - 500	20 - 500	87	49
145	Spirodiclofen	10	-	0,997	0,998	10 - 500	10 - 500	114	89
146	Spiroxamine I	50	-	0,996	0,998	10 - 500	10 - 500	120	68
147	Spiroxamine II	50	10	0,996	0,998	20 - 500	10 - 500	65	45
148	Sulprofos	10	10	0,996	0,998	10 - 500	10 - 500	258	300<
149	Tebuconazole	10	10	0,997	0,997	10 - 500	10 - 500	144	86
150	Tebufenpyrad	10	10	0,997	0,999	1 - 500	10 - 500	79	36
151	Tecnazene	10	-	0,995	0,998	2 - 500	10 - 500	121	53
152	Tefluthrin	10	-	0,996	0,997	1 - 500	10 - 500	35	21
153	Terbufos	10	10	0,995	0,997	2 - 500	10 - 500	300<	300<
154	Terbumeton	10	10	0,997	0,998	2 - 500	10 - 500	63	44
155	Terbutryn	10	10	0,997	0,999	10 - 500	10 - 500	69	43
156	Tetrachlorvinphos	10	10	0,995	0,994	10 - 500	10 - 500	-	-
157	Tetraconazole	10	10	0,994	0,999	10 - 500	10 - 500	48	13
158	Tetradifon	10	-	0,996	0,999	2 - 500	10 - 500	48	30
159	Tetramethrin	10	10	0,996	0,999	10 - 500	10 - 500	151	60
160	Tolclofos-methyl	10	10	0,996	0,998	10 - 500	10 - 500	65	33
161	Tolyfluanid	10	-	0,990	0,995	10 - 500	10 - 500	150	40
162	Triadimefon	10	10	0,997	0,999	2 - 500	10 - 500	57	43
163	Triazophos	10	10	0,996	0,998	2 - 500	10 - 500	300<	96
164	Trifloxystrobin	10	10	0,997	0,999	10 - 500	10 - 500	122	52
165	Trifluralin	10	-	0,990	0,990	2 - 500	10 - 500	101	41
166	Vinclozolin	10	10	0,994	0,998	10 - 500	10 - 500	40	39

Table 4a. Precision of the chromatographic method (n=5) for LC analysed pesticides.

No.	Compound	Intra-day variability (RSD, %)				Inter-day variability (RSD, %)			
		10 µg/kg		50 µg/kg		10 µg/kg		50 µg/kg	
		Avocado	Almonds	Avocado	Almonds	Avocado	Almonds	Avocado	Almonds
1	Acephate	3	3	1	5	11	5	7	6
2	Acetamiprid	1	1	1	1	6	8	4	9
3	Aldicarb	5	6	2	3	17	13	9	10
4	Azinphos-methyl	2	2	2	2	10	6	4	8
5	Azoxystrobin	1	3	2	2	9	8	6	11
6	Bitertanol	3	1	2	1	9	8	7	10
7	Boscalid	1	1	1	2	13	12	9	14
8	Bromuconazole	1	2	3	2	10	9	6	11
9	Bupirimate	3	2	2	2	12	15	8	16
10	Buprofezin	2	2	2	2	7	3	5	6
11	Carbaryl	4	4	1	1	6	11	6	6
12	Carbendazim	1	1	1	1	9	6	5	6
13	Chlorantraniliprole	1	2	1	3	12	6	8	8
14	Chlorpyrifos	1	1	4	3	15	11	17	10
15	Chlorpyrifos-methyl	6	5	3	9	8	15	3	18
16	Clofentezine	4	1	2	6	11	9	8	12
17	Cymoxanil	2	2	2	3	10	10	7	10
18	Cyproconazole	1	3	2	1	10	7	6	8
19	Cyprodinil	3	1	3	4	12	8	7	11
20	Cyromazine	2	5	2	5	8	10	4	7
21	Diazinon	3	3	1	4	15	3	10	3
22	Dicrotophos	2	2	1	7	13	5	10	10
23	Diethofencarb	2	1	2	2	8	9	9	11
24	Difenoconazole	5	1	1	5	17	8	10	12
25	Dimethoate	1	1	1	2	6	4	5	6
26	Dimethomorph	2	1	1	3	6	12	3	14
27	Diniconazole	1	1	2	4	7	9	4	12
28	Diphenylamine	1	1	1	1	6	3	2	1
29	Dodine	5	6	7	2	19	7	16	13
30	Ethion	5	4	4	1	18	10	16	12
31	Ethirimol	1	1	1	1	9	4	5	10
32	Ethoprophos	2	3	1	1	9	10	6	11
33	Fenamidone	1	3	1	1	10	6	9	7
34	Fenamiphos	2	1	1	3	10	10	5	9
35	Fenarimol	1	4	1	2	13	10	6	11
36	Fenazaquin	6	1	5	4	7	10	7	14
37	Fenbuconazole	3	1	3	3	11	9	8	12
38	Fenoxycarb	2	3	2	1	15	10	13	11
39	Fenpropathrin	8	1	8	3	16	10	11	7
40	Fenpropimorph	1	1	1	4	12	5	8	8
41	Fenpyroximate	2	1	8	7	6	12	7	16
42	Fenthion	1	4	3	4	12	16	9	16
43	Fluazifop	1	4	1	1	10	6	5	8
44	Flufenoxuron	5	1	8	2	18	15	13	2
45	Fluquinconazole	3	1	4	4	12	14	11	15
46	Flusilazole	1	1	1	2	10	7	5	10
47	Flutriafol	2	1	1	2	11	6	6	8
48	Formetanate	1	2	2	2	20	9	14	9
49	Haloxifop	2	1	1	2	9	12	3	12
50	Hexythiazox	5	3	7	1	20	6	15	6
51	Imazalil	4	1	1	4	10	4	7	8
52	Imidacloprid	1	1	1	1	11	10	8	9

53	Indoxacarb	6	2	1	2	9	13	5	17
54	Iprovalicarb	4	1	1	3	6	7	6	8
55	Isofenphos-Methyl	3	2	1	4	11	4	12	9
56	Isoprocarb	1	1	1	3	3	7	4	9
57	Kresoxim-methyl	1	1	1	1	6	4	2	6
58	Linuron	2	1	2	1	9	9	5	10
59	Malathion	2	3	1	2	4	11	2	10
60	Mandipropamid	3	2	1	2	8	8	5	9
61	Metalaxyl	1	1	1	3	7	9	3	9
62	Metconazole	1	1	2	2	4	8	4	10
63	Methamidophos	2	1	1	3	11	7	8	12
64	Methidathion	1	1	1	2	7	11	4	11
65	Methiocarb	1	1	2	1	7	8	7	11
66	Methoxyfenozide	1	1	1	2	4	3	6	6
67	Metobromuron	1	2	1	2	10	9	6	10
68	Monocrotophos	1	1	1	4	8	7	4	10
69	Myclobutanil	1	1	2	1	6	8	3	9
70	Nitenpyram	2	1	1	2	10	5	4	8
71	Oxamyl	2	12	2	5	20	14	14	15
72	Oxydemeton-methyl	1	1	1	4	10	9	4	11
73	Paclobutrazole	1	1	1	2	6	7	2	8
74	Pencycuron	6	4	4	3	5	6	3	10
75	Pendimethalin	3	2	4	1	8	4	6	4
76	Phenthoate	5	2	4	5	14	14	4	17
77	Phosalone	1	2	1	1	11	13	6	14
78	Phosmet	4	6	2	5	18	13	8	14
79	Phoxim	6	2	4	10	13	13	10	16
80	Pirimicarb	2	2	1	1	8	6	3	6
81	Pirimiphos-methyl	1	2	1	2	3	7	2	7
82	Prochloraz	2	1	2	3	6	8	2	11
83	Profenofos	1	1	2	2	10	10	5	13
84	Propamocarb	2	3	2	6	6	6	3	10
85	Propiconazole	3	3	2	1	7	7	4	7
86	Propoxur	1	3	1	1	4	7	2	7
87	Propyzamide	3	2	1	1	9	9	5	11
88	Pymetrozine	1	2	1	3	18	8	10	10
89	Pyraclostrobin	2	3	2	3	7	9	6	9
90	Pyrethrins	6	3	5	2	15	13	8	14
91	Pyridaben	4	3	2	4	11	15	6	17
92	Pyrimethanil	2	1	1	2	6	7	2	10
93	Pyriproxyfen	6	3	6	2	11	5	6	7
94	Quinoxifen	8	2	7	1	11	8	8	9
95	Rotenone	1	1	1	1	12	11	9	11
96	Spinosyn A	1	1	2	2	3	10	4	8
97	Spinosyn D	1	2	1	4	4	8	4	9
98	Spirodiclofen	3	7	4	4	17	18	10	4
99	Spiromesifen	6	11	2	5	7	17	4	5
100	Tebuconazole	1	2	1	1	5	8	4	10
101	Tebufenozide	1	1	1	1	6	4	6	11
102	Tebufenpyrad	5	2	4	1	7	10	5	11
103	Tetraconazole	2	2	2	1	6	10	3	10
104	Thiabendazole	1	1	1	9	11	16	7	13
105	Thiacloprid	1	1	2	8	13	6	8	10
106	Thiamethoxam	1	5	1	1	7	8	4	10
107	Thiophanate-methyl	5	2	6	3	8	11	7	14
108	Triadimefon	1	1	2	2	6	9	3	9
109	Triazophos	1	1	2	1	5	6	4	9
110	Trichlorfon	1	2	1	2	3	17	5	20
111	Triflumuron	5	1	3	2	13	12	13	13
112	Triticonazole	1	1	1	1	8	6	4	7

113 Zoxamide 4 3 3 1 6 11 4 11

Table 4b. Precision of the chromatographic method (n=5) for GC analysed pesticides.

No.	Compound	Intra-day variability (RSD, %)				Inter-day variability (RSD, %)			
		10 µg/L		50 µg/L		10 µg/L		50 µg/L	
		Avocado	Almonds	Avocado	Almonds	Avocado	Almonds	Avocado	Almonds
1	2,4-DDE	1	5	2	2	11	8	12	2
2	2,4-DDT	4	8	4	4	11	18	13	12
3	4,4-DDD	4	6	2	1	10	6	13	2
4	4,4-DDE	3	4	4	1	12	6	15	3
5	4,4-DDT	4	5	2	1	10	7	13	2
6	Acrinathrin	2	4	1	1	13	11	15	4
7	Alachlor	3	6	1	2	9	14	12	3
8	Ametryn	8	7	2	4	11	16	12	7
9	Azoxystrobin	3	6	3	3	7	13	14	7
10	Benalaxyl	8	3	2	1	15	12	11	4
11	Bifenox	11	6	3	1	6	7	8	2
12	Bifenthrin	1	4	1	1	6	14	10	4
13	Bixafen	4	3	3	2	6	14	13	5
14	Boscalid	1	5	1	1	11	13	11	7
15	Bromopropylate	2	5	2	2	10	10	13	5
16	Bupirimate	14	4	1	1	8	8	10	4
17	Buprofezin	12	-	18	8	19	-	9	16
18	Butralin	16	5	2	2	12	4	1	2
19	Butylate	1	6	2	1	8	8	11	2
20	Cadusafos	1	6	2	3	9	10	12	3
21	Carbophenothion	7	4	4	1	16	16	17	7
22	Carbosulfan	-	-	8	2	-	-	9	5
23	Chinomethionat	3	5	3	1	9	16	9	6
24	Chlorbromuron	10	7	1	3	3	10	2	3
25	Chlorfenapyr	-	-	17	3	-	-	3	5
26	Chlorfenvinphos	8	4	2	2	10	8	14	1
27	Chlorobenzilate	3	7	2	1	7	9	4	4
28	Chlorpropham	4	4	2	1	8	4	12	1
29	Chlorpyrifos	9	8	3	3	13	15	14	3
30	Chlorpyrifos-methyl	6	7	1	1	12	11	15	2
31	Chlorothalonil	10	5	10	2	3	18	2	11
32	Chlozolinate	9	8	1	1	5	15	10	2
33	Cyfluthrin	1	9	1	2	9	17	11	5
34	Cypermethrin	-	5	1	3	-	9	9	6
35	Chlorthal-dimethyl	7	5	2	1	18	7	14	3
36	Cyproconazole	6	9	2	4	5	10	10	3
37	Cyprodinil	8	6	4	1	11	7	16	2
38	Deltamethrin	6	4	3	1	8	13	9	6
39	Diazinon	8	-	5	1	18	-	12	1
40	Dichlorvos	2	9	2	2	8	13	14	4
41	Diclobutrazol	2	5	4	2	15	9	12	1
42	Dicloran	6	9	4	3	13	9	17	2
43	Dimethenamid	4	4	1	2	10	10	12	3
44	Diphenylamine	3	10	1	2	9	15	13	3
45	Endosulfan alpha	-	-	8	3	-	-	4	4
46	Endosulfan beta	-	-	2	6	-	-	13	1
47	Endosulfan sulfate	-	-	7	1	-	-	10	6
48	EPN	9	10	2	2	14	14	11	5
49	Epoxiconazole	1	7	2	1	14	8	14	1

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50	Ethion	4	5	3	3	13	9	12	4
51	Ethofenprox	3	10	1	1	6	15	10	7
52	Ethofumesate	2	8	2	4	6	13	11	1
53	Ethoprophos	3	7	1	1	9	10	14	2
54	Etrimfos	5	7	2	1	9	11	10	2
55	Fenvalerate/Esfenvalerate RR/SS	2	9	2	1	11	17	7	6
56	Fenvalerate/Esfenvalerate RS/SR	5	9	1	1	14	20	6	8
57	Fenamidone	7	9	3	1	12	19	13	14
58	Fenarimol	8	8	6	2	13	13	11	5
59	Fenazaquin	5	4	1	2	4	9	10	3
60	Fenbuconazole	1	6	1	1	7	9	11	4
61	Fenchlorphos	2	7	1	3	13	12	16	3
62	Fenhexamid	2	11	3	3	7	18	10	16
63	Fenitrothion	4	8	1	3	9	14	18	3
64	Fenpropathrin	9	10	6	1	3	14	12	5
65	Fenpropimorph	3	7	1	2	16	20	18	19
66	Fenthion	4	10	1	4	15	18	19	16
67	Flamprop-isopropyl	3	6	3	2	7	8	9	2
68	Flamprop-methyl	9	6	2	2	12	9	11	3
69	Flonicamid	2	7	2	1	8	11	16	3
70	Fluacrypyrim	-	9	2	1	-	17	12	5
71	Fluazifop-P-butyl	1	8	2	1	7	16	11	5
72	Flucythrinate	4	11	3	3	8	15	12	4
73	Fludioxonil	10	-	5	1	14	-	18	3
74	Fluquinconazole	0	8	2	2	10	14	16	6
75	Flusilazole	8	11	2	3	10	12	13	3
76	Flutolanil	4	9	2	2	4	14	9	3
77	Flutriafol	-	8	1	2	-	9	15	4
78	Fluvalinate-tau	3	3	1	1	12	13	16	6
79	Fonofos	3	7	1	3	8	15	12	6
80	Formothion	10	-	6	2	19	-	17	6
81	Fosthiazate	4	12	5	1	8	16	8	4
82	Heptachlor	10	-	3	2	19	-	15	3
83	Heptenophos	1	9	1	2	9	12	15	3
84	Hexaconazole	19	13	10	3	11	17	16	4
85	Indoxacarb	2	3	4	1	15	18	5	6
86	Iprodione	4	10	1	4	17	13	18	6
87	Iprovalicarb	15	12	5	4	12	9	13	1
88	Isazofos	9	4	5	2	9	4	11	1
89	Isocarbophos	4	7	2	2	6	18	8	10
90	Isofenphos-ethyl	6	9	1	3	10	15	15	7
91	Isofenphos-methyl	3	12	1	3	6	17	11	6
92	Kresoxim-methyl	9	5	2	1	9	9	9	2
93	Lambda-cyhalothrin	5	9	2	3	7	15	12	4
94	Lindane	3	5	4	1	6	10	13	4
95	Malathion	5	7	2	1	7	14	16	3
96	Mecarbam	-	-	6	3	-	-	6	2
97	Merphos	4	6	2	1	3	11	9	2
98	Metalaxyl	8	8	3	2	17	9	11	3
99	Methamidophos	1	-	5	3	15	-	13	4
100	Metazachlor	4	6	2	2	10	8	13	2
101	Metconazole	1	8	3	5	7	15	14	5
102	Methidathion	7	6	3	2	7	19	13	7
103	Methiocarb	7	7	2	4	20	15	9	8
104	Metolachlor	4	5	1	1	10	7	12	1
105	Methoxychlor	7	10	2	2	12	18	17	12
106	Mevinphos	5	7	1	2	8	12	9	4
107	Myclobutanyl	6	7	2	2	13	13	10	3
108	Napropamide	4	10	4	2	11	11	11	3

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109	Nuarimol	9	9	1	2	8	9	12	4
110	o-Phenylphenol	5	7	2	1	17	17	7	8
111	Ofurace	9	5	3	2	11	6	15	3
112	Oxadixyl	6	7	3	3	8	9	11	4
113	Paclobutrazol	2	-	1	5	3	-	8	7
114	Parathion-ethyl	13	-	5	1	9	-	18	6
115	Parathion-methyl	7	6	2	1	17	9	1	4
116	Pebulate	1	4	2	1	8	5	13	1
117	Penconazole	2	8	4	2	11	9	14	3
118	Pendimethalin	10	9	4	5	18	4	18	1
119	Permethrin	1	11	1	2	4	16	7	5
120	Phenothrin	7	8	3	3	16	16	13	4
121	Phenthoate	4	4	4	1	9	11	9	2
122	Phorate	6	-	5	12	19	-	16	6
123	Phosmet	3	11	2	4	15	15	20	6
124	Picolinafen	5	10	4	2	11	18	12	5
125	Picoxystrobin	9	8	2	2	10	10	12	5
126	Pyrimethanil	13	7	4	1	18	12	2	2
127	Pirimicarb	6	8	1	1	12	14	14	3
128	Pirimiphos-methyl	5	8	3	2	4	12	11	3
129	Procymidone	8	7	3	1	8	8	12	4
130	Profenofos	15	7	2	1	10	15	15	4
131	Prometon	3	7	4	2	12	9	15	2
132	Prometryn	2	8	6	2	8	10	15	1
133	Propaphos	2	17	1	4	10	20	13	14
134	Propazine	3	7	3	1	8	7	13	1
135	Propiconazole	3	5	5	1	16	8	6	3
136	Propyzamide	6	8	3	3	13	15	15	5
137	Prosulfocarb	4	8	1	3	9	14	8	3
138	Prothiofos	7	6	3	1	16	5	14	1
139	Pyrazophos	4	10	5	4	8	14	11	7
140	Pyridaben	7	8	2	1	14	16	10	6
141	Pyriproxyfen	1	7	4	2	6	13	11	5
142	Quinalphos	-	11	3	4	-	18	12	4
143	Quinoxyfen	6	7	1	1	5	11	11	4
144	Quintozene	8	-	6	2	11	-	3	2
145	Spirodiclofen	8	5	4	1	9	7	12	1
146	Spiroxamine I	-	16	4	10	-	25	19	21
147	Spiroxamine II	-	7	2	3	-	19	7	19
148	Sulprofos	4	13	1	4	9	17	14	9
149	Tebuconazole	3	6	1	3	7	8	14	4
150	Tebufenpyrad	8	11	3	3	8	15	10	4
151	Tecnazene	5	7	2	2	18	6	17	2
152	Tefluthrin	3	8	3	2	7	10	12	2
153	Terbufos	5	11	3	6	17	15	8	9
154	Terbumeton	1	8	3	2	9	10	14	2
155	Terbutryn	4	10	2	2	9	14	10	3
156	Tetrachlorvinphos	6	12	5	4	17	16	13	7
157	Tetraconazole	5	9	6	1	20	11	16	2
158	Tetradifon	7	7	4	1	7	9	11	4
159	Tetramethrin	1	10	1	4	5	13	10	5
160	Tolclofos-methyl	5	7	3	2	10	7	15	2
161	Tolyfluanid	4	5	4	1	9	8	10	4
162	Triadimefon	2	9	2	4	7	11	12	1
163	Triazophos	2	4	2	1	7	8	10	3
164	Trifloxystrobin	4	4	2	1	7	5	8	1
165	Trifluralin	1	4	2	1	18	6	19	2
166	Vinclozolin	10	7	1	2	9	8	11	3