



HAL
open science

Assessment of Pesticide Residues in Fresh Peach Samples Produced Under Integrated Crop Management in a Greek Agricultural Region on the North Greece

Ioannis V Zioris, Dimitra G Lambropoulou, Theoharis George Danis, Dimitra T. Karagiozogloy, Dr. Triantafyllos Albanis

► **To cite this version:**

Ioannis V Zioris, Dimitra G Lambropoulou, Theoharis George Danis, Dimitra T. Karagiozogloy, Dr. Triantafyllos Albanis. Assessment of Pesticide Residues in Fresh Peach Samples Produced Under Integrated Crop Management in a Greek Agricultural Region on the North Greece. Food Additives and Contaminants, 2009, 26 (09), pp.1256-1264. 10.1080/02652030903045122 . hal-00573872

HAL Id: hal-00573872

<https://hal.science/hal-00573872>

Submitted on 5 Mar 2011

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Assessment of Pesticide Residues in Fresh Peach Samples Produced Under Integrated Crop Management in a Greek Agricultural Region on the North Greece

Journal:	<i>Food Additives and Contaminants</i>
Manuscript ID:	TFAC-2008-322.R1
Manuscript Type:	Original Research Paper
Date Submitted by the Author:	13-May-2009
Complete List of Authors:	Zioris, Ioannis; University of Ioannina, Chemistry Lambropoulou, Dimitra; University of Ioannina, Chemistry Danis, Theoharis; DELCOF SA Karagiozoglou, Dimitra; DELCOF SA Albanis, Dr. Triantafyllos; University of Ioannina, Chemistry
Methods/Techniques:	Chromatography - GC/MS, Extraction, Risk assessment
Additives/Contaminants:	Pesticide residues
Food Types:	Fruit

SCHOLARONE™
Manuscripts

1
2
3
4 1 **Assessment of Pesticide Residues in Fresh Peach Samples Produced**
5
6 2 **Under Integrated Crop Management in a Greek Agricultural Region**
7
8
9 3 **on the North Greece**
10
11
12 4

13
14 5 IOANNIS V. ZIORIS¹, DIMITRA G. LAMBROPOULOU², THEOXARIS G.
15
16 6 DANIS², DESPOINA T. KARAGIOZOGLOU², and TRIANTAFYLLOS A.
17
18 7 ALBANIS^{1*}
19
20
21 8

22
23 9 ¹ *Department of Chemistry, University of Ioannina, Ioannina 45110, Greece*
24

25
26 10 ² *Department of Chemistry, Aristotle University of Thessaloniki, 54124 Thessaloniki,*
27
28 11 *Greece*
29

30
31 12 ³ *DELCOF S.A., Kopanos, Athemia 55903, Greece*
32
33
34 13

35
36 14 *Correspondence author: TRIANTAFYLLOS A. ALBANIS. E-mail: talbanis@uoi.gr
37
38 15
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3 16 **Abstract**
4

5 17 A multi-residue method using selected ion monitoring mode GC/MS has been
6
7 18 developed for the quantitative analysis of 23 widely used pesticides in fresh peaches
8
9
10 19 produced under integrated crop management process (ICM) in order to assess their
11
12 20 residue levels. The proposed methodology involved a sample extraction procedure
13
14
15 21 using liquid-liquid partition with acetonitrile followed by a clean-up step based on
16
17 22 solid-phase extraction (SPE). Fortification studies were performed at different
18
19 23 concentration levels for various types of peaches that differ in properties such as
20
21 24 appearance, flavor and pit. The data showed that the different peach matrixes had no
22
23 25 significant effect on the recoveries. The recoveries were greater than 80% for most of
24
25 26 the pesticides with a RSD below 18%. The limits of quantification (LOQs) were in
26
27 27 the range 0.002 - 0.050 mg kg⁻¹, depending on the compound. The proposed method
28
29 28 was successfully applied to the analysis of 104 fruit samples collected under
30
31 29 Integrated Pest Management (IPM) production during the 2006 cultivation period, in
32
33 30 order to assess the performance of the method with real samples and to determine
34
35 31 whether the concentration of pesticides in peaches exceed their maximum residue
36
37 32 levels (MRLs). Residues detected were lower than those established by legislation for
38
39 33 all pesticides, except diazinon, where one positive sample was detected containing
40
41 34 0.03 mg kg⁻¹.
42
43
44
45
46
47
48
49
50

51 36 **Keywords:** Peaches; analysis; pesticides; gas chromatography-mass spectrometry
52
53 37 (GC-MS); integrated crop management (ICM).
54
55
56
57
58
59
60

38 Introduction

39 Pesticides are widely used at various stages of cultivation and during post-
40 harvest storage to protect fruit and vegetables against a range of pests and fungi and
41 provide quality preservation. They play a beneficial role in agriculture, because they
42 help to combat a variety of pests that destroy crops, even though small amounts of
43 pesticide residues remain in the food supply, constituting a potential risk for the
44 human health, because of their sub-acute and chronic toxicity (European Union 2007;
45 http://europa.eu.int/comm/food/index_en.htm).

46 Farmers and growers are trying to reduce the amounts of conventional
47 chemical pesticides used, in response to demands from retailers. There is a
48 requirement, therefore, to develop environmentally sustainable systems for controlling
49 pests that are less reliant on chemical pesticides as the primary management tool. For
50 most farmers, in order to maintain profitability, this must be done without sacrificing
51 crop quality and productivity. The best way is through Integrated Pest Management
52 (IPM) and Integrated Crop Management (ICM), which combine a range of
53 complementary methods to reduce a pest population below its economic injury level
54 whilst minimizing the impact on other components of the agro-ecosystem, thus taking
55 into account the needs of producers, wider society and the environment (Kogan, 1998;
56 Smith and Reynolds 1965)

57 There is extensive literature that describes procedures for pesticide analysis in
58 food matrices (Rawn et al. 2007; Česnik et al. 2006; Lambropoulou and Albanis.
59 2002; Lambropoulou and Albanis. 2003; Lambropoulou and Albanis. 2007; Cajka et
60 al. 2008; Soler et al. 2004; Chu et al. 2005; Anastassiades et al. 2003; Kristenson .
61 2006). However, studies focused on pesticides residues on fruits that were produced
62 under ICM have not been well described (Nguyen et al. 2008; Baker et al. 2002). It

1
2
3 63 would therefore be desirable to check the effectiveness of ICM fruit production with
4
5 64 measurements in the field where ICM is applied, as a research study to help improve
6
7
8 65 regulatory approaches and protect consumers from unsafe levels.
9

10 66 Laboratories routinely monitor fruit and vegetables for pesticide residues to
11
12 67 check for compliance with statutory maximum residue limits (MRLs) and to provide
13
14
15 68 the results for consumer exposure assessment (Fussell et al. 2007). In this respect,
16
17
18 69 the present study aimed to assess the suitability of a multi-residue method as a
19
20 70 research tool for measuring low levels of pesticide on peach fruits collected in a big
21
22 71 Greek agricultural area (Imathia). Cultivation of peaches is one of the most important
23
24 72 arboriculture cultivations in Greece. The region of Imathia in Macedonia, Northern
25
26
27 73 Greece, produce the majority of the total peach crop, i.e. 600.000 tons/year of the
28
29 74 1.108 million tons/year harvested in Greece. The largest amounts of them are used by
30
31
32 75 the canning industry. Moreover, from the 7741 hectares (ha) on which the ICM is
33
34 76 applied in Greece, the 6068 ha are peach cultivation of which 3430 ha are in the
35
36 77 region of Imathia. Since the last decade, all production is under IPM with the aim to
37
38 78 minimize the use of active substances and improve the use of necessary chemicals in
39
40 79 order to keep pesticides residues inside Maximum Residue Limits (MRL). This paper
41
42 80 reports the results of the monitoring survey that was carried out for a cultivation
43
44 81 period of one year (2006) in order to evaluate the peaches quality that were produced
45
46 82 under ICM. The multi-residue method used for the quantitative determination of
47
48 83 pesticides involves a simple two-step (liquid-liquid extraction with acetonitrile
49
50
51 84 followed by cleanup using solid-phase extraction (SPE)) sample preparation method
52
53 85 followed by GC/MS detection.
54
55
56
57
58
59

60

87 **Material and methods**

1
2
3 88 *Pesticide mixture*
4

5
6 89 In ICM conventional cultivation, the only crop protection products used were those
7
8 90 allowed for the specific cultivation by the Greek Ministry of Agriculture. Presently,
9
10 91 14 acaricides, 65 insecticides, 9 herbicides and 43 fungicides (total of 131 pesticides)
11
12 92 are registered in Greece (Gianopolitis 2006). The reported number of crop protection
13
14 93 products, i.e. 131, represents the total number of pesticide formulations that might
15
16 94 contain the same active ingredient. In terms of the active ingredients, the 23 chemicals
17
18 95 selected for testing represent all the residues likely to be present in peaches (Tsakiris
19
20 96 et al. 2004).
21
22
23

24
25 97 Monitoring was performed for the following most frequently used categories
26
27 98 of crop protection products:

- 28
29 99 • Insecticides: Methamidophos, Dimethoate, Chlorpyrifos-methyl, Parathion-
30
31 100 methyl, Malathion, Chlorpyrifos, Fenthion, Ethion, Phosalone, Diazinon,
32
33 101 Methidathion, Bifethrin, Phosmet, Indoxacarb, Deltamethrin.
34
35 102 • Fungicides: Chlorothalonil, Captan, Penconazole, Myclobutanil, Tebuconazole.
36
37 103 • Acaricides: Dicofol. Propargite, Amitraz.
38
39
40

41 104 All classes are of interest because of their extensive use or potential adverse
42
43 105 health effects.
44

45
46 106 *Fresh Peaches Sampling.*
47

48
49 107 Fresh peaches were collected from four selected fields at the banks of Aliakmonas
50
51 108 River in Imathia region, during the cultivation period of 2006 and were of various
52
53 109 species. 104 samples were collected all under IPM production. All fruits had reached
54
55 110 their final size. Samples were collected as indicated in Directive 79/700/EEC
56
57 111 (Commission Directive 79/700/EEC 1979), which stipulates the European Union
58
59 112 methods of sampling for the official control of pesticide residues in and on products
60

1
2
3 113 of plant and animal origin. The four selective fields monitored for pesticides residues
4
5 114 were a) SS1 – Agia Varvara, b) SS2 – Meliki c) SS3 – Alexandria and d) SS4 – Plati.
6
7
8
9

10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

115
116 *Reagents.*

117 Chlorothalonil, Dicofol, Chlorpyrifos-methyl, Phosmet, Tebuconazole,
118 Penconazole, Myclobutanil, Propargite, Amitraz, Diazinon, Deltamethrin, Indoxacarb,
119 Bifethrin, Methidathion and Captan were supplied by Riedel de Haen (Seelze,
120 Germany), Malathion, Dimethoate, Phosalone, Fenthion, Methamidophos,
121 Chlorpyrifos, Parathion-methyl and Ethion were from Riedel de Haen (Seelze,
122 Germany) and PSC-Poly Science Corporation (Niles, Illinois, USA). All standards
123 were used without further purification and were storage at -20°C . Sodium chloride,
124 sodium sulphate and solvents (acetonitrile, toluene and acetone) of pesticide
125 analytical grade were bought from Riedel de Häen. Solid-Phase Extraction cartridges
126 ENVI-18 and ENVITM-Carb were from Supelco (Bellefonte, CA, USA).

127 A separate stock solution for each active ingredient was prepared in acetone at
128 a concentration of $100\ \mu\text{g ml}^{-1}$ and stored at 0°C . New diluted solutions containing the
129 selected pesticides were prepared from the initial stock solutions and used for the
130 fortification process.

131 *Extraction procedures.*

132 Samples of fruits were processed as received in their raw, unwashed and unpeeled
133 form. The samples were cut and blended at medium speed for 4 min. From 3 kg of
134 fresh peaches sample, a 25 g portion was homogenized with 50 ml acetonitrile by
135 mechanical shaker for 5 min. After addition of 5 g sodium chloride, the sample was
136 rehomogenized for 10 min. An aliquot of the supernatant acetonitrile layer of 13 ml
137 was concentrated through a pre-conditioned (5 ml acetonitrile) ENVI-18 SPE tube to

1
2
3 138 a test tube. After dehydration (with sodium sulfate) and concentration (under a gentle
4
5
6 139 nitrogen stream at a constant 37°C), the sample was transferred to a pre-conditioned
7
8 140 (5 ml acetonitrile: toluene, 3:1) ENVI-Carb SPE tube and eluted with a 10-ml mixture
9
10
11 141 of acetonitrile: toluene (3:1). The sample was evaporated almost to dryness and
12
13 142 reconstituted with 0.5 ml acetonitrile, which was analyzed by GC.

14
15 143 *GC-MS analysis.*

16
17
18 144 A Shimadzu (Kyoto, Japan) QP 5050A GC-MS was used with an MDN-5S fused
19
20 145 silica capillary column 30m x 0.32mmi.d. (Supelco). Helium was used as the carrier
21
22 146 gas at 87.5 kPa and 1.5 ml min⁻¹ flow rate. The injection temperature was 220 °C. The
23
24
25 147 column was programmed from 50 to 160 °C (10 min) at 5 °C min⁻¹ (first step) and
26
27 148 from 160 to 250°C (20 min) at 15°C min⁻¹ (final step). The interface was programmed
28
29 149 at 250°C. Electron ionization was used with a detector voltage of 1.2 kV, mass range
30
31
32 150 from 45 to 400 m/z, and scan speed of 1000 amu s⁻¹. The MS system was routinely
33
34 151 programmed in SIM using one target and two qualifier ions, as indicated in Table 1.
35
36 152 Groupings were defined to increase the sensitivity of the MS analysis. The injection
37
38
39 153 volume was 1 µL for all standards and samples.

40
41 154 *Quality control.*

42
43
44 155 Identification and confirmation of the target compounds was based on the quality
45
46 156 control procedures established by the EU (Soler et al. 2004). Thus, identifications of
47
48 157 pesticides in peach samples were made by comparing the retention time, identifying
49
50
51 158 the target and qualifier ions, and determining the qualifier-to-target ratios of the peak
52
53 159 in the peaches with that of a pesticide standard. Acceptance criteria for positive
54
55 160 identification consisted of retention times within (0.50 min of the expected) value and
56
57
58 161 % qualifier-to-target ratios within 20% of the standard (0.1 mg L⁻¹) for qualifier-to-
59
60 162 target abundance percentages greater than 50%. For less than 50%, the criterion for

1
2
3
4 163 the qualifier-to-target ratios was set at 30% of the calibration standard. Fruit blanks
5
6 164 and spikes were analyzed to account for any residual carry over or possible
7
8 165 contamination sources such as the glassware. The identification of pesticide residues
9
10 166 in the blanks resulted in repeating the extraction and analysis of the entire batch.

11
12
13 167 *Quantification of peach extracts.*

14
15 168 In order to avoid quantitative errors, matrix-matched standards were used in this
16
17 169 study. The homogenized samples were subsequently used as blanks and in the
18
19 170 preparation of matrix-matched standards for calibration. Matrix-matched calibration
20
21 171 standards were prepared by adding known quantities of standard mixture solutions to
22
23 172 the corresponding blank sample extracts. Matrix-matched standards at concentration
24
25 173 levels ranging from 0.25 to 10 $\mu\text{g ml}^{-1}$ were prepared by dilution of mixture-standard
26
27 174 solutions in peach final extracts prepared from unfortified samples. The internal
28
29 175 standard was added to all calibration standard solutions. Two types of peaches
30
31 176 (freestones and clingstones) and nectarines were chosen for recovery and
32
33 177 reproducibility studies. Fresh clingstone peaches were collected from a field near the
34
35 178 town of city of Veria in the middle of the harvesting period (29 August 2006). The
36
37 179 mean recoveries of selected pesticides, three replications per level and RSDr are
38
39 180 presented in Table 2.

40
41
42
43
44
45 181 *Spiking procedure.*

46
47 182 For spiking studies, a measured 25 g test portion of peach sample with no pesticides
48
49 183 detected previously was spiked with appropriate standard solutions to a final
50
51 184 concentration of 0.05, 0.10 and 0.50 mg kg^{-1} , and the Teflon centrifuge tube was
52
53 185 vigorously vortexed to distribute the pesticide residues. The same procedure described
54
55 186 in *extraction procedures* was applied to the spiked samples.

56
57
58
59
60 187

1
2
3 188 **Results and discussion**
4

5
6 189 *Analytical Performance Characteristics.*
7

8 190 The analytical performance of the proposed method was studied in order to evaluate
9
10 191 its usefulness for quantitative analyses in the studied matrices. The accuracy (as
11
12 192 recovery), linearity, precision [as repeatability (RSD_r) and reproducibility (RSD_R)],
13
14 193 matrix effect, limits of detection (LODs) and limits of quantifications (LOQs) were
15
16 194 established to validate the procedure.
17

18
19
20 195 *Linearity.*
21

22 196 Linearity was established by performing calibration sets at concentrations of 0.25, 0.5,
23
24 197 0.75, 1.0, 2.5, 5 and 10 µg ml⁻¹ (corresponding to 0.25 –10 ng on-column and 0.005–
25
26 198 0.5 mg kg⁻¹ in the sample), both in solvent and in matrix. To exclude memory effects,
27
28 199 the first series of data, obtained starting from a lower concentration, was compared
29
30 200 with the second, obtained starting from a higher concentration, for a total of four
31
32 201 replications for each point. The calibration curves were constructed by applying the
33
34 202 least-squares method and using the equation $y = mx + q$ as the regression model.
35
36
37

38
39 203 For solvent standards the regression coefficients for all 23 target compounds
40
41 204 were above 0.9900. In the presence of peach matrix, excellent linearity was still
42
43 205 obtained for the majority of the target compounds except for captan, methamidophos
44
45 206 and indoxocarb the correlation coefficients of which were below 0.990. From these
46
47 207 results it can be concluded that the GC-MS system is suitable for quantitative
48
49 208 measurement of the target pesticides in peach matrices.
50

51
52
53 209 *Precision of Method.*
54

55 210 The overall method accuracy and precision was conducted following the EU criteria
56
57 211 for validation of pesticide residue methods (SANCO/10476/2003 2003;
58
59 212 SANCO/3131/2007 2007) by analyzing fortified clingstone peach samples at three
60

1
2
3 213 levels (50, 100 and 500 $\mu\text{g kg}^{-1}$). At each level, the analysis was performed with six
4
5 214 replicates. The same protocol was applied for performance data under intermediate
6
7 215 reproducibility conditions but analyses (i.e., six blank peaches spiked at each of the
8
9 216 two fortification levels) were conducted by two analysts over a 1-month period. Table
10
11 217 2 summarizes these data. The results of intraday precision are showed in Table 2 near
12
13 218 recovery data, while those of inter-day variability, for the three peach matrices spiked
14
15 219 at 100 $\mu\text{g kg}^{-1}$, are listed in Table 1. Within- and between-day, as well as within-
16
17 220 laboratory, precisions were below 18%. Precisions at fortification level at 500 $\mu\text{g kg}^{-1}$
18
19 221 were better and below 12%.

222 *Matrix Effects.*

223 In food analysis by mass spectrometry, signal suppressions may occur during the
224 ionization process of the extracts due to the composition (salts, proteins, lipids,
225 carbohydrates etc) of the matrix under survey. This matrix effect can be minimized by
226 an efficient cleanup of the extract, but usually cannot be totally avoided. In a recent
227 comprehensive review (Hajšlova and Zrostlíková 2003) the nature of various types of
228 matrix effects was discussed together with suggestions for prevention, reduction
229 and/or compensation of their occurrence when determining troublesome analytes in
230 food matrices. In this context, for all the pesticides considered here, including
231 bromophos ethyl candidate for use as internal standard, we conducted a study aimed
232 at assessing variations of the matrix effect (if present).

233 For this purpose, we checked the matrix effects of different peaches on the
234 analysis of the tested pesticides by constructing matrix-matched calibration curves
235 and comparing their slope with those of calibration curves constructed in solvent.
236 Table 2 summarizes these data and shows that in GC/MS, the matrix seemed to be
237 slightly dependent of the particular peach extract analyzed for most of the target

1
2
3 238 analytes. However, in the case of captan, deltamethrin and bifethrin and
4
5 239 organophosphorous pesticides (chlorpyrifos and parathion methyl) the matrix
6
7
8 240 produced either suppression or enhancement with fluctuations of up to about $\pm 30\%$
9
10 241 depending also on both the matrix and each individual species. For this reason, the
11
12 242 calibration was carried out using matrix matched standards, in order to improve the
13
14
15 243 accuracy of the analysis of these compounds.

16
17
18 244 *Recovery Test.*

19
20 245 To evaluate the effectiveness of the extraction method, different recovery studies were
21
22 246 performed by spiking peach matrices at three spike levels, that is, 50, 100 and 500 μg
23
24 247 kg^{-1} . At each concentration, six measurements were performed. Two different types of
25
26
27 248 peaches (freestone and clingstone) and nectarines were also selected for pesticide
28
29 249 fortification studies based on their different properties. The purpose of choosing the
30
31 250 three different peach matrices for the pesticide fortification studies was to determine
32
33 251 whether the proposed multi-residue method is applicable to different peach matrices
34
35 252 regardless of their properties.

36
37
38
39 253 Freestone types of peaches were chosen for this study because it is
40
41 254 representative of a standard peach found commonly in Greek markets. Clingstone
42
43 255 type peach was chosen for the study based on its similarity to freestone ones in terms
44
45
46 256 of flavor, and appearance but it is different because of the tightest flesh to the pit.
47
48 257 Freestone types are usually preferred for eating fresh or for freezing, while clingstone
49
50 258 types are used primarily for canning. The nectarines differ from the other two types of
51
52 259 peaches due to its lack of fuzz on the skin.

53
54
55 260 Data are reported in Table 2 which show the 23 pesticides were recovered in
56
57 261 the range of 64-104% with 2-18% of relative standard deviation (RSD) at all spiking
58
59 262 levels. Thus, for all pesticides (except for captan and bifethrin), average recoveries
60

1
2
3 263 were in line with criteria that sets acceptable mean recovery to be between 70 and
4
5 264 120% with $RSD \leq 20\%$ (SANCO/10476/2003 2003; SANCO/3131/2007 2007)
6
7

8 265 In this study captan, showed low recoveries (<70%) in peach samples, which
9
10 266 was probably related to the sample matrix, which somehow did not fit well with the
11
12 267 chosen solvent. In addition lower recoveries are mostly linked to pesticides that may
13
14 268 not be stable or decompose during sample preparation, and GC injection. Captan is a
15
16 269 well-known problematic pesticide in multi-residue analyses being difficult to
17
18 270 determine using existing methods and recoveries lower than 70% have been also
19
20 271 reported in other studies ((Lehotay et al., 2005, Pihlström et al., 2007, Hercegová et
21
22 272 al., 2007). This example illustrates the difficulties to develop a unique procedure
23
24 273 for the extraction of a wide range of pesticides with different physical properties (i.e.:
25
26 274 polarity and/or solubility). Although the recoveries of this compound were less than
27
28 275 the guideline value, it is worth to say that they were nevertheless consistent as
29
30 276 observed from their standard deviations at any of the fortification levels (Table 2).
31
32
33
34
35

36 277 There was no significant difference in recoveries among sample types or
37
38 278 spiking levels. Average recoveries of 23 pesticides in 18 samples were around 90%.
39
40 279 Most chromatograms were clear enough to identify and determine each pesticide with
41
42 280 primary ion detection. These results demonstrate the feasibility of the studied
43
44 281 extraction method.
45
46
47

48 282 The similarity in recoveries obtained for a given pesticide in the three peach
49
50 283 matrices indicates that different fruit characteristics likely to be encountered in real
51
52 284 samples would have little impact on method performance and is indicative of the
53
54 285 robustness of this method.
55
56

57 286 *LODs and LOQs.*
58
59
60

1
2
3 287 When a MS detector is used, the first condition to be satisfied for ascertaining the
4
5 288 presence of a target compound is that the precursor ion and at least two product ions
6
7
8 289 produce signals distinguishable from the background ion current. Accordingly, a
9
10 290 definition of LOD (S/N 3) of each analyte was adopted, considering in each case the
11
12 291 ion giving the worst S/N. When more than three ions were selected for analyte
13
14 292 identification (see Table 1), LODs were estimated by selecting signals for the parent
15
16 293 ion and, among fragment ions, the two giving the best S/N. The background noise
17
18 294 estimate was based on the peak-to-peak baseline near the analyte peak. The noise
19
20 295 level depends on the matrix; therefore, there are different LODs for different samples.
21
22 296 In reference to this, LODs were estimated from the SIM chromatogram referring to
23
24 297 the analysis of $50 \mu\text{g kg}^{-1}$ of each analyte in peach, of several peach matrices. LOQs,
25
26 298 according to the EU guidelines were defined as lowest concentration that provided
27
28 299 acceptable recoveries and RSDs (<19%) (Anastassiades et al. 2003). The LOQs of
29
30 300 this method are well below the MRLs set by the EU and FDA for residues of
31
32 301 pesticides in food matrices.
33
34
35
36
37

38
39 302 *Specificity.*

40
41 303 Six repetitive analyses showed excellent similarities with reference to the retention
42
43 304 time for all pesticides (between 95% and 100%). Additionally, the similarity of ethyl
44
45 305 bromophos as the internal standard was over 99%, indicating that the analytical
46
47 306 procedure and the chromatographic column yielded consistent and specific results.
48
49

50
51 307 *Monitoring studies.*

52
53 308 The proposed procedure was applied to the analysis of 104 peach samples taken from
54
55 309 different local farmers who performed the ICM up to 3 years. Internal quality control
56
57 310 was applied in every batch of samples in order to check if the system is under control.
58
59 311 This quality control implies a matrix-matched calibration, a reagent blank, a matrix
60

1
2
3 312 blank and a spiked blank sample at $100 \mu\text{g L}^{-1}$ in order to evaluate stability of the
4
5
6 313 proposed method with time.
7

8 314 With each batch of 10 samples, a five-point calibration curve was prepared for
9
10 315 analytes concentrations between the LOQs and 10 LOQs by injections before and
11
12 316 after those of the sample extracts. In addition, 2 quality control (QC) samples were
13
14
15 317 injected in every batch of samples. The QC samples were blank peach sample
16
17 318 fortified at LOQ level and 10 times the LOQ level. All the samples were injected in
18
19 319 duplicate.
20
21

22 320 The total results from the peach samples analyzed are summarized in Table 3.
23
24 321 Statistical analysis of the quantified residual levels of the detected crop protection
25
26 322 products in peach samples from IPM system the number of detected samples, their
27
28 323 average concentration and finally the European Maximum Residues Limits are
29
30 324 presented in Table 4.
31
32

33 325 Among the 23 pesticides included in the present monitoring study only 10 of
34
35 326 them were finally detected in the peach samples. The detected pesticides were
36
37 327 chlorpyrifos, tebuconazole, chlorothalonil, phosmet, captan, malathion, diazinon,
38
39 328 bifethrin, propargite and indoxacarb, which are the most widespread-used pesticides
40
41 329 in the peaches crops in the Imathia region (Fytianos et al. 2006; Tsakiris et al. 2004).
42
43 330 The results showed an occurrence of these pesticides in a range of 1% to 46%
44
45 331 depending on the compound and the sampling station.
46
47
48
49

50 332 Chlorpyrifos (O,O-diethyl O-3,5,6-trichloro-2-pyridyl phosphorothioate) was
51
52 333 the crop protection product most frequently detected in samples collected ICM
53
54 334 cultivation systems with an occurrence up to 44.2 % (Figure 1) of the total number of
55
56 335 samples (46 positive samples). The concentrations varied between 0.025 to 0.050 mg
57
58 336 kg^{-1} (Table 3), depending on the sampling station. These findings are in agreement
59
60

1
2
3 337 with other published data showing that this insecticide is one of the most frequently
4
5 338 detected pesticides in fruit samples (Tsakiris et al. 2004; Fernandez et al. 2001;
6
7
8 339 Montemurro et al. 2002). It is worth saying that, statistically significant higher levels
9
10 340 of chlorpyrifos residues in peach samples from early varieties were observed
11
12 341 compared with the samples of late varieties. From this result a question arises
13
14
15 342 regarding the fate of this compound in the environment. To the best of our knowledge
16
17 343 the fate of this pesticide under natural environmental conditions is not thoroughly
18
19 344 investigated and thus future work will be needed to study its degradation and
20
21 345 transformation, especially under local climatic condition, for the further
22
23 346 understanding of its persistence in the food commodities.
24
25
26

27 347 Captan was detected in higher concentrations than the other pesticides and in
28
29 348 almost all the sampling places (Figure 1). However, in all cases the concentration was
30
31 349 lower than the MRL levels and ranged between 0.04 and 0.14 mg kg⁻¹. Chlorothalonil
32
33 350 was detected in five different samples and only in three from the four sampling
34
35 351 stations at low concentration levels (mean concentration 0.03 mg kg⁻¹). It is worth
36
37 352 noting that, although diazinon was found and quantified in only five different
38
39 353 samples, it had an average concentration equal or even higher (one sample) to the EU
40
41 354 MRL in all cases. This result clearly indicates that more monitoring studies and proof
42
43 355 is needed to assess if this compound can possess potential risk for the consumers'
44
45 356 health.
46
47
48
49

50 357 The other detected pesticides (tebuconazole, bifethrin, phosmet) had an
51
52 358 occurrence in the peaches that did not exceed 23%. The concentration levels ranged
53
54 359 between 0.01 and 0.06 mg kg⁻¹ depending on the pesticide and the sampling station.
55
56
57 360 Methamidophos was not detected in any samples, thus confirming previous findings
58
59
60

1
2
3 361 in peaches, produced under ICM, that this insecticide is less frequently used in
4
5
6 362 Imathia commodity (Tsakiris et al. 2004).

7
8 363 Although the study on the monitoring of the target analytes in IPM production
9
10 364 was conducted on single samples collected in the harvest period, the study gives
11
12 365 insight into the reductions that may take place under the IPM process. The
13
14
15 366 concentration levels in all the tested peach samples were lower than the MRLs
16
17 367 established for all pesticides, except diazinon, that exceed in one positive sample,
18
19
20 368 reaching the value of 0.03 mg kg^{-1} .

21 22 369 **Conclusions**

23
24 370 A simple two-step sample preparation method based on liquid-liquid extraction with
25
26
27 371 acetonitrile followed by cleanup using SPE has been developed for the determination
28
29 372 of 23 pesticides in peach samples. The proposed methodology combined with mass
30
31 373 spectrometric identification and quantification using GC/MS, gives analytical
32
33 374 performance which could be applied for the monitoring of pesticide residues in such
34
35 375 commodities at low $\mu\text{g kg}^{-1}$. The proposed sample treatment strategy is fast, easy to
36
37 376 perform and could be utilized for regular monitoring of pesticide residues in fruit or
38
39
40
41 377 other kind of food samples.

42
43 378 The usefulness of the proposed approach has been assessed by analyzing
44
45 379 peach samples from ICM cultivation. Screening analyses of peach samples from
46
47 380 different origin from Imathia prefecture (N. Greece), showed the presence of 10 from
48
49
50 381 the 23 pesticides investigated. Data obtained are new since very few studies are
51
52 382 available in the literature regarding the occurrence of pesticide residues in peach
53
54 383 cultivation, produced under ICM processes.

55
56
57 384 Summarizing this work results it is obvious that, ICM in peach cultivation is a
58
59
60 385 powerful tool for peach producers in order to minimize or completely eliminate the

1
2
3 386 pesticides residues in food chain and to the environment. Also, in the frame of ICP
4
5 387 can also evaluate the effectiveness and residues level of the active substances in order
6
7
8 388 to modify their plans for the next year cultivation period.
9

10 389

11
12
13 390 **References**

14
15 391 Anastassiades M, Lehotay SJ, Štajnbaher D, Schenk FJ. 2003. Fast and easy
16
17 392 multiresidue method employing acetonitrile extraction/partitioning and
18
19 393 "dispersive solid-phase extraction" for the determination of pesticide residues in
20
21
22 394 produce. *J AOAC Int*, 86, 412–431

23
24 395 Baker, BP. Benbrook CM., Groth III E, Lutz Benbrook K. 2002. Pesticide residues in
25
26 396 conventional, integrated pest management (IPM)-grown and organic foods:
27
28 397 insights from three US data sets *Food Additives & Contaminants* 19 (5), 427-
29
30 398 446

31
32
33 399 Cajka T, Hajslova J, Lacina O, MastovskaK, Lehotay SJ. 2008. Rapid analysis of
34
35 400 multiple pesticide residues in fruit-based baby food using programmed
36
37 401 temperature vaporiser injection–low-pressure gas chromatography–high-
38
39 402 resolution time-of-flight mass spectrometry. *Journal of Chromatography A*.
40
41 403 1186: 281–294

42
43
44 404 Česnik HB, Gregorčič A., Bolta ŠV, Kmecl V.. 2006. Monitoring of pesticide
45
46 405 residues in apples, lettuce and potato of the Slovene origin, 2001-04. *Food*
47
48 406 *Additives and Contaminants*, 23(2): 164–173

49
50
51 407 Chu XG, Hu XZ, Yao HY. 2005. Determination of 266 pesticide residues in apple
52
53 408 juice by matrix solid-phase dispersion and gas chromatography–mass selective
54
55 409 detection. *Journal of Chromatography A*. 1063: 201–210.
56
57
58
59
60

- 1
2
3 410 Commission Directive 79/700/EEC. 1979. Establishing Community methods of
4
5
6 411 sampling for the official control of pesticide residues in and on fruit and
7
8 412 vegetables.
9
10 413 European Commission Document No. SANCO/10476/2003, 2003. Quality control
11
12 414 procedures for pesticides residue analysis.
13
14 415 European Commission Document No. SANCO/3131/2007. 2007. Method validation
15
16 416 and quality control Procedures for pesticide residues analysis in food and feed.
17
18 417 Brussels.
19
20 418 European Union (EU). 2007. MRLs of pesticides, available at <http://europa.eu.int>,
21
22 419 EU, Brussels, Belgium.
23
24 420 Fussell RJ., Hetmanski MT., Colyer A, Caldow M., Smith F, and Findlay D. 2007
25
26 421 Assessment of the stability of pesticides during the cryogenic processing of
27
28 422 fruits and vegetables. *Food Additives and Contaminants*. 24(11): 1247–1256
29
30 423 Fytianos K, Raikos N, Theodoridis G, Velinova Z, and Tsoukali H 2006. Solid phase
31
32 424 microextraction applied to the analysis of organophosphorus insecticides in
33
34 425 fruits. *Chemosphere*. 65: 2090–2095
35
36 426 Gianopolitis, K., 2006. *Insecticides. Index 2006*. Agrotipos. Athens
37
38 427 Hajšlova J. and Zrostlíková J. 2003. Matrix effects in (ultra)trace analysis of pesticide
39
40 428 residues in food and biotic matrices. *Journal of Chromatography A*. 1000: 181–
41
42 429 197
43
44 430 Hercegová A, Dömötörövá M, Matisová E, Sample preparation methods in the
45
46 431 analysis of pesticide residues in baby food with subsequent chromatographic
47
48 432 determination, Review, 2007. *Journal of Chromatography A*, 1153: 54-73
49
50 433 http://europa.eu.int/comm/food/index_en.htm.
51
52
53
54
55
56
57
58
59
60

- 1
2
3 434 Kogan M. 1998. Integrated Pest Management: Historical perspectives and
4
5 435 contemporary developments. *Annual Review of Entomology*. 43: 243-70.
6
7
8 436 Kristenson EM, Brinkman UATh, Ramos L. 2006. Recent advances in matrix solid-
9
10 437 phase dispersion. *Trends Anal Chem*. 25(2): 96–111
11
12 438 Lambropoulou DA, and Albanis TA. 2002. Headspace Solid Phase Microextraction
13
14 439 applied to the analysis, of organophosphorus insecticides in strawberry and
15
16 440 cherry juices. *J. Agric. Food Chem*. 50: 3359-3365.
17
18
19 441 Lambropoulou DA and Albanis TA. 2003. Headspace Solid-Phase Microextraction in
20
21 442 combination with gas chromatography–mass spectrometry for the rapid
22
23 443 screening of organophosphorus insecticide residues in strawberries and cherries.
24
25 444 *Journal of Chromatography A*. 993: 197–203
26
27
28 445 Lambropoulou DA and Albanis TA. 2007. Methods of sample preparation for
29
30 446 determination of pesticide residues in food matrices by chromatography-mass
31
32 447 spectrometry-based techniques: a review. *Anal Bioanal Chem*. 389(6):1663-83.
33
34
35 448 Lehotay SJ, de Kok A, Hiemstra M, van Bodegraven P, 2005. Validation of a Fast and
36
37 449 Easy Method for the Determination of 229 Pesticide Residues in Fruits and
38
39 450 Vegetables Using Gas and Liquid Chromatography and Mass Spectrometric
40
41 451 Detection, *Journal of AOAC International*, 88: 595-614.
42
43
44 452 Montemurro N, Grieco F, Lacertosa G, and Visconti A. 2002. Chlorpyrifos decline
45
46 453 curves and residue levels from different commercial formulations applied to
47
48 454 oranges *J. Agric. Food Chem*. 50: 5975-5980
49
50
51 455 Nguyen TD, Han EM, Seo MS, Kim SR, Yun MY, Lee DM, Lee GH . 2008. A multi-
52
53 456 residue method for the determination of 203 pesticides in rice paddies using gas
54
55 457 chromatography/mass spectrometry. *Anal. Chim. Acta*. 619 (1) : 67-74.
56
57
58
59
60

- 1
2
3
4 458 Putnam RA, Nelson JO, and Clark JM 2003. The persistence and degradation of
5
6 459 chlorothalonil and chlorpyrifos in a cranberry bog. *J. Agric. Food Chem*, 51:
7
8 460 170-176
9
10 461 Pihlström T, Blomkvist G, Friman P, Pagard U, Österdahl B-G, 2007. Analysis of
11
12 462 pesticide residues in fruit and vegetables with ethyl acetate extraction using gas
13
14 463 and liquid chromatography with tandem mass spectrometric detection
15
16 464 *Analytical and Bioanalytical Chemistry* 389:1773–1789
17
18
19 465 Rawn DFK, Quade SC, Shields JB, Conca G, Sun WF, Gladys Lacroix MA, Smith M,
20
21 466 Fouquet A, Bélanger A. 2007. Variability in captan residues in apples from a
22
23 467 Canadian orchard. *Food Additives and Contaminants*, 24 (2): 149–155
24
25
26 468 Pico FMY., and Manes J. 2001. Pesticides residues in oranges from Valencia (Spain).
27
28 469 *Food Additives and Contaminants*, 7: 615-624.
29
30
31 470 Smith RF, Reynolds HT. 1965. Principles, definitions and scope of integrated pest
32
33 471 control. *Proceedings FAO Symposium on Integrated Pest Control*, Rome, FAO
34
35 472 1:11–15.
36
37
38 473 Soler C, Mānes J, Picó Y. 2004. Liquid chromatography–electrospray quadrupole ion-
39
40 474 trap mass spectrometry of nine pesticides in fruits. *Journal of Chromatography*
41
42 475 A, 1048: 41–49
43
44
45 476 Tsakiris IN, Danis TG., Stratis IA, Nikitovic D, Dialyna IA, Alegakis AK and
46
47 477 Tsatsakis AM. 2004. Monitoring of pesticide residues in fresh peaches produced
48
49 478 under conventional and integrated crop management cultivation. *Bull. Environ.*
50
51 479 *Contam. Toxicol.* 69:674–681
52
53
54
55 480
56
57
58
59
60

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

1 **Legends**

2 **Figure 1** Rate of detection of pesticides from the total samples of peaches

For Peer Review Only

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47

For Peer Review Only

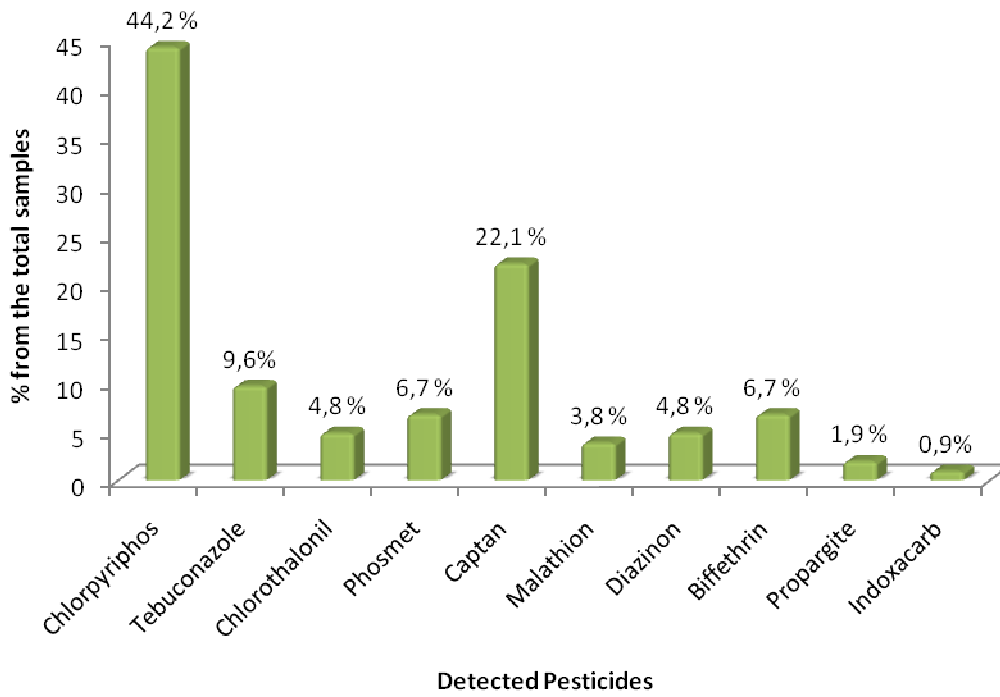


Figure 1

Review Only

Table 1. Target pesticides, , Retention time (t_R)*, Target and Qualifier ions (T, Q_1 and Q_2)*, Percentage of Qualifier – to – Target Ratios, (Q_1/T and Q_2/T)*, LODs*, LOQs*, Regression Coefficient (r^2)*, matrix effect and inder-day – precision (RSD_R)*.

Pesticides	t_R (min)	T	$Q_1(Q_1/T\%)$	$Q_2(Q_2/T\%)$	LOD (mg Kg ⁻¹)	LOQ (mg Kg ⁻¹)	Matrix effect (Slope M/S)	% RSD_R (n=6) 100 (µg Kg ⁻¹)
Methamidophos	18.00	94	141 (53)	79 (36)	0.002	0.005	1.0	13
Dimethoate	28.27	87	93 (61)	125 (58)	0.005	0.015	0.9	10
Diazinon	28.77	179	137 (98)	152 (67)	0.001	0.004	1.1	8
Chlorothalonil	29.08	266	229 (85)	264 (79)	0.002	0.005	0.9	9
Chlorpyrifos-Methyl	29.81	286	109 (66)	125 (54)	0.001	0.002	1.1	8
Parathion-Methyl	29.94	263	109 (110)	125 (99)	0.003	0.010	1.3	10
Malathion	30.45	173	93 (86)	125 (85)	0.003	0.010	1.2	12
Chlorpyrifos	30.66	97	197 (71)	314 (69)	0.001	0.003	1.3	9
Fenthion	30.77	278	109 (31)	125 (24)	0.001	0.002	1.1	12
Dicofol	31.08	139	111 (56)	251 (48)	0.001	0.004	1.0	10
Penconazole	31.52	248	159 (90)	161 (61)	0.001	0.002	1.0	9
Captan	31.90	79	107 (21)	117 (12)	0.008	0.025	0.7	18
Methidathion	32.10	145	85 (61)	93 (15)	0.015	0.050	0.9	13
Myclobutanil	32.99	179	150 (49)	288 (12)	0.001	0.002	1.1	12
Ethion	33.99	231	125 (41)	153 (36)	0.001	0.004	1.2	14
Propargite	35.50	135	173 (13)	250 (11)	0.015	0.050	1.0	15
Tebuconazole	35.96	250	125 (100)	83 (44)	0.001	0.004	0.9	11
Bifethrin	36.90	181	165 (79)	166 (33)	0.001	0.002	1.3	15
Phosmet	37.38	160	104 (8)	133 (5)	0.005	0.015	0.8	14
Phosalone	39.04	367	121 (34)	182 (29)	0.003	0.010	1.0	12
Amitraz	49.45	121	132 (52)	147 (45)	0.006	0.020	1.1	12
Indoxacarb	53.23	150	201 (69)	527 (32)	0.002	0.005	1.1	11
Deltamethrin	54.06	181	253 (81)	172 (23)	0.008	0.025	0.7	14

* - The values of these analytical parameters are referred to the analytical procedures used, according the experimental part of this work (paragraph 3)

Table 2. Mean extraction method recoveries of pesticides from fresh nectarine, freestone and clingstone peaches and \pm RSDr. Also % recoveries for Clingstone peaches for two different concentrations of pesticides.

Pesticides	% Recovery \pm RSDr (100 $\mu\text{g Kg}^{-1}$)			% Recovery for Clingstone peaches \pm RSDr	
	Freestone	Clingstone	Nectarine	50 ($\mu\text{g Kg}^{-1}$)	500 ($\mu\text{g Kg}^{-1}$)
Methamidophos	84 \pm 7	81 \pm 10	78 \pm 8	78 \pm 9	85 \pm 5
Dimethoate	97 \pm 8	104 \pm 9	95 \pm 10	91 \pm 13	102 \pm 9
Diazinon	86 \pm 8	91 \pm 5	84 \pm 7	80 \pm 8	98 \pm 3
Chlorothalonil	86 \pm 9	92 \pm 6	89 \pm 7	82 \pm 7	88 \pm 4
Chlorpyrifos-Methyl	98 \pm 9	95 \pm 8	87 \pm 11	87 \pm 10	94 \pm 5
Parathion-Methyl	91 \pm 8	97 \pm 6	90 \pm 5	87 \pm 9	97 \pm 4
Malathion	93 \pm 10	88 \pm 8	91 \pm 9	83 \pm 9	91 \pm 6
Chlorpyrifos	91 \pm 8	95 \pm 9	90 \pm 7	87 \pm 9	100 \pm 6
Fenthion	89 \pm 7	88 \pm 7	85 \pm 9	83 \pm 8	92 \pm 5
Dicofol	82 \pm 6	85 \pm 8	81 \pm 7	75 \pm 10	97 \pm 4
Penconazole	89 \pm 8	91 \pm 5	90 \pm 8	85 \pm 7	97 \pm 3
Captan	70 \pm 13	64 \pm 12	69 \pm 12	65 \pm 16	72 \pm 11
Methidathion	98 \pm 11	95 \pm 10	92 \pm 8	91 \pm 12	94 \pm 6
Myclobutanil	104 \pm 7	102 \pm 7	97 \pm 9	96 \pm 9	88 \pm 4
Ethion	103 \pm 8	99 \pm 10	95 \pm 9	94 \pm 11	84 \pm 7
Propargite	101 \pm 6	98 \pm 4	97 \pm 4	93 \pm 8	89 \pm 3
Tebuconazole	99 \pm 11	93 \pm 10	90 \pm 12	87 \pm 14	84 \pm 9
Bifethrin	71 \pm 11	73 \pm 12	68 \pm 12	67 \pm 14	78 \pm 11
Phosmet	95 \pm 8	93 \pm 7	95 \pm 9	88 \pm 9	83 \pm 6
Phosalone	102 \pm 9	99 \pm 10	95 \pm 7	95 \pm 8	85 \pm 5
Amitraz	80 \pm 8	84 \pm 9	83 \pm 9	80 \pm 10	82 \pm 6
Indoxacarb	103 \pm 9	98 \pm 6	98 \pm 7	85 \pm 9	93 \pm 5
Deltamethrin	86 \pm 9	88 \pm 8	82 \pm 7	81 \pm 12	85 \pm 7

10

11

12 **Table 3** Detected pesticide in peach samples in the four sampling stations, their average concentration in every sampling and the EU MRLs.

PESTICIDES	Average Concentration mg/Kg																EU MRLs (mg/Kg)
	SS 1 - AGIA VARVARA				SS -2 MELIKH				SS 3 - ALEXANDRIA				SS 4 - PLATI				
	June	July	August	September	June	July	August	September	June	July	August	September	June	July	August	September	
Diazinon	n.d.	n.d.	0.02	n.d.	n.d.	0.03	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.01	n.d.	0.02
Chlorothalonil	n.d.	n.d.	0.025	n.d.	n.d.	0.04	n.d.	n.d.	n.d.	n.d.	0.025	n.d.	n.d.	n.d.	n.d.	n.d.	1.00
Malathion	n.d.	0.05	n.d.	n.d.	n.d.	n.d.	0.04	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.06	n.d.	0.50
Chlorpyrifos	0.04	0.033	0.04	0.025	n.d.	0.04	0.04	0.03	0.05	0.05	0.1	0.03	0.03	0.03	0.05	0.03	0.20
Captan	0.1	0.1	0.07	0.07	0.1	0.1	0.06	0.05	0.08	0.07	0.1	0.04	n.d.	0.07	0.14	0.07	2.00
Propargite	n.d.	n.d.	0.04	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	4.00
Tebuconazole	n.d.	0.025	0.03	n.d.	n.d.	0.03	0.035	n.d.	n.d.	n.d.	0.04	n.d.	n.d.	0.03	n.d.	n.d.	1.00
Bifethrin	n.d.	0.03	0.03	n.d.	n.d.	0.03	0.03	n.d.	n.d.	n.d.	0.02	n.d.	n.d.	n.d.	0.04	n.d.	0.20
Phosmet	0.04	0.06	n.d.	n.d.	n.d.	n.d.	0.04	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.10
Indoxacarb	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.06	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	-

13
14 -no defined EU MRLs, n.d.: not detected
15
16

1
2
3
4 17 **Table 4.** Statistical analysis of the quantitated residual levels of the detected crop
5
6 18 protection products in peach samples from ICM system, number of detected samples,
7
8 19 average concentration, Range of concentration and European Maximum Residues
9
10 20 Limits

Pesticide	Number of samples (N)	Average concentration (mg/Kg)	Range of concentration (mg/Kg)	EU MRLs (mg/Kg)
Chlorpyrifos	46	0.036	0.025-0.1	0.20
Tebuconazole	10	0.032	0.025-0.04	1.00
Chlorothalonil	5	0.03	0.025-0.04	1.00
Phosmet	7	0.05	0.04-0.06	0.10
Captan	23	0.09	0.04-0.14	2.00
Malathion	4	0.05	0.04-0.06	0.50
Diazinon	5	0.02	0.01-0.03	0.02
Bifethrin	7	0.03	0.02-0.04	0.20
Propargite	2	0.04	0.04	4.00
Indoxacarb	1	0.06	0.06	0.3

21

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

22
23

For Peer Review Only