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Studying the recoveries of four representative organophosphorus pesticides from eighteen plant products belonging to different botanical categories; implications for matrix effects

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3 1 **Studying the recoveries of four representative organophosphorus pesticides from**
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5 2 **eighteen plant products belonging to different botanical categories; implications**
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8 3 **for matrix effects**
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10 4
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12 5
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14
15 6 **Abstract**

16
17 7 A study of the matrix effect was performed in order to evaluate the influence of some
18
19 8 matrices on the gas chromatographic responses of representative organophosphorus
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21 9 insecticides. Particularly, 3 fortification levels and the Maximum Residual Level
22
23 10 (MRL) of 4 organophosphorus pesticide standard solutions were added in 18 matrices
24
25 11 (15 belonging to 5 specific botanical categories and 3 botanically unclassified). The
26
27 12 recoveries of the examined pesticides were determined using a simple official
28
29 13 multiresidue method of detection, without any additional clean-up step. Recoveries
30
31 14 were estimated based on standards prepared in solvent. The recovery percentages of
32
33 15 the most polar pesticides, especially methamidophos (20.2–288.4%), were much
34
35 16 higher than those of non polar ones (chlorpyrifos and methidathion 25.7–136.4% and
36
37 17 37.6–292.6% respectively), except for quince. Pronounced matrix effects (>120%)
38
39 18 were observed to the lowest fortification levels (MRLs established by EU), of
40
41 19 dimethoate and methamidophos (i.e. the most polar analytes) in the majority of
42
43 20 product extracts. Furthermore, it was proved that there is no correlation between the
44
45 21 classification of plant products, according to their botanical characteristics, and the
46
47 22 recoveries of pesticides in the equivalent extracts. Indeed, there were significant
48
49 23 differences in the recoveries of pesticides in extracts, derived from matrices belonging
50
51 24 to the same botanical group (especially in the categories of pome fruits and citrus).
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53 25 Consequently, it was shown that, under the examined conditions, obtaining recovery
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4 26 data, derived from only one representative matrix, with purpose to validate an official
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6 27 method in its botanical category is, possibly, an erroneous practice.
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9 28

10 29 **Keywords:** *matrix effect, organophosphorus pesticide residue analysis, ethyl acetate,*
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13 30 *botanical groups, validation.*
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31 **Introduction**

32 Bearing in mind the prevalence of chemical pest control and the wide variety of
33 pesticides available, the monitoring of pesticides residues constitutes a prevalent
34 objective in chemical contaminants research that aims mainly to prevent possible risks
35 for human health. A large number of Multiresidue Extraction Methods (MRMs) is
36 applied in pesticide residue analysis, all of which offer an effective way of
37 identification and quantification of several analytes in a relatively short period
38 (Hajšlová et al. 1998). According to the EU guidance (Hill and Reynolds 1999),
39 recovery portions of target pesticides form a minimum requirement in order to
40 validate the analytical method, necessitating the availability of recovery data from
41 various pesticides and representative sample matrices (with varying chemical
42 composition and botanical characteristics) of different plant product categories. One
43 of the most frequently used methods in the analysis of non fatty matrices is the
44 extraction with ethyl acetate and gas chromatography with appropriate sensitive
45 detectors (Ministry of Welfare, 1988), while small modifications, especially in the
46 additional clean-up step, are nowadays also widely used, with acceptable recoveries
47 of pesticides (Cai et al. 1995; Dorea et al. 1995; Hajšlová et al. 1998; Navarro et al.
48 2002; Pugliese et al. 2004).

49 However, the application of MRMs has several difficulties, the main of which are
50 the suitability/compatibility of the extraction solvent to the analyzed pesticides and
51 the influence of each matrix examined on the analysis. Particularly, there have been
52 observed differences in the pesticides recovery depending on the solvent used in the
53 sample preparation (Maštovská and Lehotay 2004). In addition, the
54 quantification/recovery of the most important analytes by gas chromatography is
55 strongly affected by various factors, including the efficiency of the extraction method

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3 56 and a phenomenon, known as “matrix-induced chromatographic response
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5 57 enhancement”, which was first described by Erney et al. (1993), and causes
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8 58 excessively high recovery results. This phenomenon takes place during analysis of
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10
11 59 samples that contain a wide range of matrix components (e.g. pigments, waxes, lipids
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13 60 and other non volatile constituents) that may remain after the preparation of the
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15 61 sample and the additional step of clean-up (Godula et al. 1999). Such compounds
16
17 62 accumulate in the GC inlet and/or in the front part of a capillary column. Particularly,
18
19 63 during analysis of a pesticide(s) standard solution, more active sites in the injection
20
21 64 liner are available for the certain analyte(s), compared to those available during
22
23 65 analysis of a sample containing also matrix components (Schenck and Lehotay 2000).
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25
26 66 This is due to the fact that the latter components block the active sites of injection
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28
29 67 liner (Erney et al. 1993).

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32 68 Consequently, matrix effect is considered, nowadays, as one of the most persistent
33
34 69 sources of uncertainty in pesticide residue analysis (Cuadros-Rodriguez et al. 2002;
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36 70 Egea Gonzalez et al. 2002). However, available studies have focused on collecting
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38 71 recovery data of pesticides examining combinations of few primary crop products,
39
40 72 many pesticides and many fortification levels (Dorea et al. 1995; Hajšlová et al.
41
42 73 1998). Other studies involve determination of the pesticides recovery by many
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44 74 products belonging only to one plant commodity group (Cai et al. 1995; Egea
45
46 75 Gonzalez et al. 2002). Therefore, there is need to comparatively evaluate various
47
48 76 matrices from various botanical categories per analytical method to determine the
49
50 77 uncertainty due to matrix effect. Moreover, the recovery studies commonly involve a
51
52 78 few matrices fortified with a mixture of pesticides. Various food matrices fortified
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54 79 with one pesticide should also be included in pesticide recovery studies. This would
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56 80 clearly illustrate the matrix effect *per* pesticide.
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3 81 The objective of this work was the evaluation of the matrix effects on the recovery
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5 82 of four commonly applied pesticides of different physicochemical properties
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8 83 (especially polarity), fortified in plant products of various botanical categories, at
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10 84 three indicative levels (0.2, 0.5 and 1.5mgkg⁻¹) and MRL (when different from the
11
12 85 fortification level studied).
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17 87 **Materials and Methods**

18 88 *Materials and Reagents*

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20 89 The solvent used was ethyl acetate (Merck, Darmstadt, Germany, 110972) and was of
21
22 90 pesticide grade. Pesticide standards (chlorpyrifos, dimethoate, methamidophos and
23
24 91 methidathion) of more than 98% purity were obtained from Chem Service (Chem
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26 92 Service, West Chester, PA, USA). Stock solutions were prepared in ethyl acetate and
27
28 93 working standard mixtures were obtained with appropriate dilutions before use.
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30 94 Particularly, the standards were used for the preparation of stock standard solutions
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32 95 for each pesticide at 100mgkg⁻¹ in the used solvent and stored at -18°C. In Table I,
33
34 96 there is the list of the investigated organophosphorus pesticides along with some of
35
36 97 their physicochemical characteristics (Tomlin 1997). Anhydrous sodium sulfate for
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38 98 residue analysis was of pesticide grade (Riedel – de Haën, Hanover, Germany,
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40 99 13464).
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48 100 [Insert Table I about here]
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50 101 *Samples*

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53 102 **Eighteen different commodities were obtained from a local market for organic**
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55 103 **farming produce.** Particularly, pome fruits (pears, apples and quinces), citrus (lemons,
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57 104 mandarins and oranges), stone fruits (apricots, cherries and peaches), fruiting
58
59 105 vegetables (cucumbers, tomatoes and peppers), leafy vegetables (lettuce, spinach and
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3 106 chicory) and three other products not belonging to a specific group (kiwi fruits, table
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5 107 grapes and strawberries) were used as representative matrices in the experiment.
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8 108 These commodities were checked by gas chromatography to ensure the absence of
9
10 109 pesticide residues and their suitability for the analysis.

110 *Analytical Procedure*

111 All samples were prepared in triplicate by a general method suitable for gas
112 chromatography analysis with a nitrogen–phosphorus detector (NPD) (Ministry of
113 Welfare 1988). According to the method, 50g of the representative homogenized
114 sample of each commodity were mixed with 100mL of ethyl acetate and 50g of
115 anhydrous sodium sulfate. The mixture was blended for 2min and the extract was
116 filtered through Whatman No 1 filter paper, containing approximately 5g of
117 anhydrous sodium sulfate, into a conical flask. The clear filtrate, without additional
118 clean–up, was stored at –20°C, until it was injected into the chromatograph. The
119 storage of freeze-d extracts ranged from 1–4 days, so that the bounding reactions can
120 be avoided. Clean–up was not performed because the standard, by which the method
121 was adopted (Ministry of Welfare 1988), suggests that additional clean–up steps after
122 extraction are not always required for non fatty substances like fruits and vegetables,
123 and especially for the pesticides used in our study. Furthermore, the use of an
124 additional clean–up procedure may reduce the amount of co-extractives (Hajšlová et
125 al. 1998; Schenck and Lehotay 2000), and hence mask the potential effect of matrices
126 on pesticides recovery, which was the aim of our study.

127 *Gas Chromatographic determination*

128 A gas chromatograph (Hewlett–Packard 5890, Series II) equipped with NPD (Agilent,
129 Wilmington, USA, 19234–90167), split/splitless injector and autosampler was used.
130 The separation of sample components was performed with an Rtx[®]–5ms 30m x

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3 131 0.32mm id x 0.25 μ m film thickness (Restek, USA, 12624) capillary column. The
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6 132 injection port temperature was 260°C and the detector temperature 300°C. The oven
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8 133 temperature was programmed as follows: initial temperature 70°C for 1min, raised at
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10 134 15°Cmin⁻¹ to 130°C for 0min, raised at 5°Cmin⁻¹ to 230°C and finally raised at
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12 135 20°Cmin⁻¹ to 250°C with a residence time of 13min. Helium carrier gas at flow rate of
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15 136 8mLmin⁻¹ was used. Triplicate extracts (2 μ L) were injected and quantification of the
16
17 137 insecticides was performed by automatic integration of the peak areas (European
18
19 138 Communities 1999). Quantification/recovery of the pesticides in the fortified samples
20
21 139 was carried out by comparing the detector responses for each of the three independent
22
23 140 samples to those measured in a calibration standard, which was injected both before
24
25 141 and after each sample. It should be noticed that maintenance application of the system
26
27 142 took place at the end of a pesticide analytical “sequence”, defined as the total of
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29 143 samples prepared with one fortification level of one analyte in all 18 matrices. Product
30
31 144 extracts were analyzed in the same sequence so that the effect of matrix components
32
33 145 can be considered similar in the target analysis. Maintenance included changes
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35 146 associated with the injection site and the front part of the chromatography column
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37 147 being connected with the injection site. Specifically, at the end of an analytical
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39 148 sequence, septum and injection liner were replaced and the good operation of the
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41 149 system was evaluated by injecting the used solvent and a standard solution, containing
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43 150 the investigated pesticides. Cutting the front part of the capillary column was decided
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45 151 upon indications (such as peak width/height/tailing and integrated area) from the
46
47 152 injections of standard solutions. Furthermore, by the end of each sequence, 2 μ L of a
48
49 153 standard solution (0.1mgkg⁻¹) of pesticides mixture in ethyl acetate was injected to
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51 154 evaluate the reliability of column. In general, the performance of the GC column
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53 155 remained satisfactory for approximately 3–4 sequences.
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3 156 *Statistical analysis*
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5 157 One way analysis of variance (ANOVA) was applied in order to examine the fixed
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8 158 effects of three experimental factors (pesticide standard, fortification level, matrix) in
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10 159 the recovery of pesticides using the general linear models procedures of SPSS. Then
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12 160 least squared means of recoveries in triplicate trials were calculated and significant
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14 161 differences were estimated by post-hoc tests using Tuckey's method. A significant
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16 162 level of 0.05 was used for all statistical analysis.
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22 164 **Results and Discussion**
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24 165 The first part of this experiment includes the estimate of the NPD response in the
25
26 166 examined pesticides. Areas in curves, obtained by injections of pesticide standard
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28 167 solutions, were the means of three replicates for each concentration level. All
29
30 168 responses correspond to linear equations in the studied range of 0.01–2.5mgkg⁻¹, as
31
32 169 squared correlation coefficients in this model were found to be >0.9847 (R²=0.9959;
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34 170 R²=0.9933; R²=0.9847; R²=0.995 for chlorpyrifos, dimethoate, methamidophos and
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36 171 methidathion respectively).
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41 172 The performance of an analytical method is assessed by several criteria. The
42
43 173 recoveries of all used pesticides should be in the range 70–110% with relative
44
45 174 standard deviations (RSDs) below 20% (European Communities 1999). In this study,
46
47 175 in order to estimate the reliability of the used method, recovery trials were conducted
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49 176 at four fortification levels, chosen as representative range of pesticide concentrations
50
51 177 found in the majority of different pesticide–matrix combinations. Specifically, every
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53 178 product was fortified with the target pesticide solutions at the level of MRLs
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55 179 established by EU and at fortification levels of 0.2, 0.5 and 1.5mgkg⁻¹. The results of
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57 180 the recovery tests are presented at Tables II–V.
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3 181 [Insert Tables II-V about here]
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6 182 The type of the examined pesticides was found to influence the occurrence of
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8 183 matrix effect ($p < 0.05$), as the recoveries for the same matrix vary with the different
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10 184 pesticides. Among the used pesticides, the highest recoveries and matrix effects were
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12 185 observed to methamidophos and dimethoate, in the majority of product extracts
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14 186 (especially in the lowest fortification levels). It is notable that methamidophos was not
15
16 187 detected in the first injections after the maintenance of the GC system (changing the
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18 188 injection liner) and especially in the first samples of analysis sequence. In these cases,
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20 189 the analysis was repeated, as multiple injections of uncleaned matrix extracts were
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22 190 proved to have a potential effect on the NPD response in this analyte in contrast to the
23
24 191 non polar ones. Also, it was found that methamidophos recoveries were of poorer
25
26 192 precision in the three repeated injections, as it can be observed from RSDs presented
27
28 193 at Table IV. Our findings are in agreement with those of Cai et al. (1995), while
29
30 194 similar behavior has been reported for captan and other polar analytes (Hajšlová et al.
31
32 195 1998). In contrast to methamidophos and dimethoate, the lowest recovery portions
33
34 196 were observed to the non polar analytes chlorpyrifos and methidathion. However, the
35
36 197 only cases where matrix effect was observed in those analytes were: pepper in
37
38 198 fortification level 0.2 mg kg^{-1} and strawberries (MRL) for methidathion and cucumber
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40 199 (MRL) for chlorpyrifos (Tables II and V). These results are in agreement with Erney
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42 200 et al. (1993), who supported that changes in the recovery portion vary with the
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44 201 chemical structure of the pesticide and those compounds containing P=O bonds, like
45
46 202 methamidophos, were identified as tending to give particularly high recoveries.
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48 203 Schenck and Lehotay (2000) noticed that compounds with P=O bonds tend to exhibit
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50 204 more matrix effects rather than those with P=S bonds, like the one present in the
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52 205 molecule of dimethoate, chlorpyrifos and methidathion, because of the highest
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3 206 polarity of these bonds. Moreover, as it can be deduced from Table 1 regarding the
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5 207 physicochemical properties (especially values of $w.s.$ and $\log k_{ow}$, which are a degree
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8 208 of polarity), methamidophos and dimethoate are more polar than the other two and for
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10 209 this reason their recoveries are higher, which agrees with the statement of Hajšlová et
11
12 210 al. (1998) that the probability of the matrix effect occurrence is higher for more polar
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14 211 pesticides.

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17 212 The ratio of analyte and matrix concentration (fortification level) seems to be a
18
19 213 crucial point in the appearance of matrix effect, since there are differences in the
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21 214 recovery portions between the fortification levels for the same pesticides ($p < 0.05$).
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23 215 From the results presented in Tables II–V, it can be proved that the lower is the
24
25 216 fortification level the recovery portion is higher. The phenomenon is more evident in
26
27 217 the MRLs of 0.02 mg kg^{-1} and especially for the pesticide standard dimethoate in
28
29 218 almost all the examined matrices (Table III). This is similar to Hajšlová et al. (1998)
30
31 219 and Anastassiades et al. (2003), who noticed unacceptable recoveries and matrix
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33 220 enhancement effects at lower concentration levels of target pesticides and/or at higher
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35 221 matrix components. This behavior can be attributed to the lower competitive effect of
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37 222 the pesticide standards, when they are found in trace fortification levels, for covering
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39 223 the active sites in the injection liner (Hajšlová and Zrostlýkova 2003).

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41 224 It was also observed that in the analysis of some matrices fortified with
42
43 225 dimethoate, methamidophos and methidathion at the MRL level, the analytes were
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45 226 under the limit of determination, whereas in the case of other commodities fortified at
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47 227 the same level, the analyte showed an evident peak. Specifically, dimethoate was
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49 228 determined at the level of MRL in all matrices, apart from apricot and peach extracts.
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51 229 Almost the same performance was obtained with methamidophos, where chicory,
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53 230 pepper, kiwi and grapes fortified extracts gave no integrated peaks, at the MRL level
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3 231 of 0.01mgkg⁻¹. In samples fortified with methidathion in the level of 0.02mgkg⁻¹, the
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5 232 analyte was detected only in the strawberry extract, contrary to other examined
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8 233 matrices, as cherry, chicory, lettuce, spinach and kiwi fruit, fortified in the same level
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10 234 of MRL. Consequently, the determination of the analyte, at the same trace level in
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12 235 different matrices, is probably influenced by the type of the matrix. This performance
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15 236 was not followed by chlorpyrifos, whose MRL levels are comparatively higher and all
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17 237 peaks were easily integrated.

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20 238 Recovery portion of pesticides also depends on the chemical composition of the
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22 239 matrix ($p < 0.05$). It was found that the type of co-extracts that remains in the final
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24 240 sample leads markedly to different detector response. As a consequence, the botanical
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26 241 categories examined in the experiment can be classified according to the mean
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28 242 recovery portions of the used pesticides (especially in the three fortification levels) in
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30 243 the order: fruiting vegetables and table grapes > strawberries and leafy
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32 244 vegetables > stone fruits and kiwi fruits > pome fruits and citrus. It seems that the
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34 245 highest recoveries were observed to samples containing more non volatile compounds
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36 246 (such as chlorophylls in leafy vegetables, carotenoids in fruiting vegetables, waxes in
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38 247 grapes, lipids in strawberries) compared to samples with more volatile compounds.
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40 248 Thus, higher recoveries are possibly associated with the entrapment of non volatile
41
42 249 compounds in the injection liner which are able to cover active sites in the injection
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44 250 liner and/or the front of analytical column and may conduct to higher recoveries. The
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46 251 scientific evidence suggests that more distinct matrix effects have been reported for
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48 252 extracts derived from matrices rich in pigments and lipids (Hajšlová et al. 1998;
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50 253 Godula et al. 1999; Anastassiades et al. 2003). Also, when co-extracts, like those
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52 254 mentioned, are accumulated in the inlet, they can create new active sites, intensifying
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54 255 the presence of the phenomenon (Anastassiades et al. 2003).
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3 256 Furthermore, from Tables II–V, it can be revealed that there is no correlation
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5 257 between the classification of plant produce by botanical characteristics and the
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7 258 recoveries of pesticides in the respective extracts, since product extracts belonging to
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9 259 the same botanical category present differences in the pesticides recovery. This
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11 260 statement is more evident especially in the categories of pome fruits, in which quince
12
13 261 extracts gave extremely low recoveries in contrast with apple and pear extracts
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15 262 (Tables II–V). Similarly in the citrus category, lemon extracts gave much higher
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17 263 recoveries in contrast with mandarin and orange extracts ($p < 0.05$) (Tables II–V). On
18
19 264 the contrary, the three examined products belonging to stone fruits and leafy
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21 265 vegetables present smaller variations, while those belonging to fruiting vegetables
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23 266 present unvarying behavior in the recovery portion of pesticides ($p > 0.05$).
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29 267 In the present study, there are dramatically low recoveries in pesticides in orange
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31 268 extracts, fact opposed to other studies using ethyl acetate as the extraction solvent and
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33 269 clean-up step (Dorea et al. 1995; Hajšlová et al. 1998). Even after the required
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35 270 conditioning of the GC system and three months later, the analysis of the specific lot
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37 271 (frozen oranges), with an independent extract preparation in triplicates, gave the same
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39 272 results. On the contrary, a new lot of oranges from organic produce, analyzed by the
40
41 273 same method, gave much higher recoveries in similar combinations of pesticides and
42
43 274 fortification levels (results not shown) and the difference was more pronounce in the
44
45 275 more polar methamidophos and dimethoate at the fortification level of 1 mg kg^{-1} .
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47 276 Probably, this behavior may be attributed to the specific lot and its different chemical
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49 277 composition, depending on harvest time.
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53 278 Also, it is remarkable that recoveries of pesticides in quince extracts are extremely
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55 279 low in every pesticide and fortification level in comparison with every plant product
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57 280 extract. The existing evidence cannot help to explain this performance, as there are no
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3 281 studies examining recovery data derived from quince extracts. The fact that quinces
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5 282 contain large quantities of water-soluble pectins and the used lot was consisted of
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8 283 immature fruits, which contained higher amounts of pectins, may be the cause of this
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10 284 curious behavior, as it is presumed that these ingredients detain important quantities
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13 285 of active ingredients in the extraction step.

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15 286 Moreover, it should be noted that most matrices generally gave chromatograms
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17 287 free of peaks in the blank extracts. Nevertheless, especially in the cases of leafy
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19 288 vegetables and citrus extracts there were found some peaks in different retention times
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22 289 of both the examined pesticides in this study and other organophosphorus pesticide
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25 290 standards analyzed in our laboratory. These may be lipophilic compounds derived
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27 291 from those matrices not removed by the extraction method, as there has been observed
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29 292 similar behavior in uncleaned sample extracts in ethyl acetate (Cai et al. 1995;
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31 293 Maštovská and Lehotay 2004). The fact that the same peak in orange extracts
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34 294 appeared in every orange, either of organic produce or of conventional crop, and
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36 295 detected in the peel orange extract analyzed itself compared to the analysis of orange
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38
39 296 juice, may be the reason why some citrus peels require clean-up step, described by
40
41 297 Dorea et al. (1995).

42
43 298 Finally, it should be addressed that matrix enhancement effect is difficult to study
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45 299 because the GC system changes as matrix components are progressively deposited in
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48 300 the injection port and front of the analytical column (Schenck and Lehotay 2000).
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50 301 Moreover, the injection technique has been found to play a major role on the
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52 302 occurrence of matrix effect. Specifically, the use of cold on-column injection is
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55 303 considered as one of the most practical approaches by which, pesticides thermolysis
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58 304 and decomposition or adsorption inside the inlet could be avoided (Wylie 1996;
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60 305 Godula et al. 1999). With the specific technique, more accurate results have been

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3 306 observed, especially for troublesome analytes, compared to splitless injection as long
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6 307 as the chromatography system remains clean (Wylie 1996). Furthermore, it is likely
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8 308 that polar analytes, such as methamidophos, and matrices, containing especially non
9
10 309 volatile compounds, could be analyzed by on-column injection with the parallel use of
11
12 310 a packed column or a deactivated precolumn (to keep most of the remaining matrix
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14 311 constituents of the extract) connected to the injector site. However, the disadvantage
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16 312 of on-column injection is that it seems to be impractical for applications of complex
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18 313 or relatively uncleaned matrices, because it requires more maintenance of the column
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20 314 and thus, hot splitless injection tends to be preferable (Anastassiades et al. 2003). The
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22 315 effect of maintenance application by changing the injection liner and/or the column is
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24 316 also unpredictable, because as Godula et al. (1998) indicated, the history of the GC
25
26 317 system (especially changes in the injection port) plays an important role in the
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28 318 occurrence of matrix effects. Consequently, recoveries of pesticides are not
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30 319 reproducible and the effects of co-extracts can not be considered as stable and
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32 320 foreseeable. For these reasons, it is better to provide recovery data and validate the
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34 321 used method in only one produce, especially when the product is suspected for matrix
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36 322 effects, so that the existence of matrix effect can be checked rather than providing
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38 323 recoveries in one produce and validate the method in the whole botanical category.

324 In conclusion, the results of the present study indicate that higher pesticide
325 recoveries should be expected at more polar analytes, fortified at low concentrations
326 in matrices rich in non volatile compounds. Moreover, different recoveries may occur
327 among products of the same botanical group. Therefore, examining the recoveries of
328 target pesticides, using an official method, in only one representative plant product
329 with the purpose of validating the method for the whole botanical category is possibly
330 an erroneous practice. Indeed, the combined outcome of factors, such as analytes,

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3 331 matrix, and fortification level on the pesticide recovery can not always be predicted.
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5 332 The above suggest that validation of an official method for the analysis of pesticide
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8 333 residues should not be based only on the botanical categories of plant products. Such
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10 334 practice may be useful, for the simplification of issuing validation, when matrix-
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12 335 matched calibration standards and/or extensive clean-up of the samples are used prior
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15 336 to the final chromatographic step. Conversely, the same practice is insufficient for
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17 337 quantification with standards in neat solvent and/or in the final extract without
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19 338 additional clean-up step. However, in order to further examine the analytical
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21 339 performance of different product extracts, a matrix-matched calibration procedure for
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23 340 each product should be severally carried out. Furthermore, the analysis of each group
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25 341 of commodities fortified in many more levels, with a higher number of pesticides is
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27 342 strongly recommended and may possibly explicate the differences between the
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29 343 recovery portions of products of the same category that the current study brought out.
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401 Table I. Physicochemical properties of the target pesticides.

Pesticide (Retention time)	w.s. (mgL⁻¹)	log_{ow}	M.p. (°C)	V.p. (mPa)
Chlorpyrifos (24.6 min)	1.4	4.7	42-43.5	2.7
Dimethoate (18.9 min)	24000	0.7	43-45	0.25
Methamidophos (8.9 min)	200000	-0.8	45	2.3
Methidathion (27.1 min)	200	2.2	39-40	0.25

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403 w.s.: water solubility (20°C)

404 log_{ow}: log of n – octanol partition coefficient

405 M.p.: melting point.

406 V.p.: vapour pressure (25°C).

407 Table II. Percentage recoveries and RSDs of chlorpyrifos in the different plant
 408 products, classified by botanical characteristics, and in different fortification levels.
 409 Bold letters designate recoveries within the acceptable range of recovery (70–110%).
 410 Values in parenthesis indicate the levels of MRLs established by EU.

Plant products	Recovery \pm RSD (%)			
	1.5mgkg ⁻¹	0.5mgkg ⁻¹	0.2mg/kg ⁻¹	MRL (mgkg ⁻¹)*
<i>Pome fruits</i>				
• Pear	70.1 \pm 1.1^c	72.3 \pm 1.5^b	61.0 \pm 3.0 ^b	72.3 \pm 1.5 (0.5)
• Apple	65.7 \pm 0.1 ^b	76.5 \pm 3.4^b	92.5 \pm 15.1^c	76.4 \pm 3.4 (0.5)
• Quince	46.6 \pm 1.0 ^a	33.4 \pm 1.2 ^a	25.7 \pm 17.8 ^a	33.4 \pm 1.2 (0.5)
<i>Citrus</i>				
• Lemon	61.6 \pm 1.8 ^c	63.6 \pm 0.8 ^b	85.5 \pm 1.5^b	85.5 \pm 1.5 (0.2)
• Mandarin	54.3 \pm 6.5 ^b	63.5 \pm 1.7 ^b	89.8 \pm 5.3^b	68.2 \pm 2.8 (2.0)
• Orange	44.9 \pm 5.4 ^a	34.2 \pm 2.7 ^a	36.5 \pm 5.0 ^a	41.4 \pm 9.8 (0.3)
<i>Stone fruits</i>				
• Apricot	62.4 \pm 2.3 ^a	51.5 \pm 2.4 ^a	66.5 \pm 11.0 ^a	65.2 \pm 13.6 (0.05)
• Cherry	63.3 \pm 2.3 ^a	79.8 \pm 3.4^c	67.8 \pm 2.9 ^a	55.4 \pm 11.8 (0.3)
• Peach	62.2 \pm 0.9 ^a	58.3 \pm 5.0 ^b	70.9 \pm 10.4^a	70.9 \pm 10.4 (0.2)
<i>Leafy vegetables</i>				
• Lettuce	69.2 \pm 3.4 ^b	78.4 \pm 3.7^b	80.5 \pm 4.4^a	92.1 \pm 5.8 (0.05)
• Chicory	50.6 \pm 2.6 ^a	68.0 \pm 3.1 ^a	89.8 \pm 1.6^b	77.2 \pm 18.5 (0.05)
• Spinach	75.6 \pm 2.6^c	88.2 \pm 1.2^c	78.0 \pm 1.4^a	89.9 \pm 8.5 (0.05)
<i>Fruiting vegetables</i>				
• Cucumber	71.1 \pm 2.9^a	104.9 \pm 1.9^b	103.6 \pm 9.0^b	136.4 \pm 11.9 (0.05)
• Pepper	80.0 \pm 0.8^a	87.1 \pm 5.5^a	108.1 \pm 9.1^b	87.1 \pm 5.5 (0.5)
• Tomato	89.2 \pm 4.6^b	80.6 \pm 2.7^a	82.5 \pm 2.8^a	80.6 \pm 2.7 (0.5)
<i>Various</i>				
• Kiwi fruits	49.3 \pm 2.1	54.2 \pm 6.1	57.8 \pm 6.2	51.5 \pm 0.9 (2.0)
• Table grapes	89.5 \pm 1.1	91.0 \pm 3.4	97.0 \pm 9.7	91.0 \pm 3.4 (0.5)
• Strawberries	55.8 \pm 0.5	68.0 \pm 1.8	90.1 \pm 6.5	90.1 \pm 6.5 (0.2)

411 a, b, c: means within a plant product category and fortification level lacking a
 412 common superscript letter are different (p<0.05).

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3 413 * Some MRLs are equal to one of the rest examined concentrations (i.e. 0.2 and
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5 414 0.5mgkg⁻¹). For this reason the respective recoveries appear in two columns of the
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416 Table III. Percentage recoveries and RSDs of dimethoate in the different plant
 417 products, classified by botanical characteristics, and in different fortification levels.
 418 Bold letters designate recoveries within the acceptable range of recovery (70–110%).
 419 Values in parenthesis indicate the levels of MRLs established by EU.

Plant products	Recovery \pm RSD (%)			
	1.5mgkg ⁻¹	0.5mgkg ⁻¹	0.2mgkg ⁻¹	MRL (mgkg ⁻¹)*
<i>Pome fruits</i>				
• Pear	90.9 \pm 1.2^c	86.7 \pm 2.5^c	98.7 \pm 6.0^b	118.1 \pm 6.2 (0.02)
• Apple	71.6 \pm 5.0^b	68.4 \pm 3.8 ^b	88.9 \pm 1.5^b	97.1 \pm 15.5 (0.02)
• Quince	22.8 \pm 3.2 ^a	45.1 \pm 2.8 ^a	28.3 \pm 12.2 ^a	103.0 \pm 5.7 (0.02)
<i>Citrus</i>				
• Lemon	84.1 \pm 6.0^a	97.4 \pm 2.9^c	97.3 \pm 3.6^c	138.7 \pm 18.3 (0.02)
• Mandarin	67.9 \pm 0.5 ^a	58.3 \pm 0.2 ^a	42.0 \pm 8.5 ^a	95.2 \pm 10.6 (0.02)
• Orange	73.8 \pm 0.6^a	86.8 \pm 4.9^b	68.3 \pm 3.0 ^b	121.8 \pm 4.3 (0.02)
<i>Stone fruits</i>				
• Apricot	85.0 \pm 1.3^a	108.5 \pm 0.5^b	113.8 \pm 3.8 ^b	Not detected (0.02)
• Cherry	93.1 \pm 1.1^b	104.7 \pm 1.4^b	115.3 \pm 10.7 ^b	90.4 \pm 2.3 (1.0)
• Peach	92.4 \pm 3.7^b	78.3 \pm 0.9^a	80.5 \pm 6.6^a	Not detected (0.02)
<i>Leafy vegetables</i>				
• Lettuce	92.3 \pm 1.3^a	127.4 \pm 0.6 ^c	116.2 \pm 3.3 ^a	127.4 \pm 0.6 (0.5)
• Chicory	76.9 \pm 1.3^b	112.6 \pm 0.8 ^b	103.3 \pm 3.5^a	138.4 \pm 5.9 (0.02)
• Spinach	81.1 \pm 2.2^a	67.1 \pm 5.0 ^a	105.7 \pm 5.5^a	151.3 \pm 9.2 (0.02)
<i>Fruiting vegetables</i>				
• Cucumber	88.4 \pm 1.8^{ab}	118.1 \pm 0.5 ^b	103.2 \pm 1.4^a	157.9 \pm 14.8 (0.02)
• Pepper	86.3 \pm 2.3^b	118.8 \pm 1.3 ^b	117.6 \pm 1.9 ^b	137.9 \pm 5.4 (0.02)
• Tomato	82.9 \pm 1.4^a	87.1 \pm 6.6^a	107.0 \pm 3.6^{ab}	165.5 \pm 12.9 (0.02)
<i>Various</i>				
• Kiwi fruits	80.2 \pm 2.0	85.1 \pm 3.7	87.4 \pm 9.3	141.9 \pm 8.5 (0.02)
• Table grapes	92.9 \pm 1.8	87.0 \pm 6.4	89.0 \pm 3.3	150.0 \pm 13.5 (0.02)
• Strawberries	89.5 \pm 0.3	111.6 \pm 0.6	135.4 \pm 3.2	146.3 \pm 7.3 (0.02)

420 a, b, c: means within a plant product category and fortification level lacking a
 421 common superscript letter are different (p<0.05).

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3 422 * Some MRLs are equal to one of the rest examined concentrations (i.e. 0.2 and
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5 423 0.5mgkg⁻¹). For this reason the respective recoveries appear in two columns of the
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425 Table IV. Percentage recoveries and RSDs of methamidophos in the different plant
 426 products, classified by botanical characteristics, and in different fortification levels.
 427 Bold letters designate recoveries within the acceptable range of recovery (70–110%).
 428 Values in parenthesis indicate the levels of MRLs established by EU.

Plant products	Recovery ± RSD (%)			
	1.5mgkg ⁻¹	0.5mgkg ⁻¹	0.2mgkg ⁻¹	MRL (mgkg ⁻¹)*
<i>Pome fruits</i>				
• Pear	82.3 ± 4.8^b	82.2 ± 2.9^b	111.8 ± 2.6 ^b	99.6 ± 5.8 (0.05)
• Apple	77.7 ± 5.0^b	93.2 ± 11.2^b	106.3 ± 17.8^b	Not detected (0.05)
• Quince	32.0 ± 4.7 ^a	20.2 ± 1.8 ^a	38.3 ± 10.0 ^a	88.9 ± 6.0 (0.05)
<i>Citrus</i>				
• Lemon	103.6 ± 7.7^b	114.8 ± 3.8 ^b	105.8 ± 5.6^c	105.8 ± 5.6 (0.2)
• Mandarin	69.1 ± 1.9 ^a	78.8 ± 6.9^a	73.2 ± 6.8^b	73.2 ± 6.8 (0.2)
• Orange	58.2 ± 9.3 ^a	63.8 ± 6.6 ^a	56.8 ± 4.3 ^a	56.8 ± 4.3 (0.2)
<i>Stone fruits</i>				
• Apricot	88.0 ± 12.0^a	120.6 ± 6.3 ^b	100.0 ± 14.8^a	120.0 ± 4.3 (0.1)
• Cherry	70.9 ± 9.5^a	79.9 ± 7.3^a	88.5 ± 3.7^a	166.0 ± 15.0 (0.01)
• Peach	78.8 ± 1.4^a	83.4 ± 1.6^a	87.7 ± 8.9^a	Not detected (0.05)
<i>Leafy vegetables</i>				
• Lettuce	108.8 ± 2.3^b	97.7 ± 1.5^a	97.9 ± 1.3^a	97.9 ± 1.3 (0.2)
• Chicory	72.4 ± 3.8^a	119.3 ± 2.8 ^b	110.4 ± 4.6 ^a	Not detected (0.01)
• Spinach	98.8 ± 9.4^b	117.9 ± 2.5 ^b	128.4 ± 15.6 ^a	288.4 ± 2.7 (0.01)
<i>Fruiting vegetables</i>				
• Cucumber	96.7 ± 13.9^a	98.8 ± 3.9^a	102.1 ± 2.2^a	107.5 ± 8.2 (1.0)
• Pepper	82.7 ± 2.3^a	96.2 ± 0.9^a	108.2 ± 6.4^a	Not detected (0.01)
• Tomato	98.8 ± 3.8^a	96.8 ± 0.8^a	95.2 ± 16.8^a	Not detected (0.05)
<i>Various</i>				
• Kiwi fruits	87.9 ± 7.1	75.7 ± 6.7	92.8 ± 8.7	Not detected (0.01)
• Table grapes	76.8 ± 4.7	90.0 ± 4.1	91.0 ± 5.4	Not detected (0.01)
• Strawberries	102.2 ± 1.2	108.0 ± 5.2	103.4 ± 12.3	210.4 ± 3.5 (0.01)

429 a, b, c: means within a plant product category and fortification level lacking a
 430 common superscript letter are different (p<0.05).

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3 431 * Some MRLs are equal to one of the rest examined concentrations (i.e. 0.2 and
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5 432 0.5mgkg⁻¹). For this reason the respective recoveries appear in two columns of the
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For Peer Review Only

434 Table V. Percentage recoveries and RSDs of methidathion in the different plant
 435 products, classified by botanical characteristics, and in different fortification levels.
 436 Bold letters designate recoveries within the acceptable range of recovery (70–110%).
 437 Values in parenthesis indicate the levels of MRLs established by EU.

Plant products	Recovery \pm RSD (%)			
	1.5mgkg ⁻¹	0.5mgkg ⁻¹	0.2mgkg ⁻¹	MRL (mgkg ⁻¹)*
<i>Pome fruits</i>				
• Pear	69.8 \pm 1.4^b	62.1 \pm 3.1 ^b	74.4 \pm 1.6^b	74.2 \pm 7.2 (0.3)
• Apple	81.9 \pm 2.9^c	77.2 \pm 2.8^c	90.8 \pm 1.0^c	88.8 \pm 1.9 (0.3)
• Quince	40.5 \pm 0.8 ^a	40.2 \pm 2.2 ^a	46.0 \pm 1.7 ^a	73.6 \pm 10.8 (0.3)
<i>Citrus</i>				
• Lemon	79.7 \pm 0.3^c	86.1 \pm 1.6^b	73.0 \pm 6.4^b	81.9 \pm 8.7 (2.0)
• Mandarin	59.1 \pm 2.8 ^a	40.7 \pm 0.4 ^a	44.6 \pm 13.1 ^a	61.2 \pm 5.1 (2.0)
• Orange	44.4 \pm 0.8 ^b	37.6 \pm 5.4 ^a	44.8 \pm 14.2 ^a	53.2 \pm 4.5 (2.0)
<i>Stone fruits</i>				
• Apricot	70.9 \pm 2.5^a	85.9 \pm 2.8^b	100.9 \pm 4.2^b	100.9 \pm 4.2 (0.2)
• Cherry	76.0 \pm 2.2^a	87.9 \pm 2.2^b	90.5 \pm 10.4^b	Not detected (0.02)
• Peach	68.3 \pm 2.0 ^a	59.8 \pm 3.4 ^a	60.0 \pm 17.7 ^a	60.0 \pm 17.7 (0.2)
<i>Leafy vegetables</i>				
• Lettuce	60.3 \pm 2.1 ^a	70.9 \pm 0.7^a	76.5 \pm 13.7^a	Not detected (0.02)
• Chicory	73.9 \pm 4.5^b	76.2 \pm 2.4^b	71.0 \pm 9.4^a	Not detected (0.02)
• Spinach	53.9 \pm 1.3 ^a	68.2 \pm 1.6 ^a	73.9 \pm 8.6^a	Not detected (0.02)
<i>Fruiting vegetables</i>				
• Cucumber	84.8 \pm 3.4^b	106.4 \pm 4.9^a	104.5 \pm 3.4^a	Not detected (0.02)
• Pepper	72.0 \pm 4.1^a	102.3 \pm 2.8^a	112.2 \pm 0.5 ^a	Not detected (0.02)
• Tomato	97.1 \pm 4.8^c	93.9 \pm 4.0^a	109.5 \pm 1.3^a	109.5 \pm 1.3 (0.2)
<i>Various</i>				
• Kiwi fruits	58.7 \pm 3.4	53.5 \pm 4.1	76.6 \pm 3.7	Not detected (0.02)
• Table grapes	91.8 \pm 2.8	98.0 \pm 2.8	98.0 \pm 4.6	98.0 \pm 2.8 (0.5)
• Strawberries	60.5 \pm 1.6	86.4 \pm 2.1	81.4 \pm 5.0	292.6 \pm 8.9 (0.02)

438 a, b, c: means within a plant product category and fortification level lacking a
 439 common superscript letter are different ($p < 0.05$).

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3 440 * Some MRLs are equal to one of the rest examined concentrations (i.e. 0.2 and
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5 441 0.5mgkg⁻¹). For this reason the respective recoveries appear in two columns of the
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1 Table I. Physicochemical properties of the target pesticides.

Pesticide (Retention time)	w.s. (mgL⁻¹)	log_{ow}	M.p. (°C)	V.p. (mPa)
Chlorpyrifos (24.6 min)	1.4	4.7	42-43.5	2.7
Dimethoate (18.9 min)	24000	0.7	43-45	0.25
Methamidophos (8.9 min)	200000	-0.8	45	2.3
Methidathion (27.1 min)	200	2.2	39-40	0.25

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3 w.s.: water solubility (20°C)

4 log_{ow}: log of n – octanol partition coefficient

5 M.p.: melting point.

6 V.p.: vapour pressure (25°C).

7 Table II. Percentage recoveries and RSDs of chlorpyrifos in the different plant
 8 products, classified by botanical characteristics, and in different fortification levels.
 9 Bold letters designate recoveries within the acceptable range of recovery (70–110%).
 10 Values in parenthesis indicate the levels of MRLs established by EU.

Plant products	Recovery \pm RSD (%)			
	1.5mgkg ⁻¹	0.5mgkg ⁻¹	0.2mg/kg ⁻¹	MRL (mgkg ⁻¹)*
<i>Pome fruits</i>				
• Pear	70.1 \pm 1.1^c	72.3 \pm 1.5^b	61.0 \pm 3.0 ^b	72.3 \pm 1.5 (0.5)
• Apple	65.7 \pm 0.1 ^b	76.5 \pm 3.4^b	92.5 \pm 15.1^c	76.4 \pm 3.4 (0.5)
• Quince	46.6 \pm 1.0 ^a	33.4 \pm 1.2 ^a	25.7 \pm 17.8 ^a	33.4 \pm 1.2 (0.5)
<i>Citrus</i>				
• Lemon	61.6 \pm 1.8 ^c	63.6 \pm 0.8 ^b	85.5 \pm 1.5^b	85.5 \pm 1.5 (0.2)
• Mandarin	54.3 \pm 6.5 ^b	63.5 \pm 1.7 ^b	89.8 \pm 5.3^b	68.2 \pm 2.8 (2.0)
• Orange	44.9 \pm 5.4 ^a	34.2 \pm 2.7 ^a	36.5 \pm 5.0 ^a	41.4 \pm 9.8 (0.3)
<i>Stone fruits</i>				
• Apricot	62.4 \pm 2.3 ^a	51.5 \pm 2.4 ^a	66.5 \pm 11.0 ^a	65.2 \pm 13.6 (0.05)
• Cherry	63.3 \pm 2.3 ^a	79.8 \pm 3.4^c	67.8 \pm 2.9 ^a	55.4 \pm 11.8 (0.3)
• Peach	62.2 \pm 0.9 ^a	58.3 \pm 5.0 ^b	70.9 \pm 10.4^a	70.9 \pm 10.4 (0.2)
<i>Leafy vegetables</i>				
• Lettuce	69.2 \pm 3.4 ^b	78.4 \pm 3.7^b	80.5 \pm 4.4^a	92.1 \pm 5.8 (0.05)
• Chicory	50.6 \pm 2.6 ^a	68.0 \pm 3.1 ^a	89.8 \pm 1.6^b	77.2 \pm 18.5 (0.05)
• Spinach	75.6 \pm 2.6^c	88.2 \pm 1.2^c	78.0 \pm 1.4^a	89.9 \pm 8.5 (0.05)
<i>Fruiting vegetables</i>				
• Cucumber	71.1 \pm 2.9^a	104.9 \pm 1.9^b	103.6 \pm 9.0^b	136.4 \pm 11.9 (0.05)
• Pepper	80.0 \pm 0.8^a	87.1 \pm 5.5^a	108.1 \pm 9.1^b	87.1 \pm 5.5 (0.5)
• Tomato	89.2 \pm 4.6^b	80.6 \pm 2.7^a	82.5 \pm 2.8^a	80.6 \pm 2.7 (0.5)
<i>Various</i>				
• Kiwi fruits	49.3 \pm 2.1	54.2 \pm 6.1	57.8 \pm 6.2	51.5 \pm 0.9 (2.0)
• Table grapes	89.5 \pm 1.1	91.0 \pm 3.4	97.0 \pm 9.7	91.0 \pm 3.4 (0.5)
• Strawberries	55.8 \pm 0.5	68.0 \pm 1.8	90.1 \pm 6.5	90.1 \pm 6.5 (0.2)

11 a, b, c: means within a plant product category and fortification level lacking a
 12 common superscript letter are different (p<0.05).

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4 13 * Some MRLs are equal to one of the rest examined concentrations (i.e. 0.2 and
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6 14 0.5mgkg⁻¹). For this reason the respective recoveries appear in two columns of the
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- 16 Table III. Percentage recoveries and RSDs of dimethoate in the different plant
 17 products, classified by botanical characteristics, and in different fortification levels.
 18 Bold letters designate recoveries within the acceptable range of recovery (70–110%).
 19 Values in parenthesis indicate the levels of MRLs established by EU.

Plant products	Recovery \pm RSD (%)			
	1.5mgkg ⁻¹	0.5mgkg ⁻¹	0.2mgkg ⁻¹	MRL (mgkg ⁻¹)*
<i>Pome fruits</i>				
• Pear	90.9 \pm 1.2^c	86.7 \pm 2.5^c	98.7 \pm 6.0^b	118.1 \pm 6.2 (0.02)
• Apple	71.6 \pm 5.0^b	68.4 \pm 3.8 ^b	88.9 \pm 1.5^b	97.1 \pm 15.5 (0.02)
• Quince	22.8 \pm 3.2 ^a	45.1 \pm 2.8 ^a	28.3 \pm 12.2 ^a	103.0 \pm 5.7 (0.02)
<i>Citrus</i>				
• Lemon	84.1 \pm 6.0^a	97.4 \pm 2.9^c	97.3 \pm 3.6^c	138.7 \pm 18.3 (0.02)
• Mandarin	67.9 \pm 0.5 ^a	58.3 \pm 0.2 ^a	42.0 \pm 8.5 ^a	95.2 \pm 10.6 (0.02)
• Orange	73.8 \pm 0.6^a	86.8 \pm 4.9^b	68.3 \pm 3.0 ^b	121.8 \pm 4.3 (0.02)
<i>Stone fruits</i>				
• Apricot	85.0 \pm 1.3^a	108.5 \pm 0.5^b	113.8 \pm 3.8 ^b	Not detected (0.02)
• Cherry	93.1 \pm 1.1^b	104.7 \pm 1.4^b	115.3 \pm 10.7 ^b	90.4 \pm 2.3 (1.0)
• Peach	92.4 \pm 3.7^b	78.3 \pm 0.9^a	80.5 \pm 6.6^a	Not detected (0.02)
<i>Leafy vegetables</i>				
• Lettuce	92.3 \pm 1.3^a	127.4 \pm 0.6 ^c	116.2 \pm 3.3 ^a	127.4 \pm 0.6 (0.5)
• Chicory	76.9 \pm 1.3^b	112.6 \pm 0.8 ^b	103.3 \pm 3.5^a	138.4 \pm 5.9 (0.02)
• Spinach	81.1 \pm 2.2^a	67.1 \pm 5.0 ^a	105.7 \pm 5.5^a	151.3 \pm 9.2 (0.02)
<i>Fruiting vegetables</i>				
• Cucumber	88.4 \pm 1.8^{ab}	118.1 \pm 0.5 ^b	103.2 \pm 1.4^a	157.9 \pm 14.8 (0.02)
• Pepper	86.3 \pm 2.3^b	118.8 \pm 1.3 ^b	117.6 \pm 1.9 ^b	137.9 \pm 5.4 (0.02)
• Tomato	82.9 \pm 1.4^a	87.1 \pm 6.6^a	107.0 \pm 3.6^{ab}	165.5 \pm 12.9 (0.02)
<i>Various</i>				
• Kiwi fruits	80.2 \pm 2.0	85.1 \pm 3.7	87.4 \pm 9.3	141.9 \pm 8.5 (0.02)
• Table grapes	92.9 \pm 1.8	87.0 \pm 6.4	89.0 \pm 3.3	150.0 \pm 13.5 (0.02)
• Strawberries	89.5 \pm 0.3	111.6 \pm 0.6	135.4 \pm 3.2	146.3 \pm 7.3 (0.02)

- 20 a, b, c: means within a plant product category and fortification level lacking a
 21 common superscript letter are different ($p < 0.05$).

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3 22 * Some MRLs are equal to one of the rest examined concentrations (i.e. 0.2 and
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5 23 0.5mgkg⁻¹). For this reason the respective recoveries appear in two columns of the
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25 Table IV. Percentage recoveries and RSDs of methamidophos in the different plant
 26 products, classified by botanical characteristics, and in different fortification levels.
 27 Bold letters designate recoveries within the acceptable range of recovery (70–110%).
 28 Values in parenthesis indicate the levels of MRLs established by EU.

Plant products	Recovery \pm RSD (%)			
	1.5mgkg ⁻¹	0.5mgkg ⁻¹	0.2mgkg ⁻¹	MRL (mgkg ⁻¹)*
<i>Pome fruits</i>				
• Pear	82.3 \pm 4.8^b	82.2 \pm 2.9^b	111.8 \pm 2.6 ^b	99.6 \pm 5.8 (0.05)
• Apple	77.7 \pm 5.0^b	93.2 \pm 11.2^b	106.3 \pm 17.8^b	Not detected (0.05)
• Quince	32.0 \pm 4.7 ^a	20.2 \pm 1.8 ^a	38.3 \pm 10.0 ^a	88.9 \pm 6.0 (0.05)
<i>Citrus</i>				
• Lemon	103.6 \pm 7.7^b	114.8 \pm 3.8 ^b	105.8 \pm 5.6^c	105.8 \pm 5.6 (0.2)
• Mandarin	69.1 \pm 1.9 ^a	78.8 \pm 6.9^a	73.2 \pm 6.8^b	73.2 \pm 6.8 (0.2)
• Orange	58.2 \pm 9.3 ^a	63.8 \pm 6.6 ^a	56.8 \pm 4.3 ^a	56.8 \pm 4.3 (0.2)
<i>Stone fruits</i>				
• Apricot	88.0 \pm 12.0^a	120.6 \pm 6.3 ^b	100.0 \pm 14.8^a	120.0 \pm 4.3 (0.1)
• Cherry	70.9 \pm 9.5^a	79.9 \pm 7.3^a	88.5 \pm 3.7^a	166.0 \pm 15.0 (0.01)
• Peach	78.8 \pm 1.4^a	83.4 \pm 1.6^a	87.7 \pm 8.9^a	Not detected (0.05)
<i>Leafy vegetables</i>				
• Lettuce	108.8 \pm 2.3^b	97.7 \pm 1.5^a	97.9 \pm 1.3^a	97.9 \pm 1.3 (0.2)
• Chicory	72.4 \pm 3.8^a	119.3 \pm 2.8 ^b	110.4 \pm 4.6 ^a	Not detected (0.01)
• Spinach	98.8 \pm 9.4^b	117.9 \pm 2.5 ^b	128.4 \pm 15.6 ^a	288.4 \pm 2.7 (0.01)
<i>Fruiting vegetables</i>				
• Cucumber	96.7 \pm 13.9^a	98.8 \pm 3.9^a	102.1 \pm 2.2^a	107.5 \pm 8.2 (1.0)
• Pepper	82.7 \pm 2.3^a	96.2 \pm 0.9^a	108.2 \pm 6.4^a	Not detected (0.01)
• Tomato	98.8 \pm 3.8^a	96.8 \pm 0.8^a	95.2 \pm 16.8^a	Not detected (0.05)
<i>Various</i>				
• Kiwi fruits	87.9 \pm 7.1	75.7 \pm 6.7	92.8 \pm 8.7	Not detected (0.01)
• Table grapes	76.8 \pm 4.7	90.0 \pm 4.1	91.0 \pm 5.4	Not detected (0.01)
• Strawberries	102.2 \pm 1.2	108.0 \pm 5.2	103.4 \pm 12.3	210.4 \pm 3.5 (0.01)

29 a, b, c: means within a plant product category and fortification level lacking a
 30 common superscript letter are different ($p < 0.05$).

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3 31 * Some MRLs are equal to one of the rest examined concentrations (i.e. 0.2 and
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34 Table V. Percentage recoveries and RSDs of methidathion in the different plant
 35 products, classified by botanical characteristics, and in different fortification levels.
 36 Bold letters designate recoveries within the acceptable range of recovery (70–110%).
 37 Values in parenthesis indicate the levels of MRLs established by EU.

Plant products	Recovery \pm RSD (%)			
	1.5mgkg ⁻¹	0.5mgkg ⁻¹	0.2mgkg ⁻¹	MRL (mgkg ⁻¹)*
<i>Pome fruits</i>				
• Pear	69.8 \pm 1.4^b	62.1 \pm 3.1 ^b	74.4 \pm 1.6^b	74.2 \pm 7.2 (0.3)
• Apple	81.9 \pm 2.9^c	77.2 \pm 2.8^c	90.8 \pm 1.0^c	88.8 \pm 1.9 (0.3)
• Quince	40.5 \pm 0.8 ^a	40.2 \pm 2.2 ^a	46.0 \pm 1.7 ^a	73.6 \pm 10.8 (0.3)
<i>Citrus</i>				
• Lemon	79.7 \pm 0.3^c	86.1 \pm 1.6^b	73.0 \pm 6.4^b	81.9 \pm 8.7 (2.0)
• Mandarin	59.1 \pm 2.8 ^a	40.7 \pm 0.4 ^a	44.6 \pm 13.1 ^a	61.2 \pm 5.1 (2.0)
• Orange	44.4 \pm 0.8 ^b	37.6 \pm 5.4 ^a	44.8 \pm 14.2 ^a	53.2 \pm 4.5 (2.0)
<i>Stone fruits</i>				
• Apricot	70.9 \pm 2.5^a	85.9 \pm 2.8^b	100.9 \pm 4.2^b	100.9 \pm 4.2 (0.2)
• Cherry	76.0 \pm 2.2^a	87.9 \pm 2.2^b	90.5 \pm 10.4^b	Not detected (0.02)
• Peach	68.3 \pm 2.0 ^a	59.8 \pm 3.4 ^a	60.0 \pm 17.7 ^a	60.0 \pm 17.7 (0.2)
<i>Leafy vegetables</i>				
• Lettuce	60.3 \pm 2.1 ^a	70.9 \pm 0.7^a	76.5 \pm 13.7^a	Not detected (0.02)
• Chicory	73.9 \pm 4.5^b	76.2 \pm 2.4^b	71.0 \pm 9.4^a	Not detected (0.02)
• Spinach	53.9 \pm 1.3 ^a	68.2 \pm 1.6 ^a	73.9 \pm 8.6^a	Not detected (0.02)
<i>Fruiting vegetables</i>				
• Cucumber	84.8 \pm 3.4^b	106.4 \pm 4.9^a	104.5 \pm 3.4^a	Not detected (0.02)
• Pepper	72.0 \pm 4.1^a	102.3 \pm 2.8^a	112.2 \pm 0.5 ^a	Not detected (0.02)
• Tomato	97.1 \pm 4.8^c	93.9 \pm 4.0^a	109.5 \pm 1.3^a	109.5 \pm 1.3 (0.2)
<i>Various</i>				
• Kiwi fruits	58.7 \pm 3.4	53.5 \pm 4.1	76.6 \pm 3.7	Not detected (0.02)
• Table grapes	91.8 \pm 2.8	98.0 \pm 2.8	98.0 \pm 4.6	98.0 \pm 2.8 (0.5)
• Strawberries	60.5 \pm 1.6	86.4 \pm 2.1	81.4 \pm 5.0	292.6 \pm 8.9 (0.02)

38 a, b, c: means within a plant product category and fortification level lacking a
 39 common superscript letter are different (p<0.05).

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