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

Abstract

A study of the matrix effect was performed in order to evaluate the influence of some matrices on the gas chromatographic responses of representative organophosphorus insecticides. Particularly, 3 fortification levels and the Maximum Residual Level (MRL) of 4 organophosphorus pesticide standard solutions were added in 18 matrices (15 belonging to 5 specific botanical categories and 3 botanically unclassified). The recoveries of the examined pesticides were determined using a simple official multiresidue method of detection, without any additional clean-up step. Recoveries were estimated based on standards prepared in solvent. The recovery percentages of the most polar pesticides, especially methamidophos (20.2–288.4%), were much higher than those of non polar ones (chlorpyrifos and methidathion 25.7–136.4% and 37.6–292.6% respectively), except for quince. Pronounced matrix effects (>120%) were observed to the lowest fortification levels (MRLs established by EU), of dimethoate and methamidophos (i.e. the most polar analytes) in the majority of product extracts. Furthermore, it was proved that there is no correlation between the classification of plant products, according to their botanical characteristics, and the recoveries of pesticides in the equivalent extracts. Indeed, there were significant differences in the recoveries of pesticides in extracts, derived from matrices belonging to the same botanical group (especially in the categories of pome fruits and citrus). Consequently, it was shown that, under the examined conditions, obtaining recovery

26 data, derived from only one representative matrix, with purpose to validate an official
27 method in its botanical category is, possibly, an erroneous practice.

28

29 **Keywords:** *matrix effect, organophosphorus pesticide residue analysis, ethyl acetate,*
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

and a phenomenon, known as “matrix-induced chromatographic response enhancement”, which was first described by Erney et al. (1993), and causes excessively high recovery results. This phenomenon takes place during analysis of samples that contain a wide range of matrix components (e.g. pigments, waxes, lipids and other non volatile constituents) that may remain after the preparation of the sample and the additional step of clean-up (Godula et al. 1999). Such compounds accumulate in the GC inlet and/or in the front part of a capillary column. Particularly, during analysis of a pesticide(s) standard solution, more active sites in the injection liner are available for the certain analyte(s), compared to those available during analysis of a sample containing also matrix components (Schenck and Lehotay 2000). This is due to the fact that the latter components block the active sites of injection liner (Erney et al. 1993).

Consequently, matrix effect is considered, nowadays, as one of the most persistent sources of uncertainty in pesticide residue analysis (Cuadros-Rodriguez et al. 2002; Egea Gonzalez et al. 2002). However, available studies have focused on collecting recovery data of pesticides examining combinations of few primary crop products, many pesticides and many fortification levels (Dorea et al. 1995; Hajšlová et al. 1998). Other studies involve determination of the pesticides recovery by many products belonging only to one plant commodity group (Cai et al. 1995; Egea Gonzalez et al. 2002). Therefore, there is need to comparatively evaluate various matrices from various botanical categories per analytical method to determine the uncertainty due to matrix effect. Moreover, the recovery studies commonly involve a few matrices fortified with a mixture of pesticides. Various food matrices fortified with one pesticide should also be included in pesticide recovery studies. This would clearly illustrate the matrix effect *per* pesticide.

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81 The objective of this work was the evaluation of the matrix effects on the recovery
82 of four commonly applied pesticides of different physicochemical properties
83 (especially polarity), fortified in plant products of various botanical categories, at
84 three indicative levels (0.2, 0.5 and 1.5mgkg⁻¹) and MRL (when different from the
85 fortification level studied).

86
87 **Materials and Methods**

88 *Materials and Reagents*

89 The solvent used was ethyl acetate (Merck, Darmstadt, Germany, 110972) and was of
90 pesticide grade. Pesticide standards (chlorpyrifos, dimethoate, methamidophos and
91 methidathion) of more than 98% purity were obtained from Chem Service (Chem
92 Service, West Chester, PA, USA). Stock solutions were prepared in ethyl acetate and
93 working standard mixtures were obtained with appropriate dilutions before use.
94 Particularly, the standards were used for the preparation of stock standard solutions
95 for each pesticide at 100mgkg⁻¹ in the used solvent and stored at -18°C. In Table I,
96 there is the list of the investigated organophosphorus pesticides along with some of
97 their physicochemical characteristics (Tomlin 1997). Anhydrous sodium sulfate for
98 residue analysis was of pesticide grade (Riedel – de Haën, Hanover, Germany,
99 13464).

100 [Insert Table I about here]

101 *Samples*

102 **Eighteen different commodities were obtained from a local market for organic**
103 **farming produce.** Particularly, pome fruits (pears, apples and quinces), citrus (lemons,
104 mandarins and oranges), stone fruits (apricots, cherries and peaches), fruiting
105 vegetables (cucumbers, tomatoes and peppers), leafy vegetables (lettuce, spinach and

chicory) and three other products not belonging to a specific group (kiwi fruits, table grapes and strawberries) were used as representative matrices in the experiment. These commodities were checked by gas chromatography to ensure the absence of pesticide residues and their suitability for the analysis.

Analytical Procedure

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

Gas Chromatographic determination

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

0.32mm id x 0.25 μ m film thickness (Restek, USA, 12624) capillary column. The injection port temperature was 260°C and the detector temperature 300°C. The oven temperature was programmed as follows: initial temperature 70°C for 1min, raised at 15°Cmin⁻¹ to 130°C for 0min, raised at 5°Cmin⁻¹ to 230°C and finally raised at 20°Cmin⁻¹ to 250°C with a residence time of 13min. Helium carrier gas at flow rate of 8mLmin⁻¹ was used. Triplicate extracts (2 μ L) were injected and quantification of the insecticides was performed by automatic integration of the peak areas (European Communities 1999). Quantification/recovery of the pesticides in the fortified samples was carried out by comparing the detector responses for each of the three independent samples to those measured in a calibration standard, which was injected both before and after each sample. It should be noticed that maintenance application of the system took place at the end of a pesticide analytical “sequence”, defined as the total of samples prepared with one fortification level of one analyte in all 18 matrices. Product extracts were analyzed in the same sequence so that the effect of matrix components can be considered similar in the target analysis. Maintenance included changes associated with the injection site and the front part of the chromatography column being connected with the injection site. Specifically, at the end of an analytical sequence, septum and injection liner were replaced and the good operation of the system was evaluated by injecting the used solvent and a standard solution, containing the investigated pesticides. Cutting the front part of the capillary column was decided upon indications (such as peak width/height/tailing and integrated area) from the injections of standard solutions. Furthermore, by the end of each sequence, 2 μ L of a standard solution (0.1mgkg⁻¹) of pesticides mixture in ethyl acetate was injected to evaluate the reliability of column. In general, the performance of the GC column remained satisfactory for approximately 3–4 sequences.

156 *Statistical analysis*

157 One way analysis of variance (ANOVA) was applied in order to examine the fixed
158 effects of three experimental factors (pesticide standard, fortification level, matrix) in
159 the recovery of pesticides using the general linear models procedures of SPSS. Then
160 least squared means of recoveries in triplicate trials were calculated and significant
161 differences were estimated by post-hoc tests using Tuckey's method. A significant
162 level of 0.05 was used for all statistical analysis.

164 **Results and Discussion**

165 The first part of this experiment includes the estimate of the NPD response in the
166 examined pesticides. Areas in curves, obtained by injections of pesticide standard
167 solutions, were the means of three replicates for each concentration level. All
168 responses correspond to linear equations in the studied range of $0.01\text{--}2.5\text{mgkg}^{-1}$, as
169 squared correlation coefficients in this model were found to be >0.9847 ($R^2=0.9959$;
170 $R^2=0.9933$; $R^2=0.9847$; $R^2=0.995$ for chlorpyrifos, dimethoate, methamidophos and
171 methidathion respectively).

172 The performance of an analytical method is assessed by several criteria. The
173 recoveries of all used pesticides should be in the range 70–110% with relative
174 standard deviations (RSDs) below 20% (European Communities 1999). In this study,
175 in order to estimate the reliability of the used method, recovery trials were conducted
176 at four fortification levels, chosen as representative range of pesticide concentrations
177 found in the majority of different pesticide–matrix combinations. Specifically, every
178 product was fortified with the target pesticide solutions at the level of MRLs
179 established by EU and at fortification levels of 0.2, 0.5 and 1.5mgkg^{-1} . The results of
180 the recovery tests are presented at Tables II–V.

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[Insert Tables II-V about here]

The type of the examined pesticides was found to influence the occurrence of matrix effect ($p<0.05$), as the recoveries for the same matrix vary with the different pesticides. Among the used pesticides, the highest recoveries and matrix effects were observed to methamidophos and dimethoate, in the majority of product extracts (especially in the lowest fortification levels). It is notable that methamidophos was not detected in the first injections after the maintenance of the GC system (changing the injection liner) and especially in the first samples of analysis sequence. In these cases, the analysis was repeated, as multiple injections of uncleaned matrix extracts were proved to have a potential effect on the NPD response in this analyte in contrast to the non polar ones. Also, it was found that methamidophos recoveries were of poorer precision in the three repeated injections, as it can be observed from RSDs presented at Table IV. Our findings are in agreement with those of Cai et al. (1995), while similar behavior has been reported for captan and other polar analytes (Hajšlová et al. 1998). In contrast to methamidophos and dimethoate, the lowest recovery portions were observed to the non polar analytes chlorpyrifos and methidathion. However, the only cases where matrix effect was observed in those analytes were: pepper in fortification level 0.2mgkg^{-1} and strawberries (MRL) for methidathion and cucumber (MRL) for chlorpyrifos (Tables II and V). These results are in agreement with Erney et al. (1993), who supported that changes in the recovery portion vary with the chemical structure of the pesticide and those compounds containing P=O bonds, like methamidophos, were identified as tending to give particularly high recoveries. Schenck and Lehotay (2000) noticed that compounds with P=O bonds tend to exhibit more matrix effects rather than those with P=S bonds, like the one present in the molecule of dimethoate, chlorpyrifos and methidathion, because of the highest

206 polarity of these bonds. Moreover, as it can be deduced from Table 1 regarding the
207 physicochemical properties (especially values of w.s. and $\log k_{ow}$, which are a degree
208 of polarity), methamidophos and dimethoate are more polar than the other two and for
209 this reason their recoveries are higher, which agrees with the statement of Hajšlová et
210 al. (1998) that the probability of the matrix effect occurrence is higher for more polar
211 pesticides.

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

224 It was also observed that in the analysis of some matrices fortified with
225 dimethoate, methamidophos and methidathion at the MRL level, the analytes were
226 under the limit of determination, whereas in the case of other commodities fortified at
227 the same level, the analyte showed an evident peak. Specifically, dimethoate was
228 determined at the level of MRL in all matrices, apart from apricot and peach extracts.
229 Almost the same performance was obtained with methamidophos, where chicory,
230 pepper, kiwi and grapes fortified extracts gave no integrated peaks, at the MRL level

231 of 0.01mgkg⁻¹. In samples fortified with methidathion in the level of 0.02mgkg⁻¹, the
232 analyte was detected only in the strawberry extract, contrary to other examined
233 matrices, as cherry, chicory, lettuce, spinach and kiwi fruit, fortified in the same level
234 of MRL. Consequently, the determination of the analyte, at the same trace level in
235 different matrices, is probably influenced by the type of the matrix. This performance
236 was not followed by chlorpyrifos, whose MRL levels are comparatively higher and all
237 peaks were easily integrated.

238 Recovery portion of pesticides also depends on the chemical composition of the
239 matrix ($p < 0.05$). It was found that the type of co-extracts that remains in the final
240 sample leads markedly to different detector response. As a consequence, the botanical
241 categories examined in the experiment can be classified according to the mean
242 recovery portions of the used pesticides (especially in the three fortification levels) in
243 the order: fruiting vegetables and table grapes > strawberries and leafy
244 vegetables > stone fruits and kiwi fruits > pome fruits and citrus. It seems that the
245 highest recoveries were observed to samples containing more non volatile compounds
246 (such as chlorophylls in leafy vegetables, carotenoids in fruiting vegetables, waxes in
247 grapes, lipids in strawberries) compared to samples with more volatile compounds.
248 Thus, higher recoveries are possibly associated with the entrapment of non volatile
249 compounds in the injection liner which are able to cover active sites in the injection
250 liner and/or the front of analytical column and may conduct to higher recoveries. The
251 scientific evidence suggests that more distinct matrix effects have been reported for
252 extracts derived from matrices rich in pigments and lipids (Hajšlová et al. 1998;
253 Godula et al. 1999; Anastassiades et al. 2003). Also, when co-extracts, like those
254 mentioned, are accumulated in the inlet, they can create new active sites, intensifying
255 the presence of the phenomenon (Anastassiades et al. 2003).

Furthermore, from Tables II–V, it can be revealed that there is no correlation between the classification of plant produce by botanical characteristics and the recoveries of pesticides in the respective extracts, since product extracts belonging to the same botanical category present differences in the pesticides recovery. This statement is more evident especially in the categories of pome fruits, in which quince extracts gave extremely low recoveries in contrast with apple and pear extracts (Tables II–V). Similarly in the citrus category, lemon extracts gave much higher recoveries in contrast with mandarin and orange extracts ($p < 0.05$) (Tables II–V). On the contrary, the three examined products belonging to stone fruits and leafy vegetables present smaller variations, while those belonging to fruiting vegetables present unvarying behavior in the recovery portion of pesticides ($p > 0.05$).

In the present study, there are dramatically low recoveries in pesticides in orange extracts, fact opposed to other studies using ethyl acetate as the extraction solvent and clean-up step (Dorea et al. 1995; Hajšlová et al. 1998). Even after the required conditioning of the GC system and three months later, the analysis of the specific lot (frozen oranges), with an independent extract preparation in triplicates, gave the same results. On the contrary, a new lot of oranges from organic produce, analyzed by the same method, gave much higher recoveries in similar combinations of pesticides and fortification levels (results not shown) and the difference was more pronounced in the more polar methamidophos and dimethoate at the fortification level of 1 mg kg^{-1} . Probably, this behavior may be attributed to the specific lot and its different chemical composition, depending on harvest time.

Also, it is remarkable that recoveries of pesticides in quince extracts are extremely low in every pesticide and fortification level in comparison with every plant product 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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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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12 285 of active ingredients in the extraction step.

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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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21 289 of both the examined pesticides in this study and other organophosphorus pesticide
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23 290 standards analyzed in our laboratory. These may be lipophilic compounds derived
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25 291 from those matrices not removed by the extraction method, as there has been observed
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27 292 similar behavior in uncleaned sample extracts in ethyl acetate (Cai et al. 1995;
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29 293 Maštovská and Lehotay 2004). The fact that the same peak in orange extracts
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31 294 appeared in every orange, either of organic produce or of conventional crop, and
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33 295 detected in the peel orange extract analyzed itself compared to the analysis of orange
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35 296 juice, may be the reason why some citrus peels require clean-up step, described by
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37 297 Dorea et al. (1995).

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39 298 Finally, it should be addressed that matrix enhancement effect is difficult to study
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41 299 because the GC system changes as matrix components are progressively deposited in
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43 300 the injection port and front of the analytical column (Schenck and Lehotay 2000).
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45 301 Moreover, the injection technique has been found to play a major role on the
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47 302 occurrence of matrix effect. Specifically, the use of cold on-column injection is
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49 303 considered as one of the most practical approaches by which, pesticides thermolysis
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51 304 and decomposition or adsorption inside the inlet could be avoided (Wylie 1996;
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53 305 Godula et al. 1999). With the specific technique, more accurate results have been
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observed, especially for troublesome analytes, compared to splitless injection as long as the chromatography system remains clean (Wylie 1996). Furthermore, it is likely that polar analytes, such as methamidophos, and matrices, containing especially non volatile compounds, could be analyzed by on-column injection with the parallel use of a packed column or a deactivated precolumn (to keep most of the remaining matrix constituents of the extract) connected to the injector site. However, the disadvantage of on-column injection is that it seems to be impractical for applications of complex or relatively uncleaned matrices, because it requires more maintenance of the column and thus, hot splitless injection tends to be preferable (Anastassiades et al. 2003). The effect of maintenance application by changing the injection liner and/or the column is also unpredictable, because as Godula et al. (1998) indicated, the history of the GC system (especially changes in the injection port) plays an important role in the occurrence of matrix effects. Consequently, recoveries of pesticides are not reproducible and the effects of co-extracts can not be considered as stable and foreseeable. For these reasons, it is better to provide recovery data and validate the used method in only one produce, especially when the product is suspected for matrix effects, so that the existence of matrix effect can be checked rather than providing recoveries in one produce and validate the method in the whole botanical category.

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

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331 matrix, and fortification level on the pesticide recovery can not always be predicted.

332 The above suggest that validation of an official method for the analysis of pesticide

333 residues should not be based only on the botanical categories of plant products. Such

334 practice may be useful, for the simplification of issuing validation, when matrix–

335 matched calibration standards and/or extensive clean–up of the samples are used prior

336 to the final chromatographic step. Conversely, the same practice is insufficient for

337 quantification with standards in neat solvent and/or in the final extract without

338 additional clean–up step. However, in order to further examine the analytical

339 performance of different product extracts, a matrix–matched calibration procedure for

340 each product should be severally carried out. Furthermore, the analysis of each group

341 of commodities fortified in many more levels, with a higher number of pesticides is

342 strongly recommended and may possibly explicate the differences between the

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)	logk _{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 logk_{ow}: log of n – octanol partition coefficient

405 M.p.: melting point.

406 V.p.: vapour pressure (25°C).

Table II. Percentage recoveries and RSDs of chlorpyrifos in the different plant products, classified by botanical characteristics, and in different fortification levels. Bold letters designate recoveries within the acceptable range of recovery (70–110%). 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)

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

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413 * Some MRLs are equal to one of the rest examined concentrations (i.e. 0.2 and
414 0.5mgkg⁻¹). For this reason the respective recoveries appear in two columns of the
415 same row in the Table

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Table III. Percentage recoveries and RSDs of dimethoate in the different plant products, classified by botanical characteristics, and in different fortification levels. Bold letters designate recoveries within the acceptable range of recovery (70–110%). 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)

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

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422 * Some MRLs are equal to one of the rest examined concentrations (i.e. 0.2 and
423 0.5mgkg⁻¹). For this reason the respective recoveries appear in two columns of the
424 same row in the Table

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Table IV. Percentage recoveries and RSDs of methamidophos in the different plant products, classified by botanical characteristics, and in different fortification levels. Bold letters designate recoveries within the acceptable range of recovery (70–110%). 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)

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

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431 * Some MRLs are equal to one of the rest examined concentrations (i.e. 0.2 and
432 0.5mgkg⁻¹). For this reason the respective recoveries appear in two columns of the
433 same row in the Table

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Table V. Percentage recoveries and RSDs of methidathion in the different plant products, classified by botanical characteristics, and in different fortification levels. Bold letters designate recoveries within the acceptable range of recovery (70–110%). 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)

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

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440 * Some MRLs are equal to one of the rest examined concentrations (i.e. 0.2 and
441 0.5mgkg⁻¹). For this reason the respective recoveries appear in two columns of the
442 same row in the Table

For Peer Review Only

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).

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

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

a, b, c: means within a plant product category and fortification level lacking a 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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Table III. Percentage recoveries and RSDs of dimethoate in the different plant products, classified by botanical characteristics, and in different fortification levels. Bold letters designate recoveries within the acceptable range of recovery (70–110%). 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	90.9 ± 1.2^c	86.7 ± 2.5^c	98.7 ± 6.0^b	118.1 ± 6.2 (0.02)
• Apple	71.6 ± 5.0^b	68.4 ± 3.8 ^b	88.9 ± 1.5^b	97.1 ± 15.5 (0.02)
• Quince	22.8 ± 3.2 ^a	45.1 ± 2.8 ^a	28.3 ± 12.2 ^a	103.0 ± 5.7 (0.02)
<i>Citrus</i>				
• Lemon	84.1 ± 6.0^a	97.4 ± 2.9^c	97.3 ± 3.6^c	138.7 ± 18.3 (0.02)
• Mandarin	67.9 ± 0.5 ^a	58.3 ± 0.2 ^a	42.0 ± 8.5 ^a	95.2 ± 10.6 (0.02)
• Orange	73.8 ± 0.6^a	86.8 ± 4.9^b	68.3 ± 3.0 ^b	121.8 ± 4.3 (0.02)
<i>Stone fruits</i>				
• Apricot	85.0 ± 1.3^a	108.5 ± 0.5^b	113.8 ± 3.8 ^b	Not detected (0.02)
• Cherry	93.1 ± 1.1^b	104.7 ± 1.4^b	115.3 ± 10.7 ^b	90.4 ± 2.3 (1.0)
• Peach	92.4 ± 3.7^b	78.3 ± 0.9^a	80.5 ± 6.6^a	Not detected (0.02)
<i>Leafy vegetables</i>				
• Lettuce	92.3 ± 1.3^a	127.4 ± 0.6 ^c	116.2 ± 3.3 ^a	127.4 ± 0.6 (0.5)
• Chicory	76.9 ± 1.3^b	112.6 ± 0.8 ^b	103.3 ± 3.5^a	138.4 ± 5.9 (0.02)
• Spinach	81.1 ± 2.2^a	67.1 ± 5.0 ^a	105.7 ± 5.5^a	151.3 ± 9.2 (0.02)
<i>Fruiting vegetables</i>				
• Cucumber	88.4 ± 1.8^{ab}	118.1 ± 0.5 ^b	103.2 ± 1.4^a	157.9 ± 14.8 (0.02)
• Pepper	86.3 ± 2.3^b	118.8 ± 1.3 ^b	117.6 ± 1.9 ^b	137.9 ± 5.4 (0.02)
• Tomato	82.9 ± 1.4^a	87.1 ± 6.6^a	107.0 ± 3.6^{ab}	165.5 ± 12.9 (0.02)
<i>Various</i>				
• Kiwi fruits	80.2 ± 2.0	85.1 ± 3.7	87.4 ± 9.3	141.9 ± 8.5 (0.02)
• Table grapes	92.9 ± 1.8	87.0 ± 6.4	89.0 ± 3.3	150.0 ± 13.5 (0.02)
• Strawberries	89.5 ± 0.3	111.6 ± 0.6	135.4 ± 3.2	146.3 ± 7.3 (0.02)

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

22 * Some MRLs are equal to one of the rest examined concentrations (i.e. 0.2 and
23 0.5mgkg⁻¹). For this reason the respective recoveries appear in two columns of the
24 same row in the Table

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Table IV. Percentage recoveries and RSDs of methamidophos in the different plant products, classified by botanical characteristics, and in different fortification levels. Bold letters designate recoveries within the acceptable range of recovery (70–110%). 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)

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

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Table V. Percentage recoveries and RSDs of methidathion in the different plant products, classified by botanical characteristics, and in different fortification levels. Bold letters designate recoveries within the acceptable range of recovery (70–110%). 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	69.8 ± 1.4^b	62.1 ± 3.1 ^b	74.4 ± 1.6^b	74.2 ± 7.2 (0.3)
• Apple	81.9 ± 2.9^c	77.2 ± 2.8^c	90.8 ± 1.0^c	88.8 ± 1.9 (0.3)
• Quince	40.5 ± 0.8 ^a	40.2 ± 2.2 ^a	46.0 ± 1.7 ^a	73.6 ± 10.8 (0.3)
<i>Citrus</i>				
• Lemon	79.7 ± 0.3^c	86.1 ± 1.6^b	73.0 ± 6.4^b	81.9 ± 8.7 (2.0)
• Mandarin	59.1 ± 2.8 ^a	40.7 ± 0.4 ^a	44.6 ± 13.1 ^a	61.2 ± 5.1 (2.0)
• Orange	44.4 ± 0.8 ^b	37.6 ± 5.4 ^a	44.8 ± 14.2 ^a	53.2 ± 4.5 (2.0)
<i>Stone fruits</i>				
• Apricot	70.9 ± 2.5^a	85.9 ± 2.8^b	100.9 ± 4.2^b	100.9 ± 4.2 (0.2)
• Cherry	76.0 ± 2.2^a	87.9 ± 2.2^b	90.5 ± 10.4^b	Not detected (0.02)
• Peach	68.3 ± 2.0 ^a	59.8 ± 3.4 ^a	60.0 ± 17.7 ^a	60.0 ± 17.7 (0.2)
<i>Leafy vegetables</i>				
• Lettuce	60.3 ± 2.1 ^a	70.9 ± 0.7^a	76.5 ± 13.7^a	Not detected (0.02)
• Chicory	73.9 ± 4.5^b	76.2 ± 2.4^b	71.0 ± 9.4^a	Not detected (0.02)
• Spinach	53.9 ± 1.3 ^a	68.2 ± 1.6 ^a	73.9 ± 8.6^a	Not detected (0.02)
<i>Fruiting vegetables</i>				
• Cucumber	84.8 ± 3.4^b	106.4 ± 4.9^a	104.5 ± 3.4^a	Not detected (0.02)
• Pepper	72.0 ± 4.1^a	102.3 ± 2.8^a	112.2 ± 0.5 ^a	Not detected (0.02)
• Tomato	97.1 ± 4.8^c	93.9 ± 4.0^a	109.5 ± 1.3^a	109.5 ± 1.3 (0.2)
<i>Various</i>				
• Kiwi fruits	58.7 ± 3.4	53.5 ± 4.1	76.6 ± 3.7	Not detected (0.02)
• Table grapes	91.8 ± 2.8	98.0 ± 2.8	98.0 ± 4.6	98.0 ± 2.8 (0.5)
• Strawberries	60.5 ± 1.6	86.4 ± 2.1	81.4 ± 5.0	292.6 ± 8.9 (0.02)

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

* Some MRLs are equal to one of the rest examined concentrations (i.e. 0.2 and 0.5mgkg⁻¹). For this reason the respective recoveries appear in two columns of the same row in the Table

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