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1 **Optimization of a DI-SPME-GC-MS/MS Method for Multi-residue Analysis of Pesticides in Waters**

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14
15 **Abstract**

16 This paper discusses the optimization and validation of a complete and simple method for the
17 simultaneous determination of 48 pesticides in water by combining direct immersion solid-phase micro-
18 extraction (DI-SPME) and gas chromatography-ion trap tandem mass spectrometry (GC-ITMS/MS). For the
19 extraction, the different SPME parameters were tested and optimized. As a result, the polyacrylate fiber (PA 85
20 μm) was selected in direct immersion mode; the extraction temperature was set to 60 °C with an extraction time
21 of 45 minutes and a stirring speed of 500 rpm; the thermal desorption time of the fiber in the injector port was
22 fixed to 10 minutes at 275 °C. Concerning the analysis, MS/MS parameters were optimized and figures of merit
23 were compared. Later, the method was validated and showed good linearity in the concentration ranging from
24 0.05 to 100 $\mu\text{g L}^{-1}$. The reproducibility of measurements expressed as the relative standard deviation (% RSD)
25 was found to be satisfactory. Furthermore, the detection limits for all the compounds were between 0.001 to
26 0.458 $\mu\text{g L}^{-1}$, except for methomyl and hexachlorobenzene (1.09 and 0.99 $\mu\text{g L}^{-1}$ respectively). Finally, the
27 proposed DI-SPME-GC-MS/MS method was tested successfully for water samples collected along the
28 watershed of Abou Ali River (North Lebanon).

29
30 **Keywords:** Pesticides, GC-MS/MS, DI-SPME, Abou Ali River, water analysis

31 **1. Introduction**

32

33 Pesticides play an important role in preventing yield damage and crop destruction by controlling pests.
34 These compounds have been intensively used, in the last decades, for the purpose of increasing agricultural
35 production to meet the boost in food supply caused by the continuous growth of the global population [1].
36 However, the inappropriate and uncontrolled usage of these pesticides may lead to pollution of different
37 environmental matrices. [2]. Thus, pesticides can be found not only in sediments and in the atmosphere but also
38 in water resources including surface and groundwater [3].

39 After their application, pesticides can be transferred to groundwater systems by percolation and surface
40 water via runoff following rainfall events and/or irrigation practices [4]. The existence of pesticide residues in
41 water can cause harmful effects on human health, aquatic life and the ecosystem itself. Therefore, their
42 monitoring has been a major global concern and strict regulations have been established [5, 6]. In this context,
43 the European Union (EU) Drinking Water Directive (98/83/EC) has defined a maximum concentration of 0.1 µg
44 L⁻¹ for every single pesticide and 0.5 µg L⁻¹ for the sum of pesticides in water used for human consumption [7].
45 Furthermore, an EU Water Frame Directive (WFD, 2000/60/EC) was first implemented in October 2000. The
46 later was followed by a new EU WFD (2006/118/EC) for the protection of the aquatic environment in whose
47 Annex I, the permissible limits for the priority and hazardous substances were identified [8]. A priority
48 substance directive (2008/105/EC) was subsequently set in 2008 and was amended in 2013 by the directive
49 (2013/39/EU) in which the environmental standards and list of compounds were modified [9, 10].

50 For the analysis and quantification of pesticides in water, Gas chromatography-mass spectrometry (GC-
51 MS) is the most commonly implemented methodology. This system is distinguished by its high selectivity and
52 capability to achieve low detection limits and mass resolution; thus, making it suitable for the analysis of
53 pesticide residues from various chemical groups [11]. Moreover, the ability of the MS detector to perform
54 tandem mass spectrometry (MS/MS) promotes the analysis of pesticides in the low picogram levels, even in the
55 presence of interferences, by reducing background noise significantly [12]. Due to the low levels of pesticides in
56 environmental matrices, their diversity and different physicochemical characteristics [13], their detection
57 requires the application of a fast, reliable, green and cost-effective pre-concentration technique [14, 15]. Solid-
58 Phase Micro-Extraction (SPME) is a solvent-free [16], highly selective [17] and sensitive technique [18]
59 recently applied for the detection of a broad range of pesticides and organic compounds in water [19, 11, 20, 21,
60 22]. It is an alternative to the traditional approaches such as liquid-liquid extraction (LLE) [23] and Solid-Phase
61 Extraction (SPE) [24] [25] that are known by their extended time procedure and a large volume of toxic solvents
62 required [20].

63 The objective of this study is to develop a fully automated, simple and effective SPME-GC- ion trap (IT)
64 MS/MS method for the simultaneous analysis of 48 pesticides, belonging to 12 different chemical group (Table
65 1), in water samples. The selection of pesticides was based on field surveys, meetings with farmers, agricultural
66 engineers and suppliers in the area under study as well as previous studies depicting the pesticides that were
67 detected in the water resources in Lebanon. To the best of our knowledge, in the literature to dates, no previous
68 references have described the use of SPME for the analysis of this wide variety of chemical groups of pesticides
69 in one single run. To achieve high sensitivity and selectivity, the influence of different SPME parameters, such
70 as fiber type, extraction mode, extraction temperature, stirring speed, extraction and desorption time, on the

71 extraction proficiency were studied in details. Likewise, the conditions and parameters of the gas
72 chromatography GC and tandem MS/MS were optimized. Afterwards, the optimized method was validated by
73 assessing the linearity range (LR), the limit of detection (LOD), the limit of quantification (LOQ), precision (%
74 RSD) and the average recovery at different fortification levels. Finally, this method was used for the analysis of
75 surface water samples collected from the watershed of “Abou Ali” River in North Lebanon. The sustainability,
76 reliability and fast automation of the developed technique makes it practical to be implemented for routine
77 analysis of multiclass pesticides in laboratories.

79 2. Materials and methods

81 2.1 Chemicals, materials and reagents

82 Three separate certified standard pesticide mixtures, highly pure (> 98%) and containing 10 mg L⁻¹ of
83 each individual pesticide were purchased from LGC Standards (Germany). The composition of each mixture is
84 represented as follow: Mixture1 (cyprodinil, myclobutanil, penconazole, tebuconazole, alachlor,
85 bromopropylate, buprofezin, fludioxonil, kresoxim-methyl, metalaxyl, pendimethalin, procymidone,
86 propyzamide, trifluralin, vinclozolin, chlorpropham, propoxur); Mixture2 (aldrin, 4,4’-
87 dichlorodiphenyltrichloroethane (4,4’-DDT), 4,4’-dichlorodiphenyldichloroethylene (4,4’-DDE), 4,4’-
88 dichlorodiphenyldichloroethane (4,4’-DDD), dieldrin, endosulfan-alpha, endosulfan-beta, endosulfan-total
89 (sulfate), alpha-hexachlorohexane (alpha-HCH), beta-HCH, gamma-HCH (Lindane), delta-HCH, heptachlor-
90 exo-epoxide, Hexachlorobenzene (HCB), Methoxychlor, quintozene, chlorpyrifos, chlorpyrifos-methyl) and
91 Mixture 3 (diazinon, dichlorvos, ethion, ethoprophos, pirimiphos-methyl, bifenthrin, lambda-cyhalothrin (λ-
92 cyhalothrin), cypermethrin, amitraz, pyridaben, dimethoate, methomyl and methamidophos). The deuterated
93 internal standards, alachlor-d₁₃, and beta-endosulfan-d₄ (purity 98%) were purchased respectively from Sigma-
94 Aldrich Chemical Co (Milwaukee, WI) and ChemService (USA).

95 Working standard solution (3 mg L⁻¹) was prepared by adding precise volumes of the three pesticides
96 mixtures in acetonitrile and was stored in capped amber glass vials in the freezer. The aqueous solutions used
97 for the optimization of extraction parameters as well as the calibration solutions were prepared by spiking the
98 water with the mix working standard solution to the appropriate concentration (250 µg L⁻¹ for the optimization
99 of SPME parameters and from 0.05 to 100 µg L⁻¹ for calibration procedure).

100 The solvents used for GC were of Chromasolv HPLC-grade (>99.9 % purity); they were obtained from
101 Sigma Aldrich Chemical Co (Milwaukee, WI). Milli-Q water, with 18.2 MΩs conductivity, was generated from
102 a Simplicity water purification system (Millipore, Bedford, MA).

103 The following three commercially available SPME fibers were evaluated: polyacrylate (PA, 85 µm),
104 polydimethylsiloxane (PDMS, 100 µm) and polydimethylsiloxane (PDMS, 7 µm). These fibers were obtained
105 from Supelco (Bellefonte, PA, USA). They were conditioned to eliminate potential contaminants before usage.
106 The conditioning was done as endorsed by the manufacturer instructions, by placing the fibers in the GC
107 injector port while maintaining the helium flow. Consequently, PDMS 100 µm and PA 85 µm were kept at
108 280°C for 1 h whereas PDMS 7 µm at 340°C for 1 hour. The magnetic stirrer used was the VarioMag stirrer
109 (USA).

111 **2.2 SPME procedure**

112 A Combi-PAL auto-sampler (CTC, Sweden) coupled to the GC-MS instrument was used for the SPME
113 extraction of targeted pesticides from water samples. Aliquots of 18 mL of water samples were placed in 20 mL
114 amber glass vials. The extraction was performed by using the direct immersion (DI) mode. The PA fiber was
115 totally immersed in the aqueous phase for 45 min under a continuous magnetic stirring of 500 rpm at a
116 temperature of 60 °C. Finally, the fiber was conveyed to the GC injector port where desorption took place for 10
117 minutes in the split-less mode at 275 °C, 15 °C below the maximum temperature endorsed by the manufacturer
118 of the PA fibers, to reduce fiber contamination and preserve fiber coating. Blank sample analysis of deionized
119 water was carried out after ten extractions along with thermal desorption that was performed between two
120 consecutive extractions to eliminate the possibility of fiber contamination.

121

122 **2.3 GC-MS instrumental conditions**

123 The GC-MS analysis was executed on a Varian CP3800 gas chromatograph (GC) (Walnut Creek, CA,
124 USA) assembled with a split/splitless injector and linked to a Saturn 2200 ion trap mass spectrometer (ITMS).
125 The separation was carried out with a Varian Factor Four VF-5MS capillary column (30 m × 0.25 mm i.d., 0.25
126 µm film thickness) (Varian Inc, Lake Forest, CA). Helium (99.99%) was used as carrier gas at a flow rate of 1
127 mL min⁻¹. The oven temperature program was as follows: initial temperature 60 °C (hold 1 min); rate 30 °C/min
128 to 180 °C (hold 3 min); rate 5 °C/min to 280 °C (hold 3 min). The complete analysis time was 30 min for each
129 sample.

130 The ITMS functioned in the electron impact mode (EI) with electron energy of 70 eV. Full scan,
131 Automated Method Development (AMD) and MS/MS experiments were developed throughout this study. The
132 temperatures of the manifold, the ion source, and the transfer line were set to 150, 250 and 280 °C, respectively.

133 The analysis was executed with a filament-multiplier delay of 3 minutes and acquisition was performed
134 with a mass/charge (m/z) ratio ranging from 45-550 m/z. Furthermore, to enhance the sensitivity and linearity of
135 the MS detector, the electron multiplier voltage and the total target ion counts (TIC) were adjusted. Therefore,
136 an auto-tuning procedure was accomplished and the TIC values were set to: 65 000 in full scan MS, 25 000 in
137 AMD and 5000 in MS/MS. MS data analysis and control of the system were done by using Varian MS
138 Workstation software (Version 6).

139

140 **3. Results and discussion**

141

142 **3.1 Optimization of MS/MS operating parameters**

143 The optimization of MS/MS operating conditions involves three steps: (a) the determination of parent
144 ions (precursor ions), (b) the realization of efficient isolation and storage of the parent ion, (c) the optimization
145 of collision-induced dissociation (CID).

146 (a) The selection of the most abundant and selective ion was done and the retention time chosen
147 for each pesticide is represented in Table 1,

148 (b) The realization of efficient isolation and storage of the parent ion inside the ion trap relies on
149 the excitation radiofrequency storage level applied (ESL). ESL was calculated by MS toolkit software and the

150 “q” value was set to 0.3 for all the compounds except for methomyl and methamidophos for which the value was
151 set to 0.4 as the ESL obtained with a value of 0.3 was below the acceptable limit,

152 (c) The optimization of collision-induced dissociation (CID) was done by assessing two
153 excitation modes: non- resonant and resonant. Table 1 displays the extraction mode and the two examined
154 transitions (in bold) for each individual pesticide. The one with the highest intensity (underlined) was used for
155 quantification and the second one, for confirmation.

156

157 **3.2 Optimization of SPME parameters**

158 The optimization of SPME operative parameters is essential in order to maximize the extraction yield and
159 efficiency. According to the literature data, six factors were identified as major variables affecting extraction
160 proficiency. These factors are fiber type, extraction mode, temperature and time, in addition to the stirring speed
161 and desorption time. For optimization, the analysis was done in triplicate. The impact of ionic strength was not
162 investigated in the optimization process throughout this study since the addition of salt to the sample revealed a
163 dramatic decrease in the response and sensitivity of certain compounds [11, 12].

164 The selection of the proper fiber characteristics and the coating is critical for the SPME technique.
165 Preliminary experiments were executed to evaluate the extraction efficiencies of three commercial SPME fibers:
166 7 μm PDMS, 100 μm PDMS and 85 μm PA. As can be seen in Figure 1, the organochlorine pesticides (OCP)
167 presented different behaviors (Figure 1a). Some of them such as heptachlor-epoxide, alpha-HCH, beta-HCH,
168 Lindane, delta-HCH and HCB revealed better extraction efficiency with a PA85 fiber, while dieldrin, 4, 4'-
169 DDD, 4, 4'-DDT, Endosulphan-beta, quintozone, and methoxychlor were better extracted with a PDMS100.
170 Only 4, 4'-DDE showed better extraction efficiency when using PDMS7 and the rest of the OCP compounds
171 (Aldrin, Endosulfan-alpha, and Endosulfan-sulfate) showed the same extraction efficiency with all the tested
172 fibers. Furthermore, for the majority of the remaining selected organophosphate (OPP), carbamate
173 (Carb),pyrethroid (Pyr), Pyrimidine (P), Triazole (TA) pesticides and others (Benzamide (Benz), dicarboximide
174 (DCB), chloroactanilide (CA), acylalanine (AA), dinitroaniline (DA), Phenylpyrrole (PP) etc... (Figure 1b, c
175 and d), the 85 μm PA had the greatest extraction efficiency. Accordingly, the 85 μm PA fiber was implemented
176 for further investigations.

177 In addition to this, two SPME extraction modes were evaluated: direct immersion mode (DI-SPME) in
178 which the fiber is totally immersed in the aqueous phase of the sample and the headspace mode (HS-SPME) in
179 which the fiber is positioned in the headspace over the liquid. Figure 2a, b, c, and d clearly show that DI-SPME
180 mode had better sensitivity than HS-SPME and was capable to extract almost all the targeted compounds.
181 Taking into account these results, the DI-SPME mode was used for the development of the method.

182 The extraction temperature affects the extraction kinetically and thermodynamically. The rise in
183 temperature leads to a reduction in the extraction time, conversely it decreases the sum of analytes adsorbed on
184 the fiber [20]. In the present study, the influence of the extraction temperature was evaluated in the range
185 between 30 and 70 °C. Figure 3 shows that, for the majority of the compounds, mainly the OCPs (Figure 3a), the
186 peak area was enhanced at a temperature up to 60 °C; while after this temperature a drop in the extraction
187 efficiency was noticed. Contrariwise, for chlorpropham and cyprodinil, a temperature of 70 °C gave the best
188 extraction efficiency. However, for these compounds, the drastic decrease in the response at 60°C may be due to
189 experimental error. On the other hand, the extraction efficiency of methomyl, diazinon, and propoxur, was not
190 considerably affected by temperature. Following these results, a fixed temperature of 60 °C was set for DI-
191 SPME.

192 SPME is a partition process (equilibrium procedure) of compounds between the sample and the
193 fiber. Thus, the determination of the optimum extraction time (equilibrium time) in which the maximum amount
194 of analytes are extracted by the fiber is required [26]. The extraction time was carried out between 15 and 75
195 minutes and the peak area of analytes versus the extraction time were plotted. The results obtained (Figure 4a, b,
196 c, and d) showed that the response of the majority of the analytes increased when the extraction time reached 45
197 minutes. Between 45 and 75 minutes, the improvement in extraction efficiency was significant particularly for
198 cypermethrin, cyprodinil, tebuconazole, and trifluralin for which the best extraction efficiency was reached at 75
199 minutes. As a compromise between time and good extraction efficiency, an extraction duration of 45 minutes
200 was selected.

201 For SPME, a constant agitation of the sample should be applied during fiber exposure in order to improve
202 extraction efficiency and minimize extraction time [27]. The effect of stirring speed was evaluated at 250, 500
203 and 750 rpm. The results obtained are shown in Figure 5. The best extraction yield for all the compounds was
204 achieved at a stirring rate of 500 rpm, however, a stirring speed of 750 rpm was proven to decrease extraction
205 efficiency considerably. This can be explained by the fact that the increase in stirring speed leads to the
206 movement of the compounds to the headspace above the sample thus causing a wash of the fiber and reducing
207 extraction efficiency. This was also witnessed by Filho et al (2010) [11]. A stirring speed of 500 rpm was then
208 chosen.

209 To end with the optimization procedure, desorption time of analytes into the injector port was
210 investigated from 5 to 15 minutes at an injector temperature of 275 °C. A desorption time of 10 minutes was
211 found to be suitable to achieve the complete desorption of all the compounds (Figure 6). Thus it was selected as
212 optimum desorption time throughout this study.

213

214 3.3 Method Performance and Validation

215 The validation of the developed SPME-GC-MS/MS method was performed by calculating LR, LOD,
216 LOQ precisions and recoveries using ultra-pure water spiked at different concentrations.

217 To study the linearity of the proposed method, calibration curves were constructed by using SPME at the
218 optimized conditions, with 6 standard solutions of concentrations ranging from 0.05 to 100 µg L⁻¹, each
219 concentration analyzed in triplicate. Subsequently, graphs showing the ratio of the area of the studied pesticide
220 to the area of the internal standard versus the ratio of the concentration of the studied pesticide to the
221 concentration of the internal standard were plotted. The correction of results was done by using the closest

222 internal standards in terms of chromatographic retention time and molecular similarity (polarity, molecular
223 weight). Table A2 lists all the studied compounds and their associated internal standards. The coefficient of
224 determination (R^2) ranged between 0.994 and 1 as reported in Table 2. These results were similar and even
225 better than those reported in the literature [11, 12, 21, 25].

226 The limit of detection (LOD) and limit of quantification (LOQ) for each analyte were calculated based on
227 statistical analysis of the calibration curves using equations (1) and (2), where a is the slope, b is the intercept at
228 the origin and $s(b)$ is the standard deviation of b (according to ISO 5725 requirement).

229 (1) $LOD = \frac{b+3s(b)}{a}$ (2) $LOQ = \frac{b+10s(b)}{a}$

230 The calculated LOD and LOQ were tested experimentally. Table 2 showed that LOD and LOQ varied
231 correspondingly from 0.001 to 0.458 $\mu\text{g L}^{-1}$ and from 0.039 to 0.732 $\mu\text{g L}^{-1}$ for all the analyzed compounds,
232 except for methomyl and HCB. These values are either in the same order, Passeport et al., (2010) (0.05-0.5 μg
233 L^{-1} for LOQ) [28] and Tankiewicz et al., (2013) (0.015-0.13 for LOD and 0.045-0.38 $\mu\text{g L}^{-1}$ for LOQ) [13], or
234 better than those obtained by other researchers such as Filho et al., (2010) (0.02-0.3 $\mu\text{g L}^{-1}$ for LOD and 0.05-1
235 $\mu\text{g L}^{-1}$ for LOQ) Lafuente et al., (2016) (0.05-1 $\mu\text{g L}^{-1}$ for LOD) [21].

236 The relative recoveries were evaluated by comparing the average response of the detector ($n=3$) obtained
237 with real water samples spiked with a known concentration of studied pesticides, to the average response of the
238 detector ($n=3$) obtained with ultra-pure water spiked at the same concentration. The recovery varied between
239 75.6 to 137.31 % at 0.5 $\mu\text{g L}^{-1}$, 78.68 to 122.16 % at 5 $\mu\text{g L}^{-1}$ which proved the accuracy of the developed
240 method [29].

241 The precision of the optimized method was determined by repeatability (intra-day) and intermediate
242 precision (inter-day). The intra-day precision was calculated as the relative standard deviation (%RSD) of
243 results from five replicates executed on the same day, and the inter-day precision was calculated as %RSD of
244 results from five replicates performed within five consecutive days. The assay values for both variables were
245 below 20% for almost all the compound, these results are comparable to those obtained by other researchers [11,
246 20, 30].

247

248 3.4 Application to real water samples

249 To evaluate the performance of the optimized SPME-GC-MS/MS method, the latter was applied for the
250 analysis of 16 surface water samples taken from different locations from the watershed of Abou Ali River in
251 North Lebanon. Samples were collected in pre-cleaned amber glass bottles, stored at 4 °C and then transported
252 to the Environmental Engineering Laboratory (EEL) at the University of Balamand for analysis. All the water
253 samples were filtered through a 47 mm glass microfiber filters GF/F (Whatman) to reduce interferences from
254 particles that can damage the fiber. Descriptive statistics were applied to estimate the mean, maximum,
255 minimum and frequencies of detection of the studied pesticides. For statistical purposes, the concentration of the
256 samples that were below LOD ($<LOD$) and below LOQ ($<LOQ$), were considered equal to half of the LOD and
257 LOQ respectively. Results are represented in Table 3. Twenty out of forty-eight target pesticides were detected
258 in the analyzed water samples, emphasizing the occurrence of methomyl in almost all the samples (87.5 %), at a
259 high concentration level (2.45 $\mu\text{g L}^{-1}$). This compound also identified as Lannate is known by its high solubility
260 in water (58 g L^{-1} at 25 °C) [31] and its wide use in Lebanon not only for yield control but for the protection of
261 houses from pests. endosulfanI and alachlor also showed a frequency of detection of 87.5 % in the analyzed

262 samples[32]. Alachlor is mainly used for pre and post-emergency applications and it is one of the most
263 frequently perceived pesticides in water because of its high solubility (170.3 mg L^{-1}) [33]. For chlorpropham the
264 frequency of detection was 62.5 %, however, its concentration ($0\text{-}0.09 \text{ }\mu\text{g L}^{-1}$) was found to be within the
265 environmental quality standards set by the European Union [9]. On the other hand, dimethoate and
266 methamidophos were detected with a frequency of detection of 37.5 and 31.3 %, and their concentrations varied
267 between 0 to $0.26 \text{ }\mu\text{g L}^{-1}$ and 0 to $0.87 \text{ }\mu\text{g L}^{-1}$, correspondingly. Their presence in our surface water is explained
268 by their use for the grown of citrus fruits, pome fruits, apple trees and vegetable crops in the area under study.
269 DDD is an insecticide obtained from the biodegradation of DDT [34]. DDD was detected in five of the samples
270 analyzed with a concentration range of $0\text{-}0.18 \text{ }\mu\text{g L}^{-1}$. Researchers such as Kouzayha et al., 2013 [35] and
271 Youssef et al., 2015 [6] have also revealed the detection of DDD at trace levels in the surface water samples of
272 different rivers in south Lebanon. Finally, the frequencies for the rest of the compounds were below 25% (as
273 follows: HCB (25%), ethoprophos (18.8%), diazinon, cyprodinil and ethion (12.5%), dichlorvos, propoxur,
274 trifluralin, chlorpyrifos-methyl, pendimethalin, buprofezin, lambda-cyhalothrin and pyridaben (6.3%)).

275 These results were different from those reported by Massoud et al., (2005) [36] which confirmed the
276 absence of pesticides in the surface water samples collected along the watershed of Abou Ali River. However, It
277 was predictable that the surface water of the studied river will face serious damage in the future, not only
278 because of the results obtained in this study but also because of the intense, uncontrolled and incorrect use of
279 pesticides carried out in the agricultural areas located in this region.

280

281 **4. Conclusions**

282

283 A highly satisfactory DI-SPME-GC-MS/MS method was optimized and validated for multi-residue
284 analysis of pesticides in water. The main parameters affecting the extraction efficiency were tested and optimal
285 conditions were selected. The developed method showed good linearity, precision and high sensitivity to
286 pesticide residue analysis. The results obtained for 16 samples collected from 16 locations along the watershed
287 of Abou Ali River indicate a potential risk of environmental contamination in the area and explain the need to
288 do seasonal monitoring for these pesticides, covering all the watershed of Abou Ali River from the source to the
289 mouth.

290

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294 **Conflict of interest**

295 None.

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299

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Optimization of a DI-SPME-GC-MS/MS Method for Multi-residue Analysis of Pesticides in Waters

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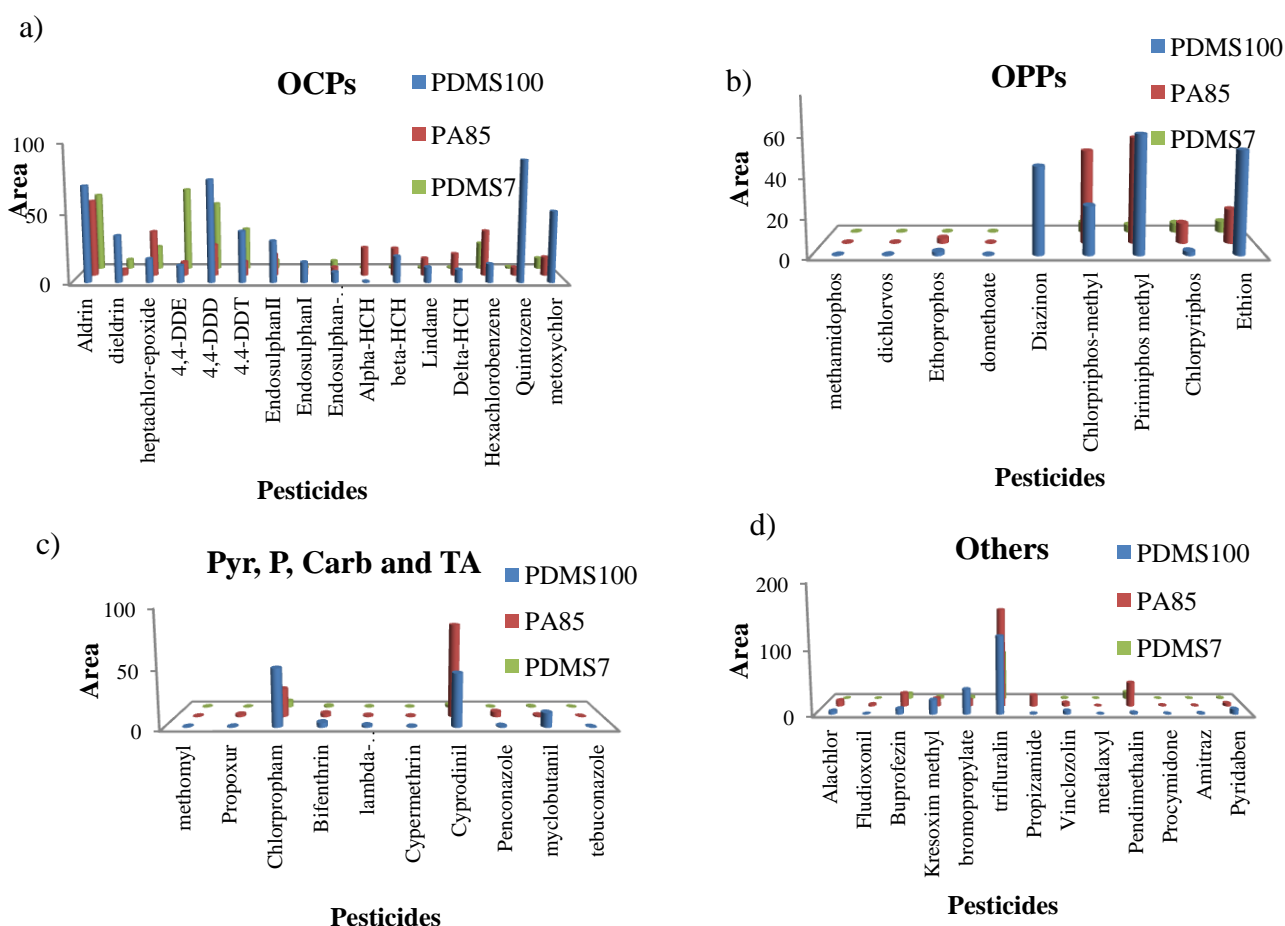


Figure 1 Impact of three SPME fibers on the extraction efficiency of the studied a) OCPs, b) OPPs, c) Carb, Pyr, P and TA d) others.

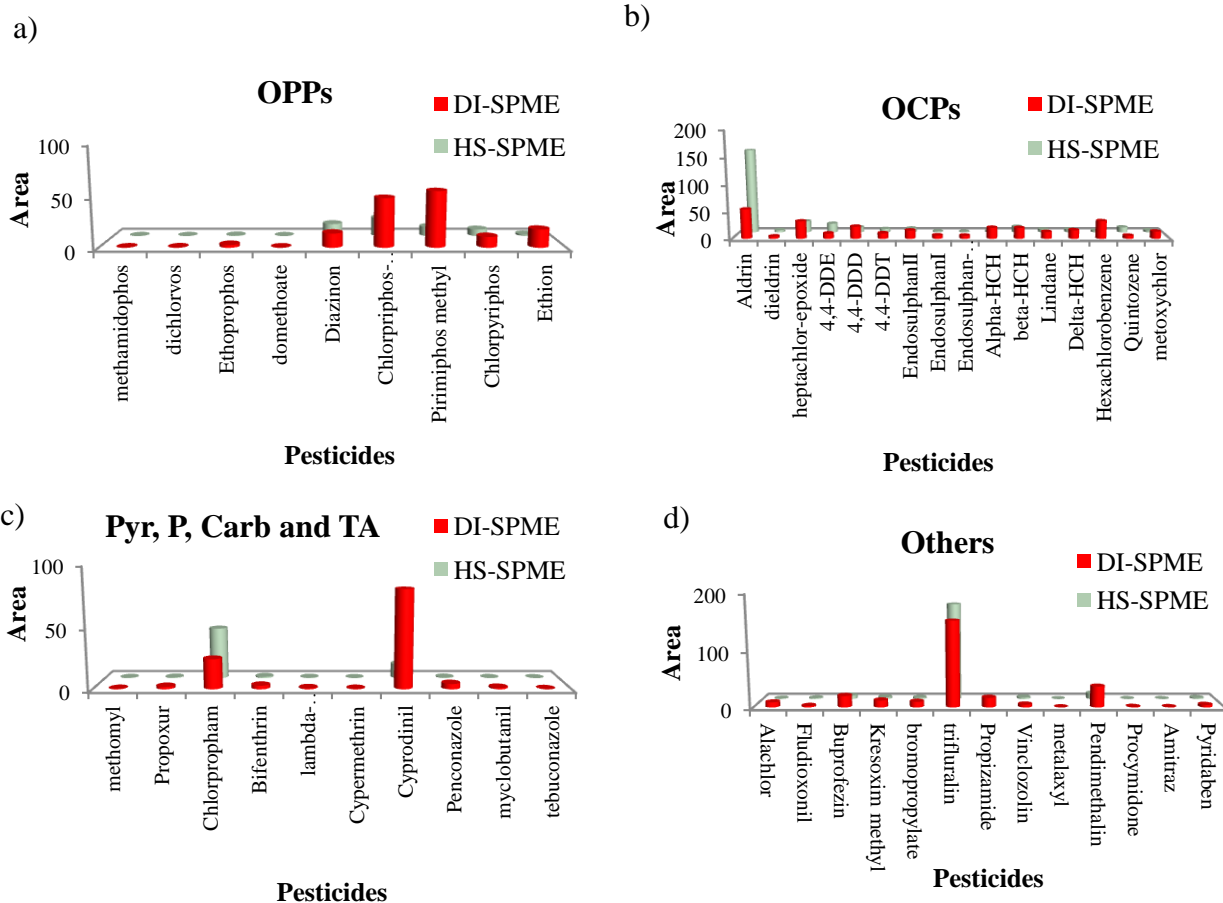


Figure 2 Effect of extraction mode (DI-SPME and HS-SPME) on the extraction efficiency of the studied a) OCPs, b) OPPs, c) Carb, Pyr, P and TA d) others.

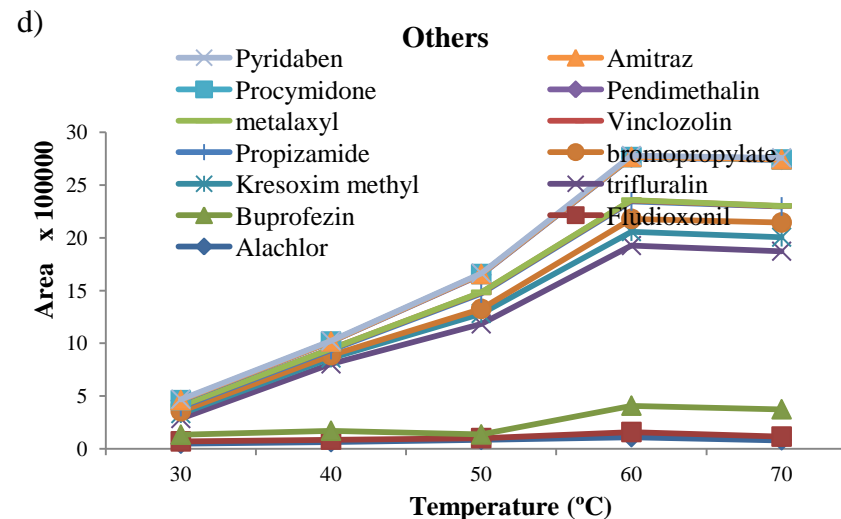
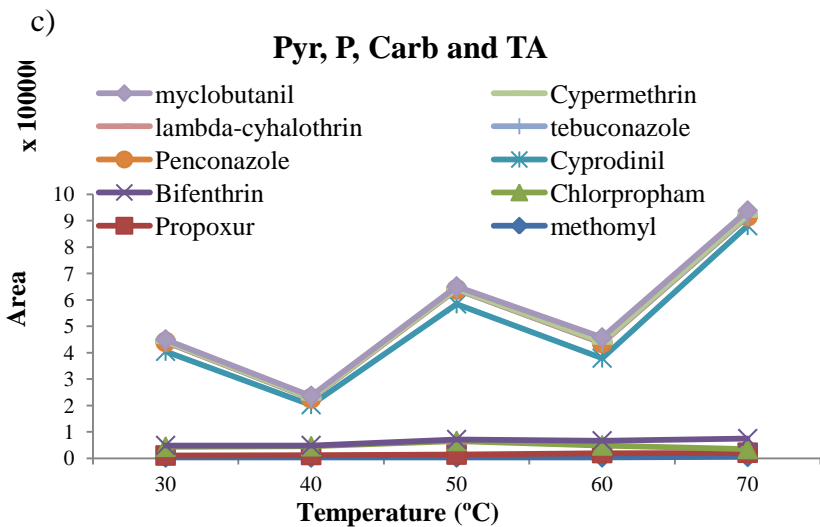
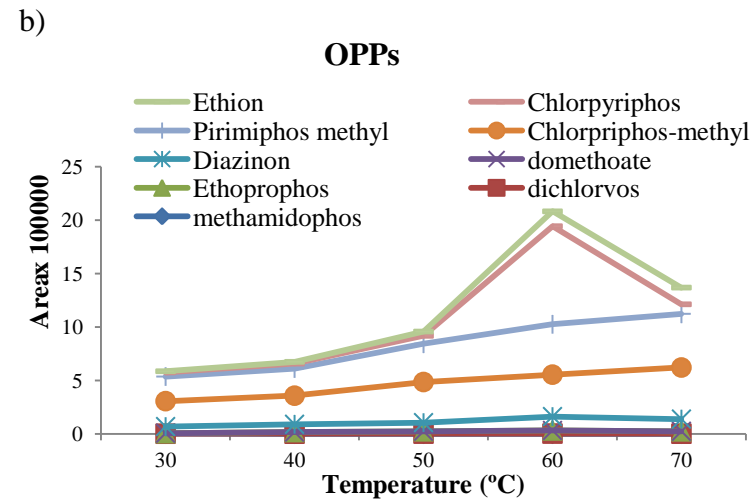
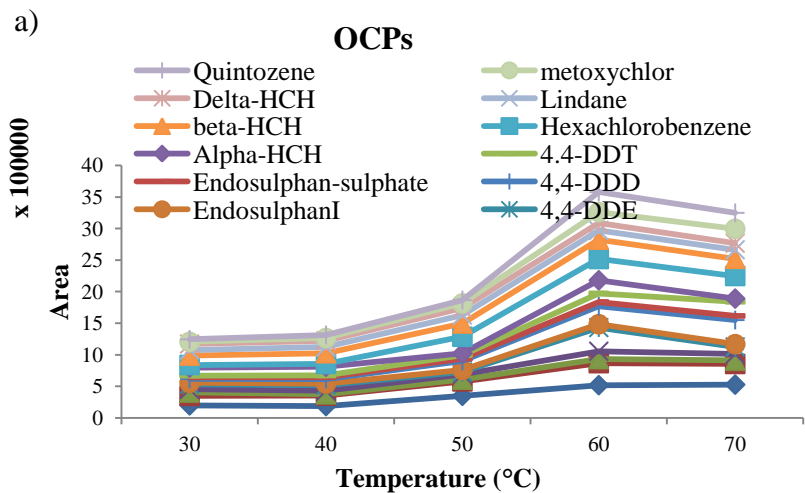


Figure 3 Effect of five extraction temperature (30, 40, 50, 60 and 70 °C) of the extraction efficiency of the studied a) OCPs, b) OPPs, c) Carb, Pyr, P and TA d) others.

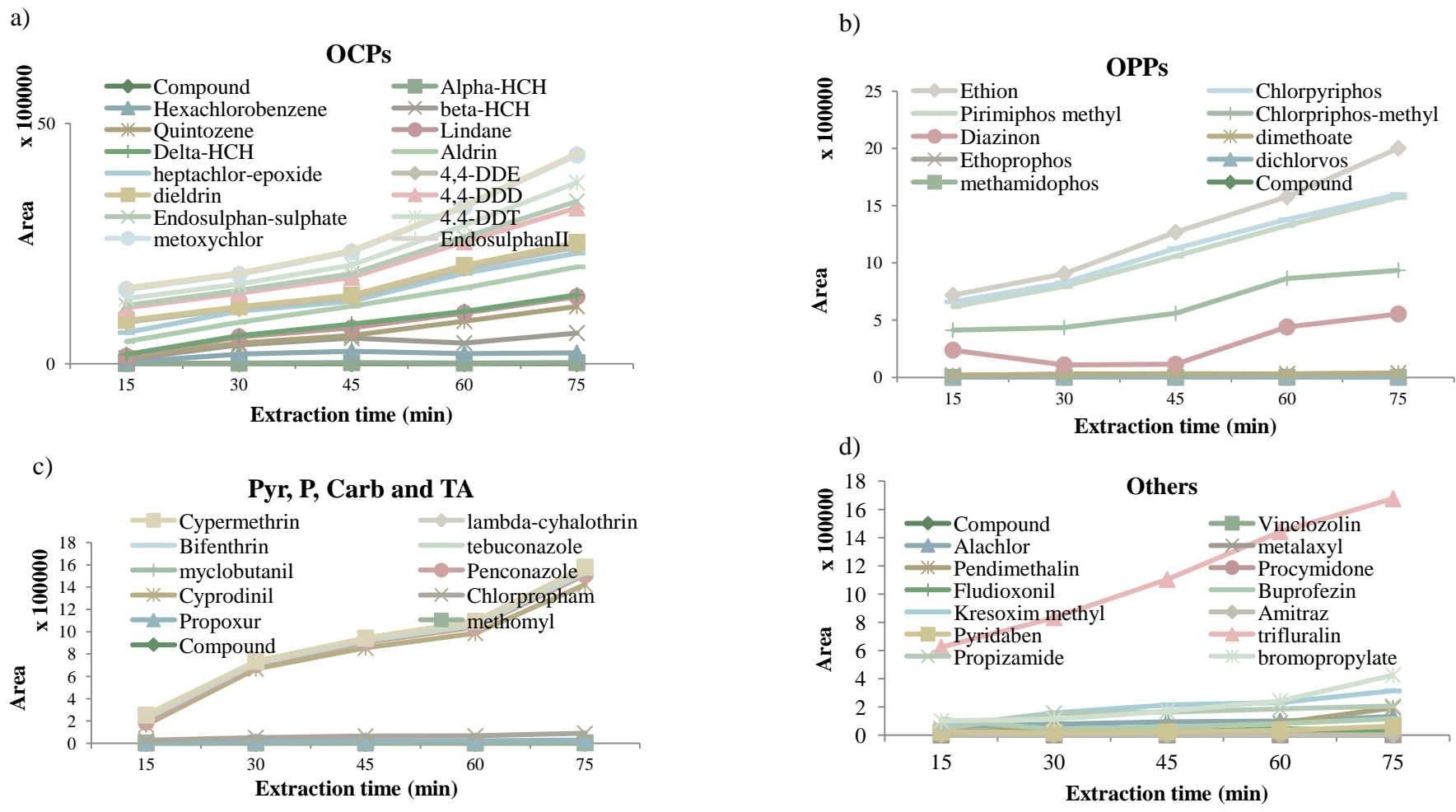


Figure 4 Effect of extraction time on the effectiveness of extraction of the studied a) OCPs, b) OPPs, c) Carb, Pyr, P and TA d) others.

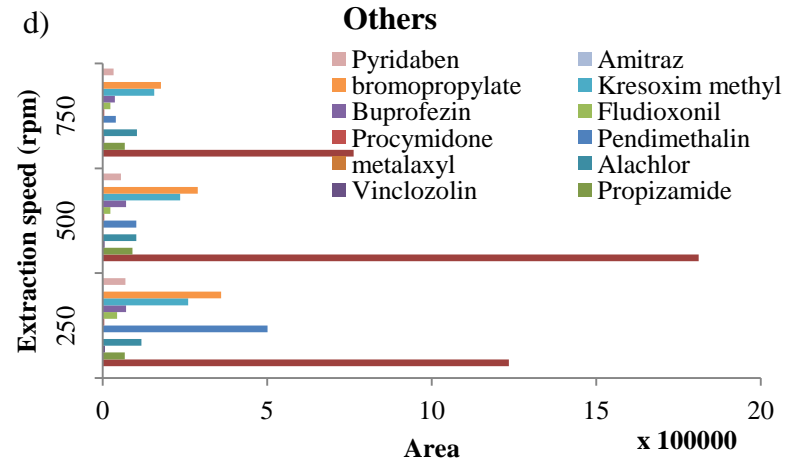
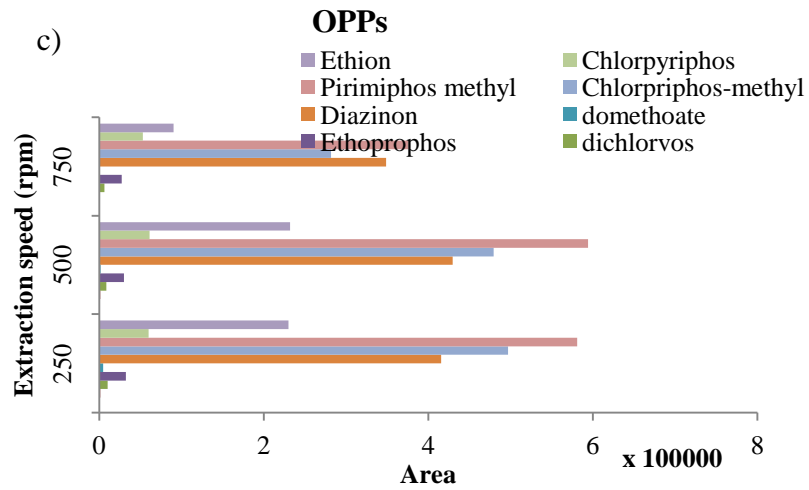
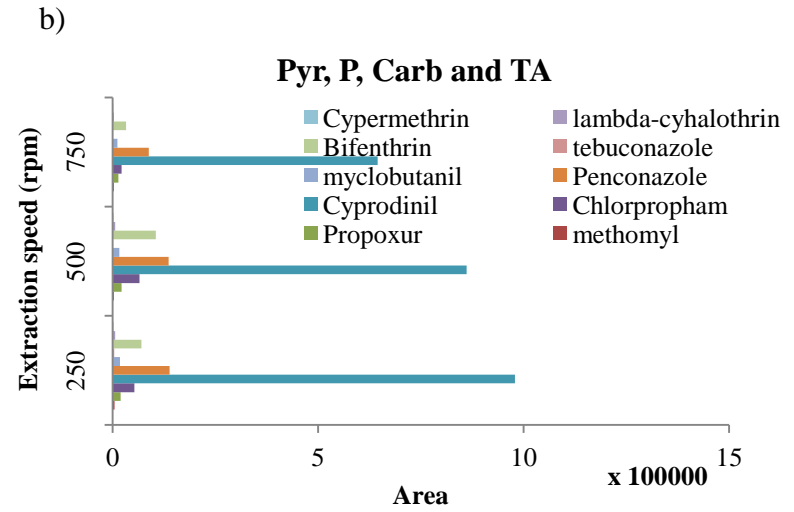
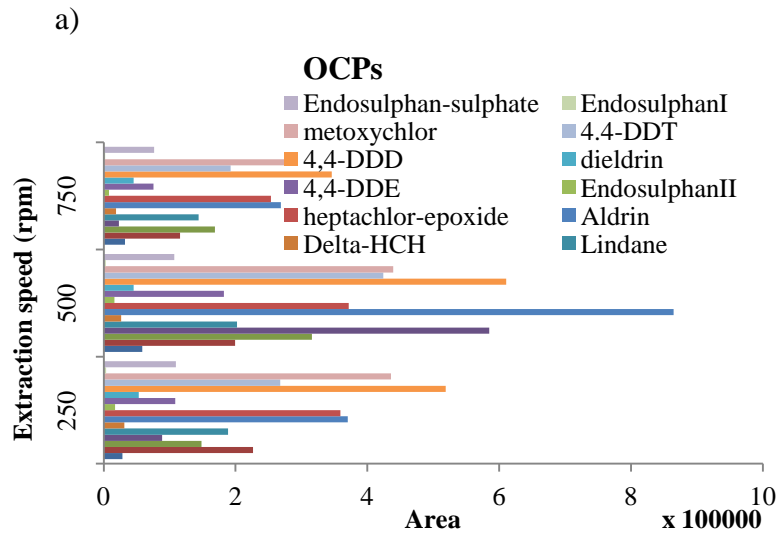


Figure 5 Effect of stirring speed on the extraction efficiency of the studied a) OCPs, b) OPPs, c) Carb, Pyr, P and TA d) others.

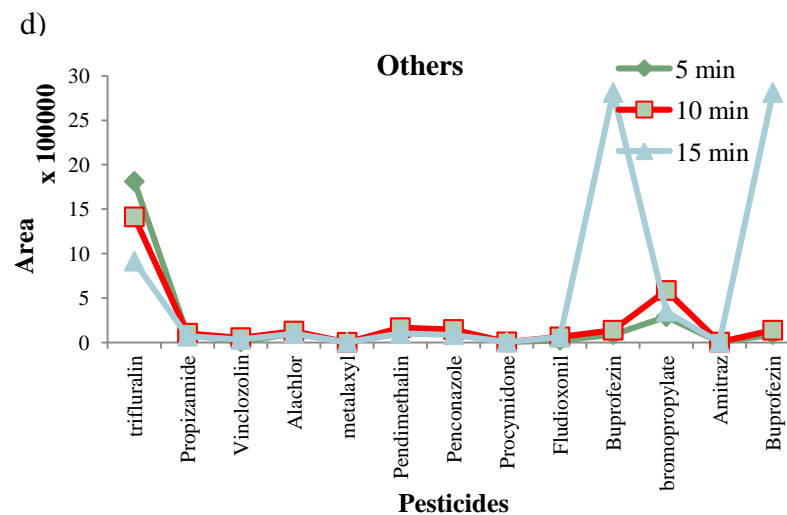
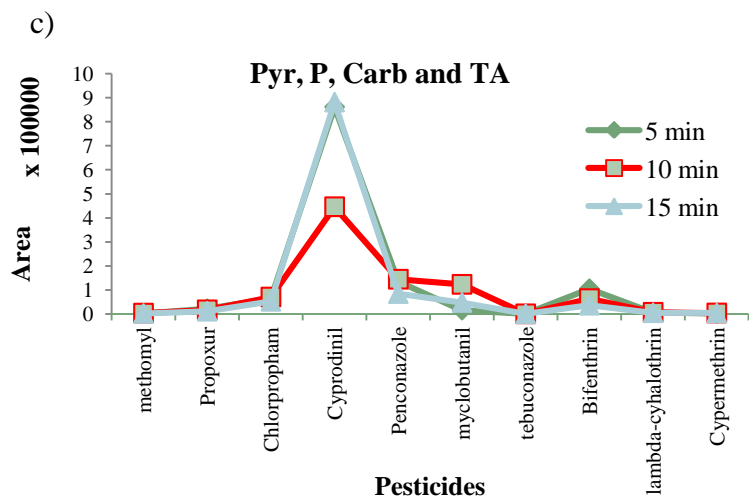
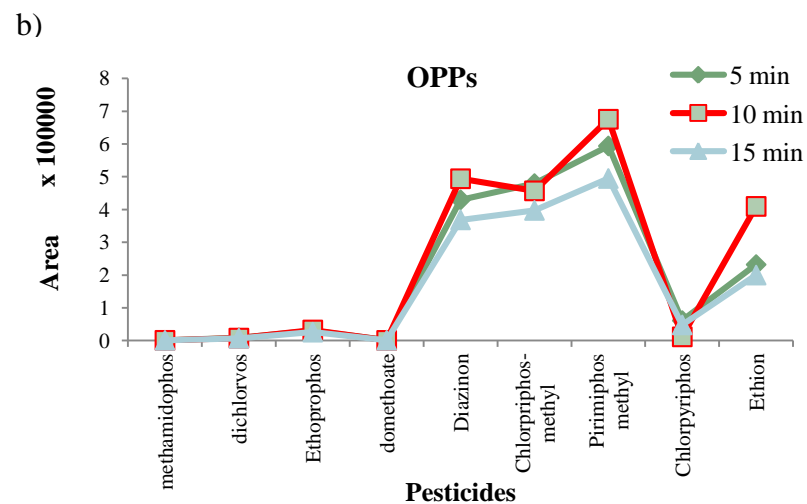
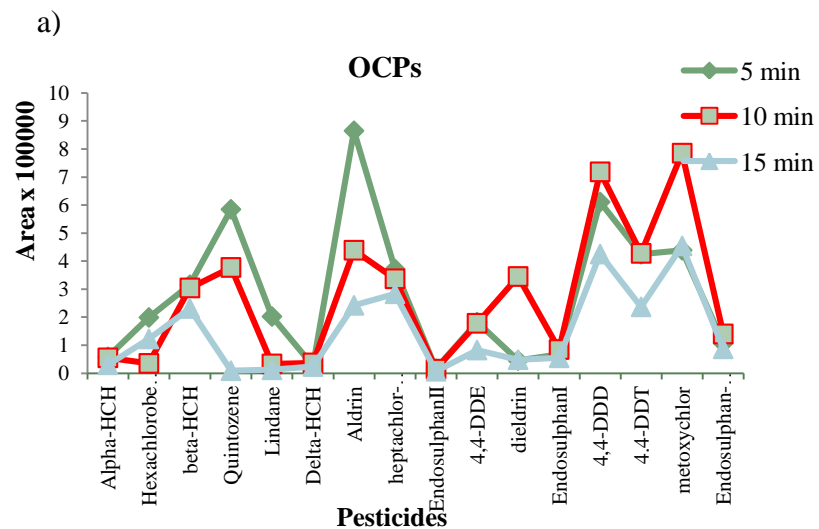


Figure 6 Effect of desorption time on the extraction efficiency of the studied a) OCPs, b) OPPs, c) Carb, Pyr, P and TA d) others.

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Table 1 Chemical group (CG) and optimized operating conditions for MS/MS analysis

PN	Pesticide	CG	PG	RT (min)	MW	ESL (V)	EM	EA	Transitions (m/z)
1	Methomyl	Carb	I	4.09	162	46	NR	17	<u>105/102.9</u>
2	Methamidophos	OPP	I	5.03	141	41.2	NR	41	<u>94/63.9</u>
3	Dichlorvos	OPP	I	5.07	220	61	NR	50	<u>185/92.8</u>
4	Propoxur	Carb	I	7.86	209	36.1	NR	34	<u>110/ 82/81.1</u>
5	Ethoprophos	OPP	I	8.18	242	52	NR	25	<u>158/93.8/113.8/130</u>
6	Trifluralin		H	8.35	335	101.1	NR	50	<u>306/264.2</u>
7	Chlorpropham	Carb	H	8.43	213	70.3	NR	25	<u>213/171/212.3</u>
8	Alpha-HCH	OCP	I	9.16	288	72.3	NR	40	<u>219/181/183/216.9</u>
9	HCB	OCP	F	9.26	282	93.2	R	0.7	<u>282/247.2</u>
10	Dimethoate	OPP	A	9.42	229	41.1	R	0.25	<u>125/78.9</u>
11	Beta-HCH	OCP	I	9.82	288	72.3	NR	41	<u>219/181/183/216.9</u>
12	Quintozene	OCP	F	9.88	293	82.2	NR	73	<u>249/214/212/177/179/246.9</u>
13	Lindane	OCP	I	10.03	288	72.3	NR	43	<u>219/181/183/217</u>
14	Diazinon	OPP	I	10.08	304	59	NR	49	<u>179/177/149/137/115/110.9</u>
15	Propizamide	Benz	H	10.10	256	57	NR	48	<u>173/145/109</u>
16	Delta-HCH	OCP	I	10.84	288	72.3	NR	42	<u>219/181/183/217</u>
17	Chlorpyriphos-methyl	OPP	I	11.59	321	94.5	NR	77	<u>286/208/241.1/144.1/271.1/180</u>
18	Vinclozolin	Dicarb	F	11.68	285	69.9	R	0.38	<u>212/172.1/177.1</u>
19	Alachlor	CA	H	11.78	269	62	NR	41	<u>188/160/186.1</u>
20	Metalaxyl	AA	F	12.04	279	67.9	NR	45	<u>206/162.1/132.1</u>

Continued Table 1

PN	Pesticide	CG	PG	RT (min)	MW	ESL (V)	EM	EA	Transitions (m/z)
21	Pirimiphos-methyl	OPP	I	12.41	305	95.8	NR	65	<u>290/150.9/262</u>
22	Chlorpyrifos	OPP	I	13.03	349	103.8	NR	44	<u>314/258.1/286</u>
23	Aldrin	OCP	I	13.22	362	86.9	R	0.44	<u>263/261.2/228.2</u>
24	Pendimethalin	DA	H	14.14	281	83.2	NR	41	<u>252/208.2/191.2/162.1</u>
25	Cyprodinil	P	F	14.20	225	73.9	R	0.55	<u>224/208.4/222.3</u>
26	Penconazole	TA	F	14.38	283	81.9	NR	60	<u>248/192/206.1</u>
27	Heptachlor epoxide	OC	I	14.50	386	116.7	R	0.3	<u>353/351.1</u>
28	Procymidone	Dicarb	F	14.83	283	93.5	NR	53	<u>283/255.2</u>
29	EndosulfanII	OCP	I	15.73	404	79.6	NR	66	<u>241/239/204.2/206.1/170.2/205.2</u>
30	Fludioxonil	PP	F	16.26	248	81.9	NR	65	<u>248/182/154.2</u>
31	4,4'-DDE	OCP	I	16.47	318	105.1	NR	73	<u>318/246.6/316.3/248.3</u>
32	Myclobutanil	TA	F	16.63	288	59	R	0.28	<u>179/151.7/125</u>
33	Dieldrin	OCP	I	16.68	378	57.7	NR	46	<u>175/132.1/173.1</u>
34	Buprofezin		I	16.70	305	57.7	R	0.27	<u>175/132</u>
35	Kresoxym-methyl		F	16.75	313	38.1	NR	35	<u>116/89.1</u>
36	EndosulfanI	OCP	I	17.81	404	79.6	R	0.31	<u>241/239/205.1</u>
37	Ethion	OPP	I	17.89	384	76.2	R	0.21	<u>231/202.9/174.9</u>
38	4,4'-DDD	OCP	I	17.95	318	77.6	NR	58	<u>235/165.2/199.2</u>
39	Endosulfansulphate	OCP	I	19.14	420	89.8	R	0.27	<u>272/270/237</u>
40	4,4'-DDT	OCP	I	19.25	352	77.6	R	0.36	<u>235/200.1/165.2/199.2</u>
41	Tebuconazole	TA	F	19.76	308	82.5	R	0.34	<u>250/249.1/125</u>
42	Bifenthrin	Pyr	I	20.91	422	59.6	R	0.33	<u>181/166.1/165.2</u>
43	Bromopropylate		A	21.03	426	112.7	R	0.23	<u>341/339.2/183/185.9</u>
44	Metoxychlor	OCP	I	21.25	344	74.9	R	0.39	<u>227/212.2/225.2/196.2/195.3</u>
45	Amitraz		A/I/S	22.81	162	53.3	NR	28	<u>162/161.1/147/141</u>
46	Lambda-cyhalothrin	Pyr	I	22.84	449	59.6	NR	58	<u>181/152</u>
47	Pyridaben		I/M	24.70	364	48.4	NR	33	<u>147/119.1/105</u>
48	Cypermethrin	Pyr	I	26.42	415	53.7	NR	34	<u>163/126.9</u>

Abbreviations:

PN: pesticide number, PG: pesticide group; I: Insecticide; A: Acaricide, F: Fungicide, H: Herbicide, M: Miticide; S: Scabicide

CG: Chemical group; OPP: organophosphate; OCP: Organochlorine; Pyr: pyrethroid, P: Pyrimidine, Carb: Carbamate, TA: Triazole / Others: Benz: Benzamide

DCB: dicarboximide; CA: chloroactanilide; AA: acylalanine; DA: dinitroaniline; PP: Phenylpyrrole etc...

RT: retention time; MW: Molecular weight; ESL: Excitation storage level; EM: Excitation mode; EA: Excitation amplitude

Table 2 Analytical parameters of the optimized SPME-GC-MS/MS method

Pesticide	Linearity Range (LR) ($\mu\text{g L}^{-1}$)	Coefficient of Determination (R^2)	Limit of detection (LOD) ($\mu\text{g L}^{-1}$)	Limit of quantification (LOQ) ($\mu\text{g L}^{-1}$)	LOQ Mean recovery and RSD % (n=3)	LOQ Precision %RSD (n=5)	Mean recovery and RSD % (n=3)		Intra-day precision %RSD (n=5)
							0.5	5	
							($\mu\text{g L}^{-1}$)	($\mu\text{g L}^{-1}$)	
Methomyl	0.5-50	0.9989	1.09	1.43	95.8 \pm 14.8	16	-	100.5 \pm 13.3	4
Methamidophos	0.05-50	0.9991	0.46	0.73	89.9 \pm 9.8	10	99.8 \pm 2.1	80.3 \pm 1.4	19
Dichlorvos	0.5-75	0.9997	0.33	0.59	76.8 \pm 1.9	10	91.1 \pm 2.5	93.4 \pm 1.4	3
Propoxur	0.05-50	0.9992	0.30	0.56	95.9 \pm 1.4	4	129.3 \pm 1.8	118.9 \pm 1.1	10
Ethoprophos	0.05-75	0.9995	0.12	0.37	92.3 \pm 5.3	6	115.7 \pm 1.4	122.2 \pm 1.6	10
Trifluralin	0.05-5	0.9957	0.01	0.08	78.5 \pm 1.1	5	80.2 \pm 2.2	101.7 \pm 5.6	19
Chlorpropham	0.05-75	1	0.02	0.06	94.2 \pm 3.1	8	95.3 \pm 1.1	98.9 \pm 5.3	8
Alpha-HCH	0.05-10	0.9992	0.04	0.09	82.8 \pm 1.7	7	84.7 \pm 1.9	88.4 \pm 2.2	18
HCB	0.5-100	0.9997	0.99	1.36	79.6 \pm 3.6	7	-	88.5 \pm 6.5	11
Dimethoate	0.05-5	0.9962	0.03	0.10	88.3 \pm 2.8	9	89.2 \pm 8.3	98.2 \pm 9.1	4
Beta-HCH	0.05-100	0.9995	0.03	0.16	81.7 \pm 2.3	3	108.1 \pm 2.6	111.8 \pm 3.1	17
Quintozene	0.05-50	0.9996	0.00	0.15	82.6 \pm 5.4	7	137.3 \pm 2.6	87.3 \pm 1.2	10
Lindane	0.05-5	0.9955	0.03	0.10	92.8 \pm 5.5	5	93.3 \pm 1.9	98.3 \pm 1.1	7
Diazinon	0.05-50	0.9998	0.00	0.10	92.1 \pm 2.3	12	105.3 \pm 8.2	92.3 \pm 5.5	12
Propizamide	0.05-75	0.9999	0.01	0.10	77.4 \pm 5.5	15	136.8 \pm 7.4	92.0 \pm 2.3	19
Delta-HCH	0.05-5	0.9968	0.04	0.10	98.3 \pm 5.7	16	99.0 \pm 7.1	98.2 \pm 2.4	9
Chlorpriphos-methyl	0.05-50	0.9994	0.01*	0.04*	86.1 \pm 4.1	9	109.1 \pm 9.5	86.7 \pm 3.7	7
Vinclozolin	0.05-75	0.9998	0.05	0.24	98.1 \pm 2.1	8	104.2 \pm 1.1	99.0 \pm 1.4	8
Alachlor	0.05-75	0.9984	0.08*	0.26	93.8 \pm 3.1	9	95.1 \pm 3.3	98.4 \pm 5.1	13
Metalaxyl	0.05-25	0.9997	0.05	0.13	88.1 \pm 1.4	6	77.7 \pm 1.4	89.5 \pm 2.5	14
Pirimiphos methyl	0.05-5	0.9989	0.01	0.04	75.2 \pm 1.8	8	79.8 \pm 1.1	99.4 \pm 2.2	9
Chlorpyriphos	0.05-5	0.9957	0.03	0.10	88.4 \pm 4.5	7	85.7 \pm 1.5	100.7 \pm 4.5	5
Aldrin	0.05-5	0.994	0.02	0.10	92.1 \pm 7.9	9	114.4 \pm 7.9	102.4 \pm 1.2	6
Pendimethalin	0.05-100	0.9995	0.25	0.65	86.6 \pm 3.9	10	91.4 \pm 2.2	83.4 \pm 2.3	13
Cyprodinil	0.05-75	0.9997	0.04	0.29	97.8 \pm 1.7	2	110.4 \pm 4.1	100.3 \pm 1.7	8
Penconazole	0.05-10	0.9999	0.02	0.04	86.4 \pm 1.7	9	88.8 \pm 2.1	100.0 \pm 1.6	18
Heptachlor-epoxide	0.05-75	0.9996	0.13	0.40	87.3 \pm 1.9	2	90.9 \pm 2.9	100.0 \pm 5.1	6
Procymidone	0.05-75	0.9995	0.13	0.36	98.1 \pm 1.1	15	119.1 \pm 1.5	104.3 \pm 1.2	14
Endosulfan II	0.05-5	0.9979	0.02	0.06	84.9 \pm 3.4	4	119.4 \pm 1.4	100.3 \pm 1.5	4
Fludioxonil	0.05-75	0.999	0.13	0.55	82.5 \pm 2.9	13	105.9 \pm 3.1	83.6 \pm 2.5	13

Continued Table 2

Pesticide	Linearity Range (LR) ($\mu\text{g L}^{-1}$)	Coefficient of Determination (R^2)	Limit of detection (LOD) ($\mu\text{g L}^{-1}$)	Limit of quantification (LOQ) ($\mu\text{g L}^{-1}$)	LOQ Mean recovery and RSD % (n=3)	LOQ Precision %RSD (n=5)	Mean recovery and RSD % (n=3)		Intra-day precision %RSD (n=5)
							0.5	5	
							($\mu\text{g L}^{-1}$)	($\mu\text{g L}^{-1}$)	
4,4'-DDE	0.05-25	0.9953	0.02*	0.06*	93.9 \pm 4.3	16	128.7 \pm 13.7	98.2 \pm 6.1	19
Myclobutanil	0.05-100	0.9999	0.02	0.18	89.3 \pm 1.1	11	124.1 \pm 9.1	100.5 \pm 4.2	19
Dieldrin	0.05-75	0.9996	0.26	0.54	99.9 \pm 1.3	5	116.7 \pm 8.6	100.3 \pm 4.4	6
Buprofezin	0.05-25	0.9997	0.01	0.09	90.9 \pm 1.4	11	90.6 \pm 1.1	100.1 \pm 6.4	16
Kresoxim methyl	0.05-25	0.9998	0.03	0.10	89.6 \pm 1.3	13	100.1 \pm 1.3	100.1 \pm 1.6	19
EndosulfanI	0.05-50	0.9992	0.07*	0.23*	89.4 \pm 5.5	15	136.8 \pm 10.1	78.7 \pm 1.5	11
Ethion	0.05-50	0.9996	0.08*	0.28	99.3 \pm 2.1	6	121.3 \pm 7.1	96.0 \pm 3.9	10
4,4'-DDD	0.05-5	0.9961	0.03	0.10	98.5 \pm 1.4	4	108.4 \pm 7.1	101.0 \pm 3.1	6
Endosulfan-sulphate	0.05-100	1	0.05	0.10	81.8 \pm 1.7	6	82.6 \pm 2.5	97.4 \pm 4.9	15
4,4'-DDT	0.05-100	1	0.02	0.09	91.3 \pm 1.1	4	108.2 \pm 6.2	107.9 \pm 1.1	7
Tebuconazole	0.05-5	0.9946	0.02	0.10	89.4 \pm 4.1	10	112.3 \pm 9.9	102.4 \pm 3.5	11
Bifenthrin	0.05-100	1	0.03	0.09	91.5 \pm 1.4	4	113.1 \pm 5.7	97.3 \pm 1.9	19
Bromopropylate	0.05-100	0.9994	0.07	0.43	94.8 \pm 3.7	9	119.9 \pm 9.5	81.2 \pm 3.7	7
Metoxychlor	0.05-5	0.9979	0.02	0.06	86.9 \pm 1.7	17	87.5 \pm 3.6	100.7 \pm 4.8	14
Amitraz	0.05-100	0.9992	0.21	0.62	81.3 \pm 1.4	4	122.6 \pm 9.3	80.7 \pm 2.7	14
Lambda-cyhalothrin	0.05-5	0.9963	0.02	0.08	99.8 \pm 2.5	12	104.6 \pm 1.1	100.8 \pm 1.1	13
Pyridaben	0.05-50	0.9998	0.16	0.29	100.4 \pm 1.3	11	110.4 \pm 8.8	118.6 \pm 9.2	8
Cypermethrin	0.05-5	0.9975	0.04	0.09	73.9 \pm 3.1	13	75.6 \pm 3.1	100.7 \pm 7.2	8

*Calculated by Signal to noise ratio (S/N) of 3 for LOD and 10 for LOQ; “-“was not detected

Table 3 mean, concentration range and frequency of detection of target pesticides in 16 surface water samples

Compounds	Mean ($\mu\text{g L}^{-1}$)	Concentration Range ($\mu\text{g L}^{-1}$)	Frequency of detection (%)
Methomyl	1.462	nd-2.46	87.5
Methamidophos	0.170	nd -0.87	31.3
Dichlorvos	0.018	nd -0.29	6.3
Propoxur	0.017	nd -0.28	6.3
Ethoprophos	0.027	nd -0.18	18.8
Trifluralin	0.006	nd -0.09	6.3
Chlorpropham	0.023	nd -0.09	62.5
HCB	0.170	nd -0.68	25
Dimethoate	0.042	nd -0.26	37.5
Diazinon	0.013	nd -0.10	12.5
Chlorpyrifos-methyl	0.005	nd -0.08	6.3
Alachlor	0.267	nd -0.92	87.5
Pendimethalin	0.020	nd -0.33	6.3
Cyprodinil	0.044	nd -0.38	12.5
Buprofezin	0.028	nd -0.45	6.3
EndosulfanI	0.100	nd -0.11	87.5
Ethion	0.017	nd -0.14	12.5
4,4'-DDD	0.046	nd -0.18	31.3
Lambda-cyhalothrin	0.010	nd -0.16	6.3
Pyridaben	0.025	nd -0.39	6.3

nd: not detected

