



## Determination of Pesticides in the Respirable Fraction of Airborne Particulate Matter by High-Performance Liquid Chromatography – Tandem Mass Spectrometry

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Keywords:	pesticides, respirable fraction of airborne particulate matter, pesticide spreading operations, tractor cabs, High-Performance Liquid Chromatography – Tandem Mass Spectrometry (HPLC-MS/MS)

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1 **Determination of Pesticides in the Respirable Fraction of Airborne Particulate Matter by**  
2 **High-Performance Liquid Chromatography – Tandem Mass Spectrometry**

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14 **Abstract**

15 Potential harmful effects of pesticides include risks to human health of workers involved in the wet  
16 spray application in cultivated areas. Inhalation exposure depends on several factors including  
17 pesticide concentrations in the respirable fraction of airborne particulate matter (PM<sub>4</sub>). In order to  
18 ensure a high level of protection, the use of tractors with cabs provides protection against dusts,  
19 aerosols and vapours. Since tractors not providing maximum protection are still in use, PM<sub>4</sub> was  
20 sampled during spreading operations in agricultural fields inside and outside the tractor cab. Sample  
21 preparation technique based on accelerated solvent extraction and solid phase extraction clean-up,  
22 was optimized before analysis of nine pesticides in PM<sub>4</sub>. Meptyldinocap, deltamethrin,  
23 myclobutanil, fluopyram, methoxyfenozide, dimethomorph, fluopicolide, cyflufenamid,

metrafenone were simultaneously analyzed by HPLC/ESI-MS-MS. The results demonstrated the efficacy of the tractor cabs used in the sampling sites.

## Keywords

Pesticides; High-Performance Liquid Chromatography – Tandem Mass Spectrometry (HPLC-MS/MS); electrospray ionization (ESI); respirable fraction of airborne particulate matter; pesticide spreading operations; tractor cabs.

## 1. Introduction

Though pesticides have a key role in the increase of agricultural productivity, some measures must be taken to avoid any potential adverse health effects in workers who may be exposed to chemicals (Dosemeci 2002; Harris 2010). Agricultural pesticide spraying is an especially important operation because of its impact on involved operators. In addition to exposure due to residue that could be absorbed through the skin after dermal contact with chemicals, inhalation is an important route of exposure for workers involved in chemical treatments (Giles 1995; Dougherty 2000; Ramwell 2005).

Formulated pesticide products contain active ingredients, with the balance solvents and stabilizers and are often spread in combinations in the form of an aqueous mixture, so providing concurrent substances in ambient air that can be transported depending on their physical properties and can be adsorbed onto soil and bioconcentrated into the biota.

As a result of agricultural use, PM may simultaneously contain molecules with different chemical and physical properties. Their quantitative extraction and the simultaneous chromatographic analysis of all active ingredients, purified by additives and coformulants, is still a challenge (Coscollà 2008; Schreck 2008; Coscollà 2013a; Coscollà 2013b; Coscollà 2017; López 2017).

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3 46 Up to now, analytical method has been developed above all to determine pesticides in food and in  
4  
5 47 water. Methods for pesticide extraction from environmental water samples involve liquid-liquid  
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7 48 extraction with a large solvent consuming, solid-phase extraction methods, and solid-phase  
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9  
10 49 microextraction; solid phase extraction disks were also tested as an alternative (Urruty 1996; Riley  
11  
12 50 2005). The most popular pretreatment methods for pesticide extractions from food also involve  
13  
14 51 liquid-liquid and solid phase extraction; microextraction techniques were also developed (Ravelo-  
15  
16 52 Pérez 2009); QuEChERS methods have also been tested (Lehotay 2005). Soxhlet, pressurized liquid  
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18 53 (PLE), and microwave assisted extractions (MAE) have been used for pesticide extraction from  
19  
20  
21 54 particulate matter. PLE and MAE are less time and organic solvent consumption (Coscollà 2009).

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23  
24 55 As for chromatographic analysis, gas chromatography coupled to mass spectrometry and liquid  
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26 56 chromatography coupled to tandem MS (LC-MS/MS) are the most used detection techniques in  
27  
28 57 pesticide residue analysis. Alder in 2006 stated that LC-MS/MS methods were more successful in  
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30  
31 58 terms of number of pesticides simultaneously analyzed, increased sensitivity, and selectivity (Alder  
32  
33 59 2006).

34  
35  
36 60 Pesticides can be applied to crops by tractors, creating high-density chemical clouds. To improve  
37  
38  
39 61 the worker safety, tractors with closed filtered air cabs are used to reduce operator exposure to  
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41 62 airborne contaminants during the process of chemical treatments. To ensure a high level of  
42  
43 63 protection, proper cab filtration system reducing dusts, aerosols and vapors, should be used and  
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45 64 filters should be replaced based on filter efficiency. In case of using cabs providing a low protection  
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47 65 factor (Hall 2002; Heitbrink 2003; Balsari 2010), with filter only ensuring the reduction of dusts,  
48  
49 66 occurrence of airborne pesticides inside the cabs, particularly in the respirable fraction (PM<sub>4</sub>;  
50  
51 67 aerodynamic diameter less than or equal to 4 µm) of atmospheric particulate matter, causing  
52  
53 68 potential deposition at inner sites of the respiratory tract, may determine inhalation hazard.  
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56 69 Therefore, airborne concentration of pesticides can be used to correctly estimate an aspect of  
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58 70 potential personnel exposure (Ross 2000; Coscollà 2009).

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3 71 To date, data on pesticide concentrations in the respirable fraction of the airborne particulate matter,  
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5 72 during the spreading of formulated products, are scarce, despite such data allow a more accurate  
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7 73 risk assessment and consequently a better prevention strategy (Clausnitzer 1996; Coscollà 2011).  
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10  
11 74 The aim of present paper was the determination of airborne pesticide concentrations inside tractor  
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13 75 cabs during the operation of spreading, to assess the safety level of the vehicle. Among the many  
14  
15 76 frequently used commercial formulations, nine of them were taken into consideration in this study.  
16  
17 77 Table 1 reports a description of the pesticides contained in the commercial products (Kodandaram  
18  
19 78 2013; EPA Chemistry Dashboard). Since the determination of many pesticides together is especially  
20  
21 79 important when analyzing airborne particulate matter collected in areas where formulated pesticide  
22  
23 80 products are spread in combinations, a method for their simultaneous determination in particulate  
24  
25 81 matter is investigated. The optimized method was then applied to samples of PM<sub>4</sub>, collected inside  
26  
27 82 and outside tractor cabs, used for spreading pesticides. A discussion of the results is provided in this  
28  
29 83 paper. It is noteworthy to point out that for the first time pesticide measures have been carried out  
30  
31 84 within tractor cabs to evaluate the degree of operator's protection.  
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## 35 36 85 **2. Experimental**

### 37 38 39 86 **2.1 Instrumentation**

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43 87 Low Volume Universal XR Pumps (SKC inc; AMS Analitica, Pesaro, Italy), operating at 0.15 m<sup>3</sup> h<sup>-1</sup>  
44  
45 88 (2.5 L min<sup>-1</sup>), were used with the aid of cyclones for the collection of the respirable fraction of  
46  
47 89 particulate matter.  
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49  
50  
51 90 A microbalance (Sartorius ME5; weight uncertainty ±2 µg) and a conditioning climatic cabinet  
52  
53 91 (Activa Climatic Cabinet, Aquaria, Milan, Italy) were utilized for filter weighting procedure.  
54

55  
56 92 Particulate matter extraction was carried out by Accelerated Solvent Extraction (ASE 200–Dionex;  
57  
58 93 ThermoFisher Scientific, Rodano, Milan, Italy).  
59  
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3 94 Evaporation was carried out by a Glas-Col SE 500 evaporator (Bioanalitica Strumenti srl, Milan,  
4  
5 95 Italy) under a nitrogen stream at a temperature of about 60° C.  
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8  
9 96 A vacuum manifold 12-Port model SPE (Alltech, Casalecchio di Reno, Bologna, Italy) was used to  
10  
11 97 quickly elute the analytes from the solid phase cartridges at a constant flow.  
12

13  
14 98 Pesticides were analyzed by liquid chromatography/ion electrospray ionization-tandem mass  
15  
16 99 spectrometry (HPLC/ESI-MS/MS), in selected reaction monitoring (SRM) mode, by an Agilent  
17  
18 100 1290 series binary HPLC pump system, fitted with an autosampler (20 µL) Agilent G4226A,  
19  
20 101 coupled to an Agilent Jet Stream 6460 triple quadrupole mass spectrometer with an IonSpray source  
21  
22 102 (Agilent Technologies Italia S.p.A., Cernusco sul Naviglio, Milan, Italy).  
23  
24

## 25 26 103 **2.2 Reagents and materials**

27  
28  
29 104 Particulate matter was collected onto polytetrafluoroethylene membrane disc filters (diameter: 37  
30  
31 105 mm, porosity: 2.0 µm) (Pall Corporation - VWR International s.r.l., Milan, Italy).  
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33

34  
35 106 The chromatographic method was developed using a Luna® C<sub>18</sub> Phenomenex HPLC Column 5 µm  
36  
37 107 particle size, L × I.D. 15 cm × 2.1 mm, fitted with a guard column (Phenomenex, Castel Maggiore,  
38  
39 108 BO, Italy).  
40  
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42  
43 109 A solid-phase clean-up was performed by applying the extracts to Strata-X cartridges (200 mg / 6  
44  
45 110 mL) (Phenomenex, Castel Maggiore, Bologna, Italy).  
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47  
48  
49 111 Ultra-gradient acetonitrile, water, and methanol were from Romil Chemicals Ltd (Cambridge,  
50  
51 112 U.K.).  
52

53 113 Ammonium formate was from Carlo Erba Reagents S.p.A. (Arese, Milan, Italy).  
54

55 114 Meptyldinocap (purity 95.1%), deltamethrin (purity 98.0%), myclobutanil (purity 99.4%),  
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57 115 fluopyram (purity 99.9%), methoxyfenozide (purity 99.8%), dimethomorph (purity 99.9%),  
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3 116 fluopicolide (purity 99.9%), cyflufenamid (purity 98.0%), and metrafenone (purity 98.1%) were  
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5 117 from Sigma-Aldrich S.r.l., Milan, Italy.

### 118 **2.2.1 Standard preparation**

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10 119 For infusion into the mass spectrometer, the calibration curves, and the spiked samples preparation,  
12  
13 120 the stock standard solutions of the analytes were prepared by dissolving meptyldinocap,  
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15 121 deltamethrin, myclobutanil, fluopyram, methoxyfenozide, dimethomorph, fluopicolide,  
16  
17 122 cyflufenamid, and metrafenone in water:methanol, 50:50 (v/v), or water, or acetonitrile ( $1 \text{ mg mL}^{-1}$ )  
18  
19 123 and storing them at  $-20^{\circ}\text{C}$  in amber vials. Working solutions were prepared by successive dilution  
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21 124 of the stock standard solutions.

### 125 **2.3 Sampling of pesticides**

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28 126 Three sampling campaigns were performed in the warm season of 2016 in two vineyards and one  
29  
30 127 melon field, during the pesticide spreading, by placing two pumps inside and two pumps outside the  
31  
32 128 cab within which the operator was seated. The sampling time was concordant with the pesticide  
33  
34 129 spreading period, lasting about two hours. Field blanks were placed both inside and outside the cab.

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38 130 In the first campaign at the vineyard, spraying operation had a duration of 100 minutes. The  
39  
40 131 formulated pesticides were mixed with water, with a total volume in the tank sprayer of 1800 L.  
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42 132 The sprayed mixture was composed by the following active ingredients: methoxyfenozide,  
43  
44 133 dimethomorph, meptyldinocap. The concentrations of active ingredients in the mixture were 267,  
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46  
47 134 500, and  $595 \text{ mg L}^{-1}$ , respectively. The volume applied was  $1800 \text{ L ha}^{-1}$ .

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50  
51 135 In the second vineyard, spraying operation had a duration of 151 minutes. The formulated pesticides  
52  
53 136 were mixed with water, with a total volume in the tank sprayer of 1800 L. Pesticide mixture sprayed  
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55 137 was composed by a mixture containing fluopicolide, fluopyram, myclobutanil. The concentration of

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2  
3 138 active ingredients in the mixture were 157, 208,  $1.14 \cdot 10^8$  mg L<sup>-1</sup>, respectively. The volume applied  
4  
5 139 was 1800 L ha<sup>-1</sup>.  
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9 140 In these two spraying operations a mist blower sprayer with fan shaped diffusors was trailed by a  
10  
11 141 tractor with the cab filtration efficiency only ensuring the reduction of large aerosol particles.  
12

13  
14 142 In the melon field, spraying operation had a duration of 62 minutes. The formulated pesticides were  
15  
16 143 mixed with water, with a mean volume of the tank sprayer of 3000 L. The sprayed mixture  
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18 144 contained deltamethrin, cyflufenamid, and metrafenone. The concentration of active ingredients in  
19  
20 145 the mixture were 17, 25, 125 mg L<sup>-1</sup>, respectively. The volume applied was 6000 L ha<sup>-1</sup>.  
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24 146 The sprayer machine utilized was a boom sprayer - trailed tank that directs the spray downwards,  
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26 147 and the tractor cabs were certificated for particles with diameters typically from 3.0 µm or greater.  
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30 148 Filters were weighed before and after the sampling using a microbalance after conditioning in  
31  
32 149 climatic cabinet for 24 h, at 20° C and 50 % relative humidity. All filters were stored in aluminum  
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34 150 foils in refrigerator, and then processed following the procedure illustrated below (Yusà 2009).  
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#### 37 151 **2.4 Sample preparation**

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40 152 Particulate matter extraction was carried out by inserting filters into ASE cells, between two layers  
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42 153 of diatomaceous earth. Two successive extraction cycles, with a mixture of acetonitrile/water 90:10,  
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44 154 were carried out, collecting the solvents in a single vial. The ASE operating conditions were: heat  
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47 155 up time 5', static time 5', flush volume 60%, purge time 300 sec, pressure 1500 psi, T 100° C (Adou  
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49 156 2001).  
50

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52  
53 157 After evaporation by an evaporator under a nitrogen stream at a temperature of about 60° C, a solid-  
54  
55 158 phase clean-up was performed by applying the extracts to Strata-X cartridges, previously activated  
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57 159 with 5 mL of acetonitrile, 5 mL of ultra-gradient methanol, and 5 mL of water. Pesticides, after  
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3 160 purification with 5 mL of water, were eluted with 5 mL of methanol and 10 mL of acetonitrile/water  
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5 161 90:10. A vacuum manifold was used to quickly elute the analytes from the solid phase cartridges at  
6  
7 162 a constant flow.  
8

## 10 163 2.5 LC/MS/MS analysis

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14 164 The eluates from the SPE cartridges were evaporated, and re-solubilized in 100  $\mu\text{L}$  of methanol,  
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16 165 before the analysis. Pesticides were analyzed by injecting 5  $\mu\text{L}$  of solution onto the HPLC column.  
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18  
19  
20 166 The chromatographic method, using the  $\text{C}_{18}$  column maintained at 40  $^{\circ}\text{C}$ , included the following  
21  
22 167 gradient elution with 10 mM aqueous ammonium formate (Carlo Erba Reagents S.p.A., Arese,  
23  
24 168 Milan, Italy), as “A” and acetonitrile as “B” at a flow rate of 0.2  $\text{mL min}^{-1}$ : 0–3 min: 20% B; 3-3.1  
25  
26 169 min: 20% B  $\rightarrow$  85% B; 3.1-14 min: 85% B  $\rightarrow$  100% B.; 14-16 min: 100% B.  
27

28  
29  
30 170 Infusion of each pesticide into the mass spectrometer was performed with solutions of 10  $\text{ng mL}^{-1}$  in  
31  
32 171 water:methanol, 50:50 (v/v), or water or acetonitrile, all added with ammonium formate 10 mM at a  
33  
34 172 flow rate of 10  $\mu\text{L min}^{-1}$ , to acquire MS and MS/MS spectra of all the analytes. The optimized  
35  
36 173 parameter settings for ESI were: nebulizer voltage, 2.5 kV cell acceleration voltage 0 V for  
37  
38 174 myclobutanil and 1 V for all other pesticides; gas temperatures 120 $^{\circ}\text{C}$  for sheath and 300 $^{\circ}\text{C}$  for  
39  
40 175 auxiliary gas (both nitrogen); gas flow 13  $\text{L min}^{-1}$  for both of them; nebulizer 60 psi, capillary  
41  
42 176 voltage 3 kV. Collision energy ranged from 5 to 30 eV depending on the pesticide. MS/MS data for  
43  
44 177 deltamethrin, myclobutanil, fluopyram, dimethomorph, fluopicolide, and metrafenone were  
45  
46 178 collected in positive ion mode and the transitions  $m/z$   $(\text{M}+\text{NH}_4)^+$  523  $\rightarrow$   $m/z$  506, 281;  $m/z$   $(\text{M}+\text{H})^+$   
47  
48 179 289  $\rightarrow$   $m/z$  125, 70;  $m/z$   $(\text{M}+\text{H})^+$  397  $\rightarrow$   $m/z$  208, 173;  $m/z$   $(\text{M}+\text{H})^+$  388  $\rightarrow$   $m/z$  301, 165;  $m/z$  383  
49  
50 180  $(\text{M}+\text{H})^+$   $\rightarrow$   $m/z$  365, 173; and  $(\text{M}+\text{H})^+$  409  $\rightarrow$   $m/z$  227, 209 were chosen for the successive  
51  
52 181 experiments in SRM mode, respectively. MS/MS data for meptyldinocap, methoxyfenozide, and  
53  
54 182 cyflufenamid were collected in negative ion mode and the transitions  $m/z$   $(\text{M}-69)^-$  295  $\rightarrow$   $m/z$  163,  
55  
56 183 193;  $m/z$   $(\text{M}-\text{H})^-$  367  $\rightarrow$   $m/z$  149, 105;  $m/z$   $(\text{M}-\text{H})^-$  411  $\rightarrow$   $m/z$  391, 218 were chosen for the  
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3 184 successive experiments in SRM mode, respectively. The underlined transitions were the most  
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5 185 abundant and were used for quantitative analysis (Ortelli 2004; Mandal 2010; Mastovska 2010;  
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7 186 Sack 2011; Baker 2013; Zhang 2014; Hanot 2015; Dias 2016).  
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10  
11 187 As shown in figure 1, the analytes were acquired with the respective transitions, according to the  
12  
13 188 retention times, in two windows of elution from 0 to 9 min and from 9 minutes to the run end.  
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15  
16 189 The optimized method allowed detection of all the target analytes, by extraction from airborne  
17  
18 190 particulate matter, purification and HPLC/ESI-MS-MS analysis.  
19

### 20 21 22 191 **3 Results and discussion**

#### 23 24 25 192 **3.1 Method recovery**

26  
27  
28 193 As for recovery study, PM<sub>4</sub> was collected in parallel for two hours on six filters at the Botanical  
29  
30 194 Garden of the University "La Sapienza" and three of them were spiked with a pesticide standard  
31  
32 195 solution at concentrations of 1 mg L<sup>-1</sup>, the other filters were spiked with the solution at 0.2 mg L<sup>-1</sup>.  
33

34  
35 196 The spiked filters were extracted, and the solutions were evaporated and purified using the  
36  
37 197 described method, then analyzed in triplicate. The results showed that the recoveries for pesticides  
38  
39 198 at concentration of 0.2 mg L<sup>-1</sup> ranged from 65 to 88%, and for pesticides at a concentration of 1 mg L<sup>-1</sup>  
40  
41 199 from 74 to 95%, as reported in table 2.  
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#### 44 45 200 **3.2 Calibration curves, limits of detection and quantification, and linearity.**

46  
47  
48 201 Accelerated solvent extraction may co-extract interfering substances together with pesticides from  
49  
50 202 the atmospheric particulate matter (Choi 2001). Therefore, matrix effect was simulated by sampling  
51  
52 203 PM on five filters at the Botanical Garden of the University "La Sapienza". The filters were added  
53  
54 204 with pesticide standard solutions at growing concentrations, over a working range from each  
55  
56 205 pesticide limit of quantification to 0.8 mg L<sup>-1</sup>, and processed as described above.  
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3 206 Limits of detection and quantification were calculated by diluting the 0.2 mg L<sup>-1</sup> spiked filter  
4  
5 207 solution down to obtain a peak signal three or ten times the background noise, respectively (See tab.  
6  
7 208 2).

8  
9  
10 209 After extraction and purification, the solutions were analyzed in triplicate and the results were used  
11  
12 210 to build calibration curves for each pesticide to be used for the quantitative analysis of  
13  
14 211 environmental samples. As for the linearity, the calibration curves showed linear regression  
15  
16 212 coefficients > 0.994 (See tab. 2).

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20  
21 213 To assess the matrix effect, the ratio between the slope of the matrix matched calibration curves and  
22  
23 214 solvent-based calibration curves built from pesticide standard solutions was calculated and the  
24  
25 215 results emphasized that quantification of pesticides needs to be carried out using matrix-matched  
26  
27 216 calibration curves since the use of standard calibration curves would introduce significant errors in  
28  
29 217 the quantitative analysis (Pomata 2014).

30  
31  
32  
33 218 Solvent-based calibration curves built from pesticide standard solutions were only used for  
34  
35 219 quantifying the solutions coming from recovery studies.

### 37 38 220 **3.3 Occurrence of pesticides in air, results and discussion**

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40  
41 221 The first campaign, lasting 100 minutes, at the vineyard, was conducted on May 25<sup>th</sup>. The blank and  
42  
43 222 the four sampled filters, two internal and two external to the cab, were subjected to the procedure  
44  
45 223 described. The analyses were focused on Dimethomorph, methoxyfenozide and meptyldinocap.

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48  
49 224 The results showed concentrations lower than the limit of instrumental detection for all the analytes  
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51 225 in PM<sub>4</sub> collected inside the cab. The extracts of particulate matter sampled outside the cab showed  
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53 226 small concentrations of all the analytes and as for meptyldinocap a small amount was also found on  
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55 227 the field blank filter. Table 3 reports the values in ng of pesticides found on each filter. The results

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3 228 of the two filters positioned next to each other were averaged and since there were only two  
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5 229 samples available, the standard deviation was calculated by the method.  
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8 230 The second sampling campaign, lasting 151 minutes, at the vineyard, was conducted on June 21<sup>st</sup>.  
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10 231 The blank and the four sampled filters, two internal and two external to the cab, were subjected to  
11  
12 232 the procedure described. The analyses were focused on fluopicolide, fluopyram, and myclobutanil.  
13  
14 233 As in the first campaign, the results showed concentrations lower than the limit of instrumental  
15  
16 234 detection for all the analytes in PM<sub>4</sub> collected inside the cab. The extracts of particulate matter  
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18  
19 235 sampled outside the cab and the field blank filters showed small concentrations of all the analytes.  
20  
21 236 Table 3 reports the values in ng of pesticides found on each filter, with averaged results of the two  
22  
23 237 filters positioned next to one another and the standard deviation calculated by the method.  
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26  
27 238 In the present sampling campaign, particles larger than 4 µm diameter collected on the basis of the  
28  
29 239 cyclone were carefully retrieved, then extracted and analyzed.  
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32  
33 240 Table 4 reports the comparison between the pesticide concentration values of inhalable and  
34  
35 241 respirable fractions in ng m<sup>-3</sup>, calculated dividing the ng by the cubic meters of air sampled (377.5x10<sup>-3</sup>  
36  
37 242 m<sup>3</sup>), and shows higher concentrations of pesticides in larger particles.  
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41 243 In both the sampling campaigns, the particulate matter PM<sub>4</sub> inside the cab was higher than PM  
42  
43 244 sampled outside (data not shown), but no pesticides were found in the filter extracts. This suggests  
44  
45 245 small particles can be generated from the operator movement inside the cab (Hall 2002). Vice versa  
46  
47 246 all the pesticides were found outside the cab even in PM<sub>4</sub>. These results demonstrated the product  
48  
49 247 sprayed has not penetrated inside the cab, thus not representing a danger to the operator, despite  
50  
51 248 cabs are generally more efficient at removing aerosols larger than 3.0 µm (Hall 2002).  
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3 249 The small amounts found outside the cab arise from the fact that the sampler is not directly affected  
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5 250 by pesticide emission, as positioned upstream of the direction in which the pesticide is sprayed and  
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7 251 moves in the opposite direction together with the tractor.  
8

9  
10 252 The higher concentrations of pesticides were found in the extracts of PM at aerodynamic diameter  
11  
12 253 higher than 4  $\mu\text{m}$ , sampled outside the cab, whereas  $\text{PM}_{<4}$  inside the cab showed concentrations  
13  
14 254 lower than the limits of detection. Apparently, using large droplet size sprays not only minimizes  
15  
16 255 drift, it also yields low but non-zero concentrations of pesticides in respirable particulate matter.  
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18 256 The fact that outside pesticides are found even in small particulates is expected. Even if most of the  
19  
20 257 literature indicate that pesticide spray is typically larger than 100  $\mu\text{m}$ , Hall (2002) found noticeable  
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22 258 mass of sprayed aerosol in sizes less than 3  $\mu\text{m}$ , suggesting that pesticide spray that does not deposit  
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24 259 could become a much smaller particle due to evaporation.  
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28  
29 260 Instead, despite pesticide vapour pressure ranged within  $10^{-4} - 10^{-6}$  Pa, external blank filters  
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31 261 passively sampled the sprayed pesticides, perhaps because the filters, insufficiently protected,  
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33 262 underwent splashes.  
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36  
37 263 The third sampling campaign, lasting 62 minutes, at the melon field, was conducted on July 23<sup>rd</sup>.  
38

39 264 The blank and the four sampled filters, two internal and two external to the cab, were subjected to  
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41 265 the procedure. The analyses were focused on deltamethrin, cyflufenamid, and metrafenone. All the  
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43 266 results showed concentrations lower than the limit of instrumental detection for all the analytes.  
44

45 267 Meteorological conditions including high temperature (average temperature 31°C) and brisk breeze  
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47 268 together with the shorter period of sampling may be the cause of the results (Baldi 2006). Moreover  
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49 269 the different spraying method may have caused a low diffusion of the pesticide mixture towards the  
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51 270 sampler positioned outside the tractor (Hanafi 2016).  
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55 271 **4 Conclusion**  
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3 272 Despite being very effective in helping to increase agricultural yields, studies related with pesticides  
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5 273 in ambient air, mainly focused to achieve a better knowledge of risks to human health, need to be  
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7 274 powered. Occupational exposure can occur to operators while applying pesticide mixtures. Inhaled  
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9 275 pesticides not only may cause serious injury to human tissues, they also can be transferred through  
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11 276 the lungs into the bloodstream. Pesticide application equipment can strongly influence occupational  
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13 277 hazards and health risks. In order to reduce occupational exposition, the use of a closed cab on a  
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15 278 tractor is recommended; also appropriate weather conditions are to be considered during pesticide  
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18 279 application. Air-filtering systems of the tractor cabs also influence workers respiratory protection  
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20 280 and pesticide particle size distribution is important to estimate the filter efficiency. In order to  
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22 281 evaluate air infiltration into tractor cabs with air-filtering devices able to capture dust particles, but  
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24 282 not to remove aerosols and vapors, that are often used to protect the agricultural worker during  
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26 283 pesticide applications, in this study an analytical method for the determination of nine pesticides  
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28 284 was investigated and applied to the respirable fraction of PM, collected during pesticide spreading,  
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30 285 inside and outside the spreading tractor's cab. The optimized analytical method, applied to PM  
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32 286 samples, proved to be suitable for the measure of slight differences in pesticide contents.  
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34 287 Furthermore it turned out to be successful to detect a broad range of chemicals since it allows the  
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36 288 simultaneous determination of compounds with different chemical and physical properties.  
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38 289 Pesticide concentrations found in PM<sub>4</sub> sampled inside the tractor cabs were lower than method  
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40 290 limits of detection, demonstrating that there is no penetration of the smaller particles inside the  
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42 291 cabin. The higher concentrations of pesticides were found outside the cab in the larger fraction of  
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44 292 particulate matter. Nevertheless, the presence of pesticides, detected in PM<sub>4</sub> outside the cab,  
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46 293 demonstrates that a possible exposure might affect members of the public whether pesticide  
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48 294 application occurs near to homes, schools, nursing homes, hospitals, environmentally sensitive  
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50 295 areas, organic farms and so on.  
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57 296 **Acknowledgments**

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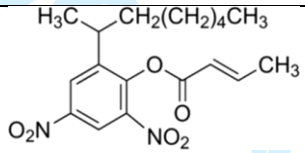
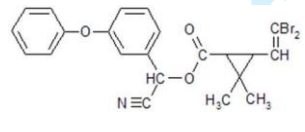
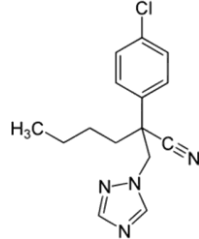
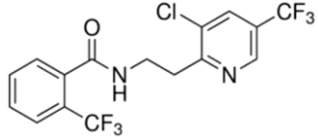
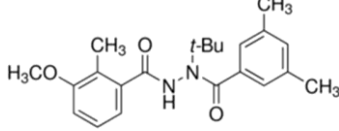
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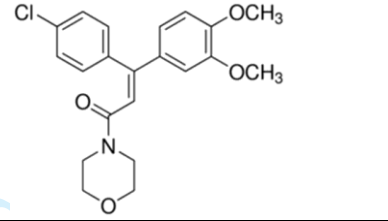
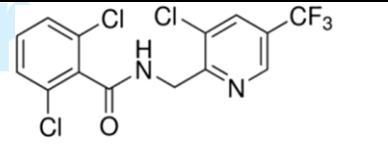
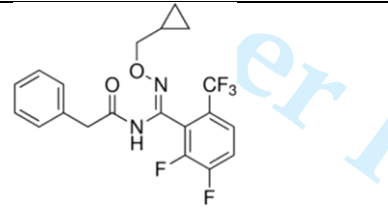
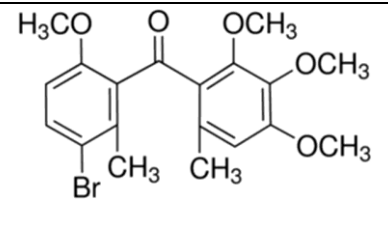
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type, and physicochemical properties (half-life in days, vapor pressure in mmHg, and Log P in octanol-water), of pesticides under study, and crops where they are used.

	chemical class type	structure	cultures	Half-life (days)	Vapor pressure (mmHg)	Log P (Octanol -Water)
meptyldinocap	dinitrophenol fungicide		grapes, cucurbits crops, strawberries	3.54	1.08e-06	5.70
deltamethrin	synthetic pyrethroid insecticide		corn, coffee, hops, artichokes, fruits	3.35	3.32e-09	5.95
myclobutanil	conazole fungicide		table and wine grapes, fruit trees, strawberry, melon, watermelon, and zucchini, cucumber, pumpkin, tomato, bell pepper, artichoke cultivations	3.35	5.71e-07	2.94
fluopyram	pyridinyl ethylbenzamide fungicide		table grapes, pome and stone fruit, vegetables	3.54	7.06e-09	4.12
methoxyfenozide	diacylhydrazine insecticide		pome fruit trees	3.35	9.38e-09	3.70

1 2 3 4 5 6 7 8 9 10	dimethomorph	morpholine fungicide		grapevines, tomatoes potatoes	4.27	4.49e-09	2.68
11 12 13 14 15	fluopicolide	benzamide and pyridine fungicide		grapes	3.54	2.76e-07	3.73
16 17 18 19 20 21 22	cyflufenamid	amidoxine fungicide		Cereals, curcubits including cucumber, courgette, melon, summer squash	3.54	2.71e-09	3.48
23 24 25 26 27 28 29 30 31	metrafenone	benzophenone fungicide		barley and wheat, is also used on grapes, tomato, bell pepper eggplant, cucumber, zucchini, melon, watermelon cultivations	7.27	1.92e-06	3.44

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414 Table 2. Recovery values at concentrations 0.2 and 1 mg L<sup>-1</sup>; limits of detection and quantification  
 415 expressed in ng mL<sup>-1</sup>; and correlation coefficients, for the nine pesticides in study.

	Rec% ± RSD (0.2 mg L <sup>-1</sup> )	Rec% ± RSD (1 mg L <sup>-1</sup> )	Limit of Detection (ng mL <sup>-1</sup> )	Limit of Quantification (ng mL <sup>-1</sup> )	Correlation Coefficient
meptyldinocap	88±3	85±2	9.9	19.2	0.998
deltametrina	69±5	78±4	86.7	108.8	0.998
myclobutanil	76±4	74±2	19.9	60.9	0.995
fluopyram	76±2	88±2	78	258	0.995
fluopicolide	81±2	75±5	4.1	12.6	0.998
methoxyfenozide	70±2	76±3	3.4	12	0.997
dimethomorph	75±5	75±3	1.1	12.2	0.998
cyflufenamid	83±2	77±4	35.8	44.3	0.994
metrofenone	65±3	95±2	3.6	4.7	0.994

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418 Table 3. Mass of pesticides (ng) in airborne particulate matter during May 25<sup>th</sup> and June 21<sup>st</sup> 2016  
 419 campaigns at vineyards. (LOD: Limit of Detection)

		Internal filters	External filters	Internal blank filters	External blank filters
May 25 <sup>th</sup>	Meptyldinocap (ng)	<LOD	22.1±0.2	<LOD	12.2±0.1
	Dimethomorph (ng)	<LOD	5.9±0.3	<LOD	<LOD
	Methoxyfenozide (ng)	<LOD	7.8±0.6	<LOD	<LOD
June 21 <sup>st</sup>	Myclobutanil (ng)	<LOD	7.5±0.5	<LOD	5.6±0.4
	Fluopyram (ng)	<LOD	22.4±0.4	<LOD	18.3±0.2
	Fluopicolide (ng)	<LOD	4.6±0.2	<LOD	2.1±0.1

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3 421 Table 4. Concentration of pesticides (ng m<sup>-3</sup>) in airborne particulate matter during June 21<sup>st</sup> 2016  
4 422 campaign at a vineyard. (LOD: Limit of Detection)

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	Internal filters PM <sub>4</sub>	Internal sampling PM <sub>&gt;4</sub>	External filters PM <sub>4</sub>	External sampling PM <sub>&gt;4</sub>
Myclobutanil ng m <sup>-3</sup>	<LOD	<LOD	19.9	314
Fluopyram ng m <sup>-3</sup>	<LOD	<LOD	59.3	69
Fluopicolide ng m <sup>-3</sup>	<LOD	<LOD	12.2	170

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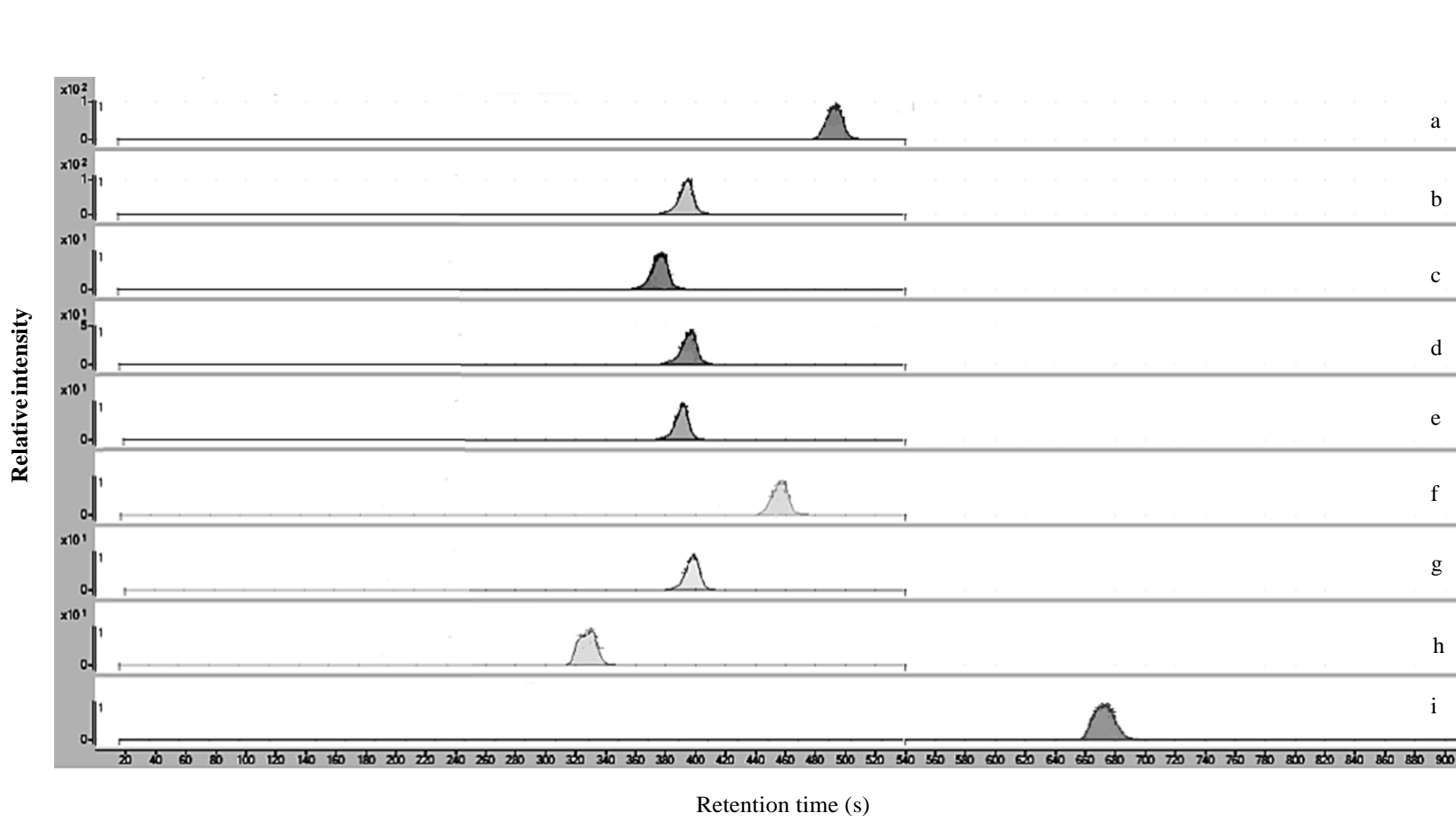


Figure 1. Chromatogram of the nine pesticides analyzed in HPLC-MS/MS in selected reaction monitoring mode. Peak identification: (a) metrafenone, (b) fluopyram, (c) dimethomorph, (d) fluopicolide, (e) myclobutanyl, (f) cyflufenamid, (g) methoxyfenazide, (h) meptyldinocap, (i) deltametrina. Analytical condition: column Luna® C18 5  $\mu$ m particle size, L  $\times$  I.D. 15 cm  $\times$  2.1 mm; mobile phase: solvent A 10 mM aqueous ammonium formate and solvent B acetonitrile; gradient: 0–3 min 20% B, 3–3.1 min 20%B  $\rightarrow$  85% B, 3.1–14 min 85% B  $\rightarrow$  100% B, 14–16 min 100% B; flow rate: 0.2 mL min<sup>-1</sup>.