<table>
<thead>
<tr>
<th>Journal:</th>
<th><em>Analytical Letters</em></th>
</tr>
</thead>
<tbody>
<tr>
<td>Manuscript ID</td>
<td>LANL-2017-0494</td>
</tr>
<tr>
<td>Manuscript Type:</td>
<td>Original Research Paper</td>
</tr>
<tr>
<td>Date Submitted by the Author:</td>
<td>31-May-2017</td>
</tr>
<tr>
<td>Complete List of Authors:</td>
<td>Di Filippo, Patrizia; Istituto Nazionale Assicurazione contro gli Infortuni sul Lavoro, DIT; Università degli Studi di Roma La Sapienza Facolta di Scienze Matematiche Fisiche e Naturali, Chemistry Pomata, Donatella; Istituto Nazionale Assicurazione contro gli Infortuni sul Lavoro, DIT Riccardi, Carmela; Istituto Nazionale Assicurazione contro gli Infortuni sul Lavoro, DIT Buiarelli, Francesca; University, Chemistry De Gennaro, Martina; Università degli Studi di Roma La Sapienza Facolta di Scienze Matematiche Fisiche e Naturali, Chemistry Console, Carla; Istituto Nazionale Assicurazione contro gli Infortuni sul Lavoro, DIT Laurendi, Vincenzo; Istituto Nazionale Assicurazione contro gli Infortuni sul Lavoro, DIT Puri, Daniele; Istituto Nazionale Assicurazione contro gli Infortuni sul Lavoro</td>
</tr>
<tr>
<td>Keywords:</td>
<td>pesticides, respirable fraction of airborne particulate matter, pesticide spreading operations, tractor cabs, High-Performance Liquid Chromatography – Tandem Mass Spectrometry (HPLC-MS/MS)</td>
</tr>
</tbody>
</table>
Determination of Pesticides in the Respirable Fraction of Airborne Particulate Matter by High-Performance Liquid Chromatography – Tandem Mass Spectrometry

Patrizia Di Filippo\textsuperscript{a,b,}, Donatella Pomata\textsuperscript{a,b}, Carmela Riccardi\textsuperscript{a,b}, Francesca Buiarelli\textsuperscript{b}, Martina De Gennaro, Carla Console, Vincenzo Laurendi, Daniele Puri.

\textsuperscript{a} Dipartimento Innovazioni Tecnologiche e Sicurezza degli Impianti Prodotti e Insediamenti Antropici, Istituto Nazionale Assicurazione Infortuni sul Lavoro, Via Roberto Ferruzzi 38/40, 00143 Rome, Italy.

\textsuperscript{b} Department of Chemistry, Sapienza University of Rome, Piazzale Aldo Moro, 5 – 00185, Rome, Italy.

\textsuperscript{c} Dipartimento Innovazioni Tecnologiche e Sicurezza degli Impianti Prodotti e Insediamenti Antropici, Istituto Nazionale Assicurazione Infortuni sul Lavoro, Via di Fontana Candida, 1 – 00040, Monteporzio Catone, Rome, Italy.

*e-mail: p.difilippo@inail.it, tel. +39(06)49693306

Abstract

Potential harmful effects of pesticides include risks to human health of workers involved in the wet spray application in cultivated areas. Inhalation exposure depends on several factors including pesticide concentrations in the respirable fraction of airborne particulate matter (PM\textsubscript{4}). In order to ensure a high level of protection, the use of tractors with cabs provides protection against dusts, aerosols and vapours. Since tractors not providing maximum protection are still in use, PM\textsubscript{4} was sampled during spreading operations in agricultural fields inside and outside the tractor cab. Sample preparation technique based on accelerated solvent extraction and solid phase extraction clean-up, was optimized before analysis of nine pesticides in PM\textsubscript{4}. Meptyldinocap, deltamethrin, myclobutanil, fluopyram, methoxyfenozide, dimethomorph, fluopicolide, cyflufenamid, 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).
Up to now, analytical method has been developed above all to determine pesticides in food and in water. Methods for pesticide extraction from environmental water samples involve liquid-liquid extraction with a large solvent consuming, solid-phase extraction methods, and solid-phase microextraction; solid phase extraction disks were also tested as an alternative (Urruty 1996; Riley 2005). The most popular pretreatment methods for pesticide extractions from food also involve liquid–liquid and solid phase extraction; microextraction techniques were also developed (Ravelo-Pérez 2009); QuEChERS methods have also been tested (Lehotay 2005). Soxhlet, pressurized liquid (PLE), and microwave assisted extractions (MAE) have been used for pesticide extraction from particulate matter. PLE and MAE are less time and organic solvent consumption (Coscollà 2009).

As for chromatographic analysis, gas chromatography coupled to mass spectrometry and liquid chromatography coupled to tandem MS (LC–MS/MS) are the most used detection techniques in pesticide residue analysis. Alder in 2006 stated that LC–MS/MS methods were more successful in terms of number of pesticides simultaneously analyzed, increased sensitivity, and selectivity (Alder 2006).

Pesticides can be applied to crops by tractors, creating high-density chemical clouds. To improve the worker safety, tractors with closed filtered air cabs are used to reduce operator exposure to airborne contaminants during the process of chemical treatments. To ensure a high level of protection, proper cab filtration system reducing dusts, aerosols and vapors, should be used and filters should be replaced based on filter efficiency. In case of using cabs providing a low protection factor (Hall 2002; Heitbrink 2003; Balsari 2010), with filter only ensuring the reduction of dusts, occurrence of airborne pesticides inside the cabs, particularly in the respirable fraction (PM$_{10}$; aerodynamic diameter less than or equal to 4 µm) of atmospheric particulate matter, causing potential deposition at inner sites of the respiratory tract, may determine inhalation hazard. Therefore, airborne concentration of pesticides can be used to correctly estimate an aspect of potential personnel exposure (Ross 2000; Coscollà 2009).
To date, data on pesticide concentrations in the respirable fraction of the airborne particulate matter, during the spreading of formulated products, are scarce, despite such data allow a more accurate risk assessment and consequently a better prevention strategy (Clausnitzer 1996; Coscollà 2011).

The aim of present paper was the determination of airborne pesticide concentrations inside tractor cabs during the operation of spreading, to assess the safety level of the vehicle. Among the many frequently used commercial formulations, nine of them were taken into consideration in this study. Table 1 reports a description of the pesticides contained in the commercial products (Kodandaram 2013; EPA Chemistry Dashboard). Since the determination of many pesticides together is especially important when analyzing airborne particulate matter collected in areas where formulated pesticide products are spread in combinations, a method for their simultaneous determination in particulate matter is investigated. The optimized method was then applied to samples of PM₄, collected inside and outside tractor cabs, used for spreading pesticides. A discussion of the results is provided in this paper. It is noteworthy to point out that for the first time pesticide measures have been carried out within tractor cabs to evaluate the degree of operator’s protection.

2. Experimental

2.1 Instrumentation

Low Volume Universal XR Pumps (SKC inc; AMS Analitica, Pesaro, Italy), operating at 0.15 m³ h⁻¹ (2.5 L min⁻¹), were used with the aid of cyclones for the collection of the respirable fraction of particulate matter.

A microbalance (Sartorius ME5; weight uncertainty ±2 µg) and a conditioning climatic cabinet (Activa Climatic Cabinet, Aquaria, Milan, Italy) were utilized for filter weighting procedure.

Particulate matter extraction was carried out by Accelerated Solvent Extraction (ASE 200–Dionex; ThermoFisher Scientific, Rodano, Milan, Italy).
Evaporation was carried out by a Glas-Col SE 500 evaporator (Bioanalitica Strumenti srl, Milan, Italy) under a nitrogen stream at a temperature of about 60° C.

A vacuum manifold 12-Port model SPE (Alltech, Casalecchio di Reno, Bologna, Italy) was used to quickly elute the analytes from the solid phase cartridges at a constant flow.

Pesticides were analyzed by liquid chromatography/ion electrospray ionization-tandem mass spectrometry (HPLC/ESI-MS/MS), in selected reaction monitoring (SRM) mode, by an Agilent 1290 series binary HPLC pump system, fitted with an autosampler (20 µL) Agilent G4226A, coupled to an Agilent Jet Stream 6460 triple quadrupole mass spectrometer with an IonSpray source (Agilent Technologies Italia S.p.A., Cernusco sul Naviglio, Milan, Italy).

### 2.2 Reagents and materials

Particulate matter was collected onto polytetrafluoroethylene membrane disc filters (diameter: 37 mm, porosity: 2.0 µm) (Pall Corporation - VWR International s.r.l., Milan, Italy).

The chromatographic method was developed using a Luna® C₁₈ Phenomenex HPLC Column 5 µm particle size, L × I.D. 15 cm × 2.1 mm, fitted with a guard column (Phenomenex, Castel Maggiore, BO, Italy).

A solid-phase clean-up was performed by applying the extracts to Strata-X cartridges (200 mg / 6 mL) (Phenomenex, Castel Maggiore, Bologna, Italy).

Ultra-gradient acetonitrile, water, and methanol were from Romil Chemicals Ltd (Cambridge, U.K.).

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

Meptyldinocap (purity 95.1%), deltamethrin (purity 98.0%), myclobutanil (purity 99.4%), fluopyram (purity 99.9%), methoxyfenozide (purity 99.8%), dimethomorph (purity 99.9%).

URL: http://mc.manuscriptcentral.com/laln E-mail: analyticalletters@email.wcu.edu
fluopicolide (purity 99.9%), cyflufenamid (purity 98.0%), and metrafenone (purity 98.1%) were from Sigma-Aldrich S.r.l., Milan, Italy.

2.2.1 Standard preparation

For infusion into the mass spectrometer, the calibration curves, and the spiked samples preparation, the stock standard solutions of the analytes were prepared by dissolving meptyldinocap, deltamethrin, myclobutanil, fluopyram, methoxyfenozide, dimethomorph, fluopicolide, cyflufenamid, and metrafenone in water:methanol, 50:50 (v/v), or water, or acetonitrile (1 mg mL$^{-1}$) and storing them at -20°C in amber vials. Working solutions were prepared by successive dilution of the stock standard solutions.

2.3 Sampling of pesticides

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

In the first campaign at the vineyard, spraying operation had a duration of 100 minutes. The formulated pesticides were mixed with water, with a total volume in the tank sprayer of 1800 L. The sprayed mixture was composed by the following active ingredients: methoxyfenozide, dimethomorph, meptyldinocap. The concentrations of active ingredients in the mixture were 267, 500, and 595 mg L$^{-1}$, respectively. The volume applied was 1800 L ha$^{-1}$.

In the second vineyard, spraying operation had a duration of 151 minutes. The formulated pesticides were mixed with water, with a total volume in the tank sprayer of 1800 L. Pesticide mixture sprayed was composed by a mixture containing fluopicolide, fluopyram, myclobutanil. The concentration of...
active ingredients in the mixture were 157, 208, $1.14 \times 10^8$ mg L$^{-1}$, respectively. The volume applied was 1800 L ha$^{-1}$.

In these two spraying operations a mist blower sprayer with fan shaped diffusors was trailed by a tractor with the cab filtration efficiency only ensuring the reduction of large aerosol particles.

In the melon field, spraying operation had a duration of 62 minutes. The formulated pesticides were mixed with water, with a mean volume of the tank sprayer of 3000 L. The sprayed mixture contained deltamethrin, cyflufenamid, and metrafenone. The concentration of active ingredients in the mixture were 17, 25, 125 mg L$^{-1}$, respectively. The volume applied was 6000 L ha$^{-1}$.

The sprayer machine utilized was a boom sprayer - trailed tank that directs the spray downwards, and the tractor cabs were certificated for particles with diameters typically from 3.0 µm or greater.

Filters were weighed before and after the sampling using a microbalance after conditioning in a climatic cabinet for 24 h, at 20° C and 50 % relative humidity. All filters were stored in aluminum foils in refrigerator, and then processed following the procedure illustrated below (Yusà 2009).

## 2.4 Sample preparation

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

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

2.5 LC/MS/MS analysis

The eluates from the SPE cartridges were evaporated, and re-solubilized in 100 µL of methanol,
before the analysis. Pesticides were analyzed by injecting 5 µL of solution onto the HPLC column.

The chromatographic method, using the C₁₈ column maintained at 40 °C, included the following
gradient elution with 10 mM aqueous ammonium formate (Carlo Erba Reagents S.p.A., Arse,
Milan, Italy), as “A” and acetonitrile as “B” at a flow rate of 0.2 mL min⁻¹: 0–3 min: 20% B; 3-3.1
min: 20% B → 85% B; 3.1-14 min: 85% B → 100% B.; 14-16 min: 100% B.

Infusion of each pesticide into the mass spectrometer was performed with solutions of 10 ng mL⁻¹
in water:methanol, 50:50 (v/v), or water or acetonitrile, all added with ammonium formate 10 mM at a
flow rate of 10 µL min⁻¹, to acquire MS and MS/MS spectra of all the analytes. The optimized
parameter settings for ESI were: nebulizer voltage, 2.5 kV; cell acceleration voltage 0 V for
methylbutilanil and 1 V for all other pesticides; gas temperatures 120° C for sheath and 300° C for
auxiliary gas (both nitrogen); gas flow 13 L min⁻¹ for both of them; nebulizer 60 psi, capillary
voltage 3 kV. Collision energy ranged from 5 to 30 eV depending on the pesticide. MS/MS data for
deltamethrin, methylbutilanil, flupyram, dimethomorph, flupicolide, and metrafenone were
collected in positive ion mode and the transitions m/z (M+NH₄)⁺ 523 → m/z 506, 281; m/z (M+H)⁺
289 → m/z 125, 70; m/z (M+H)⁺ 397→ m/z 208, 173; m/z (M+H)⁺ 388 → m/z 301, 165; m/z 383
(M+H)⁺ → m/z 365, 173; and (M+H)⁺ 409 → m/z 227, 209 were chosen for the successive
experiments in SRM mode, respectively. MS/MS data for meptyldinocap, methoxyfenozide, and
cyflufenamid were collected in negative ion mode and the transitions m/z (M-69)⁻ 295 → m/z 163,
193; m/z (M-H)⁻ 367 → m/z 149, 105; m/z (M-H)⁻ 411 → m/z 391, 218 were chosen for the

URL: http://mc.manuscriptcentral.com/lanl E-mail: analyticalletters@email.wcu.edu
successive experiments in SRM mode, respectively. The underlined transitions were the most abundant and were used for quantitative analysis (Ortelli 2004; Mandal 2010; Mastovska 2010; Sack 2011; Baker 2013; Zhang 2014; Hanot 2015; Dias 2016).

As shown in figure 1, the analytes were acquired with the respective transitions, according to the retention times, in two windows of elution from 0 to 9 min and from 9 minutes to the run end.

The optimized method allowed detection of all the target analytes, by extraction from airborne particulate matter, purification and HPLC/ESI-MS-MS analysis.

3 Results and discussion

3.1 Method recovery

As for recovery study, PM$_4$ was collected in parallel for two hours on six filters at the Botanical Garden of the University "La Sapienza" and three of them were spiked with a pesticide standard solution at concentrations of 1 mg L$^{-1}$, the other filters were spiked with the solution at 0.2 mg L$^{-1}$. The spiked filters were extracted, and the solutions were evaporated and purified using the described method, then analyzed in triplicate. The results showed that the recoveries for pesticides at concentration of 0.2 mg L$^{-1}$ ranged from 65 to 88%, and for pesticides at concentration of 1 mg L$^{-1}$ from 74 to 95%, as reported in table 2.

3.2 Calibration curves, limits of detection and quantification, and linearity.

Accelerated solvent extraction may co-extract interfering substances together with pesticides from the atmospheric particulate matter (Choi 2001). Therefore, matrix effect was simulated by sampling PM on five filters at the Botanical Garden of the University "La Sapienza". The filters were added with pesticide standard solutions at growing concentrations, over a working range from each pesticide limit of quantification to 0.8 mg L$^{-1}$, and processed as described above.
The results showed concentrations lower than the limit of instrumental detection for all the analytes in PM4 collected inside the cab. The extracts of particulate matter sampled outside the cab showed small concentrations of all the analytes and as for meptyldinocap a small amount was also found on the field blank filter. Table 3 reports the values in ng of pesticides found on each filter. The results emphasized that quantification of pesticides needs to be carried out using matrix-matched calibration curves since the use of standard calibration curves would introduce significant errors in the quantitative analysis (Pomata 2014).

Solvent-based calibration curves built from pesticide standard solutions were only used for quantifying the solutions coming from recovery studies.

### 3.3 Occurrence of pesticides in air, results and discussion

The first campaign, lasting 100 minutes, at the vineyard, was conducted on May 25th. The blank and the four sampled filters, two internal and two external to the cab, were subjected to the procedure described. The analyses were focused on Dimethomorph, methoxyfenozide, and meptyldinocap. The results showed concentrations lower than the limit of instrumental detection for all the analytes in PM4 collected inside the cab. The extracts of particulate matter sampled outside the cab showed small concentrations of all the analytes and as for meptyldinocap a small amount was also found on the field blank filter. Table 3 reports the values in ng of pesticides found on each filter. The results...
of the two filters positioned next to each other were averaged and since there were only two samples available, the standard deviation was calculated by the method.

The second sampling campaign, lasting 151 minutes, at the vineyard, was conducted on June 21st. The blank and the four sampled filters, two internal and two external to the cab, were subjected to the procedure described. The analyses were focused on fluopicolide, fluopyram, and myclobutanil. As in the first campaign, the results showed concentrations lower than the limit of instrumental detection for all the analytes in PM$_4$ collected inside the cab. The extracts of particulate matter sampled outside the cab and the field blank filters showed small concentrations of all the analytes.

Table 3 reports the values in ng of pesticides found on each filter, with averaged results of the two filters positioned next to one another and the standard deviation calculated by the method.

In the present sampling campaign, particles larger than 4 µm diameter collected on the basis of the cyclone were carefully retrieved, then extracted and analyzed.

Table 4 reports the comparison between the pesticide concentration values of inhalable and respirable fractions in ng m$^{-3}$, calculated dividing the ng by the cubic meters of air sampled ($377.5 \times 10^3$ m$^3$), and shows higher concentrations of pesticides in larger particles.

In both the sampling campaigns, the particulate matter PM$_4$ inside the cab was higher than PM sampled outside (data not shown), but no pesticides were found in the filter extracts. This suggests small particles can be generated from the operator movement inside the cab (Hall 2002). Vice versa all the pesticides were found outside the cab even in PM$_4$. These results demonstrated the product sprayed has not penetrated inside the cab, thus not representing a danger to the operator, despite cabs are generally more efficient at removing aerosols larger than 3.0 µm (Hall 2002).
The small amounts found outside the cab arise from the fact that the sampler is not directly affected by pesticide emission, as positioned upstream of the direction in which the pesticide is sprayed and moves in the opposite direction together with the tractor.

The higher concentrations of pesticides were found in the extracts of PM at aerodynamic diameter higher than 4 µm, sampled outside the cab, whereas PM$_{<4}$ inside the cab showed concentrations lower than the limits of detection. Apparently, using large droplet size sprays not only minimizes drift, it also yields low, but non-zero concentrations of pesticides in respirable particulate matter. The fact that outside pesticides are found even in small particulates is expected. Even if most of the literature indicate that pesticide spray is typically larger than 100 µm, Hall (2002) found noticeable mass of sprayed aerosol in sizes less than 3 µm, suggesting that pesticide spray that does not deposit could become a much smaller particle due to evaporation.

Instead, despite pesticide vapour pressure ranged within $10^{-4}$ – $10^{-6}$ Pa, external blank filters passively sampled the sprayed pesticides, perhaps because the filters, insufficiently protected, underwent splashes.

The third sampling campaign, lasting 62 minutes, at the melon field, was conducted on July 23rd. The blank and the four sampled filters, two internal and two external to the cab, were subjected to the procedure. The analyses were focused on deltamethrin, cyflufenamid, and metrafenone. All the results showed concentrations lower than the limit of instrumental detection for all the analytes. Meteorological conditions including high temperature (average temperature 31°C) and brisk breeze together with the shorter period of sampling may be the cause of the results (Baldi 2006). Moreover the different spraying method may have caused a low diffusion of the pesticide mixture towards the sampler positioned outside the tractor (Hanafi 2016).

4 Conclusion
Despite being very effective in helping to increase agricultural yields, studies related with pesticides in ambient air, mainly focused to achieve a better knowledge of risks to human health, need to be powered. Occupational exposure can occur to operators while applying pesticide mixtures. Inhaled pesticides not only may cause serious injury to human tissues, they also can be transferred through the lungs into the bloodstream. Pesticide application equipment can strongly influence occupational hazards and health risks. In order to reduce occupational exposition, the use of a closed cab on a tractor is recommended; also appropriate weather conditions are to be considered during pesticide application. Air-filtering systems of the tractor cabs also influence workers respiratory protection and pesticide particle size distribution is important to estimate the filter efficiency. In order to evaluate air infiltration into tractor cabs with air-filtering devices able to capture dust particles, but not to remove aerosols and vapors, that are often used to protect the agricultural worker during pesticide applications, in this study an analytical method for the determination of nine pesticides was investigated and applied to the respirable fraction of PM, collected during pesticide spreading, inside and outside the spreading tractor’s cab. The optimized analytical method, applied to PM samples, proved to be suitable for the measure of slight differences in pesticide contents. Furthermore it turned out to be successful to detect a broad range of chemicals since it allows the simultaneous determination of compounds with different chemical and physical properties. Pesticide concentrations found in PM$_4$ sampled inside the tractor cabs were lower than method limits of detection, demonstrating that there is no penetration of the smaller particles inside the cabin. The higher concentrations of pesticides were found outside the cab in the larger fraction of particulate matter. Nevertheless, the presence of pesticides, detected in PM$_4$ outside the cab, demonstrates that a possible exposure might affect members of the public whether pesticide application occurs near to homes, schools, nursing homes, hospitals, environmentally sensitive areas, organic farms and so on.

Acknowledgments
This work was supported by Istituto Nazionale per l’Assicurazione contro gli Infortuni sul Lavoro (Italy)/Ricerca Obbligatoria/2016-2018

References


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.

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

URL: http://mc.manuscriptcentral.com/lanl E-mail: analyticalletters@email.wcu.edu
<p>| | | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>dimethomorph</td>
<td>morpholine</td>
<td>fungicide</td>
<td>grapevines, tomatoes</td>
<td>4.27</td>
<td>4.49e-09</td>
<td>2.68</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>potatoes</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>fluopicolide</td>
<td>benzamide and pyridine</td>
<td>fungicide</td>
<td>grapes</td>
<td>3.54</td>
<td>2.76e-07</td>
<td>3.73</td>
</tr>
<tr>
<td>cyflufenamid</td>
<td>amidoxine</td>
<td>fungicide</td>
<td>Cereals, curcubits</td>
<td>3.54</td>
<td>2.71e-09</td>
<td>3.48</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>including cucumber,</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>courgette, melon,</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>summer squash</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>metrafenone</td>
<td>benzophenone</td>
<td>fungicide</td>
<td>barley and wheat,</td>
<td>7.27</td>
<td>1.92e-06</td>
<td>3.44</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>is also used on grapes,</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>tomato, bell pepper</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>eggplant, cucumber,</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>zucchini, melon,</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>watermelon cultivations</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 2. Recovery values at concentrations 0.2 and 1 mg L\(^{-1}\); limits of detection and quantification expressed in ng mL\(^{-1}\); and correlation coefficients, for the nine pesticides in study.

<table>
<thead>
<tr>
<th>Pesticide</th>
<th>Rec% ± RSD (0.2 mg L(^{-1}))</th>
<th>Rec% ± RSD (1 mg L(^{-1}))</th>
<th>Limit of Detection (ng mL(^{-1}))</th>
<th>Limit of Quantification (ng mL(^{-1}))</th>
<th>Correlation Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>meptyldinocap</td>
<td>88±3</td>
<td>85±2</td>
<td>9.9</td>
<td>19.2</td>
<td>0.998</td>
</tr>
<tr>
<td>deltametrina</td>
<td>69±5</td>
<td>78±4</td>
<td>86.7</td>
<td>108.8</td>
<td>0.998</td>
</tr>
<tr>
<td>myclobutanil</td>
<td>76±4</td>
<td>74±2</td>
<td>19.9</td>
<td>60.9</td>
<td>0.995</td>
</tr>
<tr>
<td>fluopyram</td>
<td>76±2</td>
<td>88±2</td>
<td>78</td>
<td>258</td>
<td>0.995</td>
</tr>
<tr>
<td>fluopicolide</td>
<td>81±2</td>
<td>75±5</td>
<td>4.1</td>
<td>12.6</td>
<td>0.998</td>
</tr>
<tr>
<td>methoxyfenozide</td>
<td>70±2</td>
<td>76±3</td>
<td>3.4</td>
<td>12</td>
<td>0.997</td>
</tr>
<tr>
<td>dimethomorph</td>
<td>75±5</td>
<td>75±3</td>
<td>1.1</td>
<td>12.2</td>
<td>0.998</td>
</tr>
<tr>
<td>cyflufenamid</td>
<td>83±2</td>
<td>77±4</td>
<td>35.8</td>
<td>44.3</td>
<td>0.994</td>
</tr>
<tr>
<td>metrofenone</td>
<td>65±3</td>
<td>95±2</td>
<td>3.6</td>
<td>4.7</td>
<td>0.994</td>
</tr>
</tbody>
</table>
Table 3. Mass of pesticides (ng) in airborne particulate matter during May 25th and June 21st 2016 campaigns at vineyards. (LOD: Limit of Detection)

<table>
<thead>
<tr>
<th></th>
<th>Internal filters</th>
<th>External filters</th>
<th>Internal blank filters</th>
<th>External blank filters</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>May 25th</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Meptyldinocap (ng)</td>
<td>&lt;LOD</td>
<td>22.1±0.2</td>
<td>&lt;LOD</td>
<td>12.2±0.1</td>
</tr>
<tr>
<td>Dimethomorph (ng)</td>
<td>&lt;LOD</td>
<td>5.9±0.3</td>
<td>&lt;LOD</td>
<td>&lt;LOD</td>
</tr>
<tr>
<td>Methoxyfenozide (ng)</td>
<td>&lt;LOD</td>
<td>7.8±0.6</td>
<td>&lt;LOD</td>
<td>&lt;LOD</td>
</tr>
<tr>
<td><strong>June 21st</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Myclobutanil (ng)</td>
<td>&lt;LOD</td>
<td>7.5±0.5</td>
<td>&lt;LOD</td>
<td>5.6±0.4</td>
</tr>
<tr>
<td>Fluopyram (ng)</td>
<td>&lt;LOD</td>
<td>22.4±0.4</td>
<td>&lt;LOD</td>
<td>18.3±0.2</td>
</tr>
<tr>
<td>Fluopicolide (ng)</td>
<td>&lt;LOD</td>
<td>4.6±0.2</td>
<td>&lt;LOD</td>
<td>2.1±0.1</td>
</tr>
</tbody>
</table>
Table 4. Concentration of pesticides (ng m\(^{-3}\)) in airborne particulate matter during June 21\(^{st}\) 2016 campaign at a vineyard. (LOD: Limit of Detection)

<table>
<thead>
<tr>
<th></th>
<th>Internal filters PM(_{4})</th>
<th>Internal sampling PM(_{4})</th>
<th>External filters PM(_{4})</th>
<th>External sampling PM(_{4})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Myclobutinil ng m(^{-3})</td>
<td>&lt;LOD</td>
<td>&lt;LOD</td>
<td>19.9</td>
<td>314</td>
</tr>
<tr>
<td>Fluopyram ng m(^{-3})</td>
<td>&lt;LOD</td>
<td>&lt;LOD</td>
<td>59.3</td>
<td>69</td>
</tr>
<tr>
<td>Fluopicolide ng m(^{-3})</td>
<td>&lt;LOD</td>
<td>&lt;LOD</td>
<td>12.2</td>
<td>170</td>
</tr>
</tbody>
</table>
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) methoxyfenozide, (h) meptyldinocap, (i) deltametrina. Analytical condition: column Luna® C18 5 µm particle size, L × I.D. 15 cm × 2.1 mm; mobile phase: solvent A 10 mM aqueous ammonium formate and solvent B acetonitrile; gradient: 0–3 min 20% B, 3.1-3.1 min 20% B → 85% B, 3.1-14 min 85% B → 100% B, 14-16 min 100% B; flow rate: 0.2 mL min⁻¹.