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# Retrospective screening of pesticide metabolites in ambient air using liquid chromatography coupled to high-resolution mass spectrometry

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ABSTRACT

A new methodology for the retrospective screening of pesticide metabolites in ambient air was developed, using liquid chromatography coupled to Orbitrap high-resolution mass spectrometry (UHPLC-HRMS), including two systematic workflows (i) post-run target screening (suspect screening) and (ii) non-target screening. An accurate-mass database was built and used for the post-run screening analysis. The database contained 240 pesticide metabolites found in different matrixes such as air, soil, water, plants, animals and humans. For non-target analysis, a "fragmentation-degradation" relationship strategy was selected. The proposed methodology was applied to 31 air samples (PM10) collected in the Valencian Region (Spain). In the post-target analysis 34 metabolites were identified, of which 11 (3-ketocarburan, carbofuran-7-phenol, carbendazim, desmethylisoproturon, ethiofencarb-sulfoxide, malaoxon, methiocarb-sulfoxide, N-(2-ethyl-6-methylphenyl)-L-alanine, omethoate, 2-hydroxy-terbuthylazine, and THPAM) were confirmed using analytical standards. The semiquantitative estimated concentration ranged between 6.78 and 198.31 pg $m^{-3}$. Likewise, two unknown degradation products of malaoxon and fenhexamid were elucidated in the non-target screening.



## 1. Introduction

A wide variety of pesticides can be applied in agriculture and their use depends on a range of factors including the specific pest and crop of interest. During 2010, about 208.000 tonnes of pesticide-active ingredients were used in Europe (EU-15) [1] and more than 300 active substances are nowadays authorised by the European Union for their application on various crops according to the Regulation (EC) 1107/2009 [2].

Following application, pesticides are partitioned among soil, water and the atmosphere, and a deep concern has been expressed for the possible effects of the active substances and their metabolites on human health and the environment. Once released in the environment, pesticides are susceptible of biological and chemical degradation, which may result in the formation of a range of different compounds, commonly termed "metabolites" (this includes biological metabolites, transformation and degradation products, reaction products). Once formed in a specific compartment (e.g. soil) where pesticides undergo transformations that give place to a wide pattern of metabolites, these can move to other compartments such as groundwater or air. Generally, metabolites show lower toxicity than the parent compound, however, in some instances metabolites are more toxic, or hold certain biological activity (relevant metabolites), such as oxygen analogs (oxons) in air samples [3]. Like the original molecules, metabolites and their transformation products can also be present in the atmosphere. The presence of pesticide metabolites in the atmosphere could be linked to the chemical degradation of parent compounds in air and to volatilization or wind erosion of metabolites formed in soil or water.

All this may add up to a large number of compounds entering the atmosphere, and it is interesting to note that unlike in water, soil and food, not many of all possible metabolites have been monitored in air, and that there is a very scarce knowledge related with their occurrence, fate and impact, showing that there is a need for more studies in these fields [4–6].

Triple quadrupole (QqQ) based mass spectrometers coupled to gas and liquid chromatographs are the most important analysers used for multiresidue pesticide analysis. This is because of their

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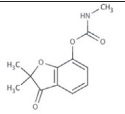
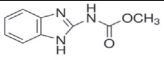
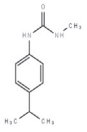
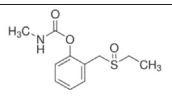
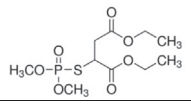
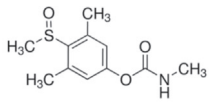
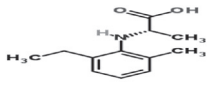
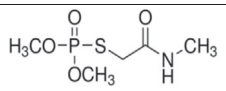
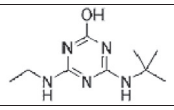
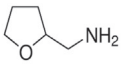
**Table 1**
Pesticide metabolites identified and confirmed with standards in the for post-run target screening (suspected screening) ($n=31$).

| Metabolite | CAS number | Structure | Parent | Monitored Mass[a] $[M+H]^+$ | Δm (ppm) $([M+H]^+)$ | Δm (ppm) (FRAG. 1) | Retention time of standard (min) | Range of Retention time of samples (min) | Number of detected samples | Average/ Estimated range level (pg $m^{-3}$)[1] |
|---|---|---|---|---|---|---|---|---|---|---|
| 3-ketocarbofuran | 16709-30-1 |  | Carbofuran | 236.09173 | -0.62 | 0.83 | 6.37 | 6.39 | 1 | 98.64 |
| Carbendazim | 10605-21-7 |  | Methyl-Thiophanate | 192.07675 | 0.57-1.23 | 0.32-1.64 | 5.36 | 5.27-5.41 | 28 | 33.54/ 19.62-184.57 |
| Carbofuran-7-phenol | 1563-38-8 |  | Carbofuran | 165.09100 | 0.15-0.56 | 1.72-2.56 | 4.04 | 4.02-4.06 | 3 | 71.12/ 51.77-93.33 |
| Desmethylisoproturon | 34123-57-4 |  | Isoproturon | 193.13354 | -0.36-0.57 | 0.19-1.77 | 7.45 | 7.42-7.46 | 2 | 17.01/ 12.82-21.19 |
| Ethiofencarb-sulfoxide | 53380-22-6 |  | Ethiofencarb | 241.07726 | -1.11-(-0.53) | 0.57-0.83 | 5.80 | 5.88-5.91 | 2 | 34.36/ 26.08-42.63 |
| Malaoxon | 1634-78-2 |  | Malathion | 315.06618 | 1.67-2.24 | 2.14-2.34 | 6.90 | 6.89-6.95 | 2 | 39.87/ 37.63-42.11 |
| Methiocarb-sulfoxide | 2635-10-1 |  | Methiocarb | 242.08454 | 2.67-3 | 1.62-1.96 | 5.84 | 5.86-5.88 | 2 | 23.10/ 21.20-25.0 |
| N-(2-ethyl-6-methylphenyl)-L-alanine | 82508-03-0 |  | Metolachlor | 208.13320 | 2.33-2.75 | 1.82-1.99 | 7.01 | 6.94-7.07 | 6 | 43.71/ 25.44-89.47 |
| Omethoate | 1113-02-6 |  | Dimethoate | 214.02974 | -0.22-1.83 | 0.72-1.83 | 4.43 | 4.36-4.48 | 12 | 102.37/ 16.01-198.31 |
| Terbuthylazine-2-OH | 66753-07-9 |  | Terbuthylazine | 212.15059 | 1.73-2.87 | 1.58-2.56 | 5.98 | 5.97-6.08 | 15 | 36.33/ 12.77-86.45 |
| THPAM | 4795-29-3 |  | Captan | 102.09134 | 1.23-1.99 | 1.25-1.47 | 7.76 | 7.73-7.78 | 3 | 9.71/ 6.78-13.18 |

[a]All isotopic pattern>90 %.

excellent quantitation and identification properties for a group of target compounds. However, these instruments have certain limitations: they require acquisition parameter optimization for each analyzed compound, the number of analyzed compounds is limited, only compounds from a target list can be detected and retrospective data analysis is impossible [7]. Consequently, these techniques are "blind" to any compound present in the sample but not included in the list of monitored analytes. As an alternative, the use of liquid chromatography coupled to high resolution mass spectrometry (LC-HRMS) has an increasing use in this field. The main advantage of LC-HRMS, such as TOF and Orbitrap, is that enables the acquisition of unlimited number of species by means of accurate mass measurements (1–5 ppm) combined with high resolving power (25000–50000 FWHM) [8,9]. On the other hand, LC-HRMS could achieve similar sensibility than multi-residue methods developed for the analysis of pesticides using LC-MS/MS [10,11].

In a previous paper we worked on a LC-HRMS strategy mainly focused on the parent pesticides [11]. In this paper, we developed an analytical strategy for retrospective screening analysis of pesticide metabolites (transformation products) in ambient air, based on a comprehensive database containing about 240 metabolites (suspect screening) and in the use of the "fragmentation-