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Combined target and post-run target strategy for a comprehensive analysis of pesticides in ambient air using liquid chromatography-Orbitrap high resolution mass spectrometry

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ABSTRACT

A comprehensive strategy for the analysis of current airborne pesticides has been developed using liquid chromatography coupled to high resolution mass spectrometry. The methodology includes both quantitative target analysis and post-run target screening analysis. The quantitative method was validated after a previous statistical optimisation of the main factors governing the ion source ionization and a study of the single-stage Orbitrap fragmentation through the HCD cell. The quantitative method presented recoveries ranging from 73 to 116%, with precision (RSD) lower than 20%, for the 35 substances in the scope of the target method. The full-scan accurate mass data were acquired with a resolving power of 50000 FWHM (scan speed, 2 Hz), and alternating two acquisition events, ESI+ without fragmentation and ESI+ with fragmentation. The method-LOQ was 6.5 pg m^{-3} for most of the target pesticides. For post-target screening a customized theoretical database, that included pesticides, metabolites and other substances such as emerging flame retardants was built up. For identification, accurate exact mass with less than 5 ppm, and some diagnostic ions including isotopes and/or fragments were used.

The strategy was applied to ten samples collected in a rural area of Valencia (Spain). Four pesticides, namely carbendazim, metalaxyl, myclobutanil and terbuthylazine, were detected in concentrations from 16 pg m^{-3} to 174 pg m^{-3}. Some pesticides and metabolites (endothal, fenfuram, terbuthylazine-2-OH), in addition to two flame retardants were tentatively identified in the post-run target screening analysis.

1. Introduction

About 208.000 tonnes of pesticide active ingredients were used in Europe (EU-15) during 2010 [1]. Likewise, more than 300 active substances are nowadays authorised by the European Union for their application on various crops according to the Directive 91/414/CEE. During the spray application of pesticides, a fraction of the dosage applied to the target area is deposited onto adjacent non-target areas (spray drift) and another fraction is lost into the atmosphere. After application, wind erosion of soil particles containing sorbed pesticides and volatilization from soil and plants may represent further significant pesticide input into the troposphere for several days or even weeks after application [2,3]. As a result of this massive use and their subsequent emission into the atmosphere, a large number of currently used pesticides (CUPs) is found in ambient air in concentrations ranging from few pg m^{-3} to several ng m^{-3} [4–6]. In the atmosphere pesticides are distributed between the particle and the gas phases.

Two recent studies have reviewed the main analytical methods used for determination of CUPs in the atmosphere; both in the particulate and gaseous phase [7,8]. Gas chromatography coupled to mass spectrometry (GC-MS) in SIM mode (simple quadrupole analyzer) [9] and mass spectrometry in tandem (triple quadrupole analyzer) [10] are currently the most employed techniques for the GC-amenable pesticides. However, the number of non-GC-amenable pesticides, either because of their poor volatility or their thermal instability has increased considerably in recent years; consequently, methods using liquid chromatography coupled to MS working in tandem mode (MS/MS) have been developed. In a recent work, Coscolla et al. [11] published a method for the determination of 30 CUPs in fine airborne particulate matter using liquid chromatography-tandem mass spectrometry with a triple quadrupole analyzer. Nevertheless, apart from this and a few other

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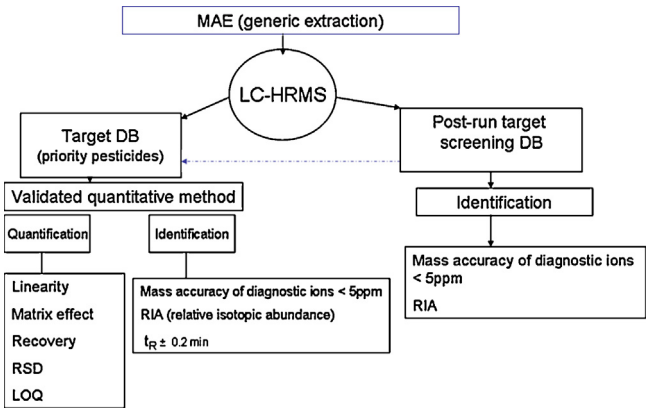

Fig. 1. Analytical strategy which combines quantitative target and post-target screening analysis.

works, the LC-MS/MS methods are not as extensively used in ambient air as in food and water analysis of pesticides.

For pesticide determination in food and environmental analysis LC coupled to high-resolution mass spectrometers (HRMS) has become increasingly popular with many papers published in the last four years [12,13]. The use of HRMS, such as TOF or Orbitrap, for multiresidue analysis is largely driven by the advantages of using the full-scan acquisition mode with high sensitivity, combined with high resolving power (>50000 FWHM) and accurate mass measurement (1–5 ppm) [14]. This powerful analytical tool allows the development of analytical strategies that combine (i) target analysis (determination of specific priority analytes for which standards are available and for which accurate mass, retention time window, isotopic pattern and fragments are reliable identification tools); (ii) post-run target or retrospective screening analysis based on an accurate-mass customized database of known parent molecules and some diagnostic fragment ions or isotopic pattern, and (iii) non-target with no selection of analytes to be searched [15,16].

The presence of pesticides in ambient air in a rural area shows its own specific profile that is linked to the main protection plant products used in agricultural practices in the area (priority pesticides) [17]. The concentration of these specific pesticides needs to be quantitatively determined for exposure and risk assessment purposes. On the other hand, other pesticides may be present owing to its use in nearby areas (transport), or illegal use. Likewise, degradation products or metabolites of pesticides could be of health interest if they present a biological activity similar to that of the parent molecule. All this may constitute a large number of compounds whose inclusion in a quantitative method is not justified unless the substances have a significant presence.

Taking into account all of the above, in this study we have developed an analytical strategy that combines quantitative target analysis for priority pesticides with post-target screening analysis (identification) based on a comprehensive customized database (see Fig. 1). The analytical methodology was applied to PM 10 samples (particulate matter with diameter < 10 μm) collected from the monitoring network of the Regional Valencia Government (Spain). To our knowledge, no work has previously reported analysis of CUPs in ambient air using liquid chromatography-high resolution mass spectrometry.

2. Experimental

2.1. Chemicals and reagents

High purity standard pesticides, omethoate (97%), thiamethoxam (98.5%), carbendazim (99%), pirimicarb-desmethyl (99.5%), thiabendazole (98.5%), imidacloprid (99%), dimethoate (98%) acetamiprid (99%), pirimicarb (98.7%), carbofuran (99%), imazalil (97.5%), diuron (98%), metalaxyl (99.5%), pyrimethanil (99%), fluazifop (96%), azoxystrobin (99.5%), methidathion (98.5%), terbuthylazine (99.5%), fluquinconazole (99%), cyproconazole (99%), fenbuconazole (98.7%), myclobutanil (99%), fenoxycarb (99.5%), fenhexamid (99.5%), iprovalicarb (97.5%), flusilazole (99.5%), benalaxyl (99.5%), tebuconazole (98.5%), difenoconazole (98.7%), cyprodinil (97.5%), bitertanol (98%), prochloraz (99.5%), triflumizole (98.5%), tebufenpyrad (98%) and buprofezin (99%), were supplied by Dr. Ehrenstorfer (Augsburg, Germany).

Individual stock standards were prepared weighting 10 mg of pure standard using a 5-decimal analytical balance and dissolving each compound in 50 ml of acetone. They were stored in capped amber vials at −21 °C. Mix working solutions at 10 and 1 mg l^{-1} were prepared with methanol. Calibration solutions were prepared by adding variable volumes of the mix working solutions in the PM 10 blank filters.

Methanol and acetonitrile were HPLC grade supplied by Scharlau (Barcelona, Spain). Acetone, ethyl acetate and water were of HPLC grade and were purchased from Merck (Darmstadt, Germany). Glacial acetic acid (Reag. Ph. Eur.) and formic acid 98% were provided by Panreac (Barcelona, Spain). Ammonium acetate for HPLC (97%) was purchased from Scharlau (Barcelona, Spain). Ammonium formate, solution Ultra (100 ml, 10 M in water) was provided by Fluka (Steinheim, Switzerland).

Statistical data manipulation and numerical analysis of data resulting from experimental design were carried out using the statistical package MINITAB for Windows, Release 14 (Minitab Inc., Birmingham, UK).

2.2. Sampling and site characterization

PM 10 samples were collected using a large-volume sampler from Digitel (Madrid, Spain) and quartz fiber filters of 150 mm of diameter, supplied by Munktell filter AB (Falun, Sweden). A sampling flow of 30 m^3 h^{-1} for 24 h that provides a total volume of air around 760 m^3 was used.

Samples were collected in Alzira (42,543 inhabitants), a city in the centre of the Valencia region (43 km from Valencia city), which has many citrus crops, such as orange trees, in its vicinity. The sampling station was placed in a rural area, at approximately 1 km from the city of Alzira (0°27′28″W, 39°09′00″N). A total of 10 samples were collected from June to July 2013. Samples were measured at about 3 m above ground level.

2.3. Sample preparation

When a wide-scope analysis is applied, non selective sample preparation is preferred in order to extract the highest number of compounds. A generic extraction method developed in a previous work using microwave extraction (MAE) with ethyl acetate was employed [11]. MAE of pesticides from PM 10 samples was carried out using a Mars system from CEM corporation (Mathews, NC, USA) equipped with Teflon® TFM 100 ml extraction vessels. The extraction conditions were as follows: a temperature of 50 °C was applied for 20 min, using a power of 1200 W, and 30 ml of ethyl acetate were added. After cooling, the reactor was opened and the extracts were filtered. After 100 μl of diethylene glycol (keeper) were added to the extract, it was concentrated with Turbo Vap 500 (Zymark, Idstein, Germany). The extracts were re-dissolved with 1 ml of water:methanol (70:30) and filtered through a 0.22 μm GHP Acrodisc filter from Pall Life Science (Ann Arbor, USA) prior to the LC–HRMS determination.