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Risk assessment of airborne pesticides in a Mediterranean region of Spain

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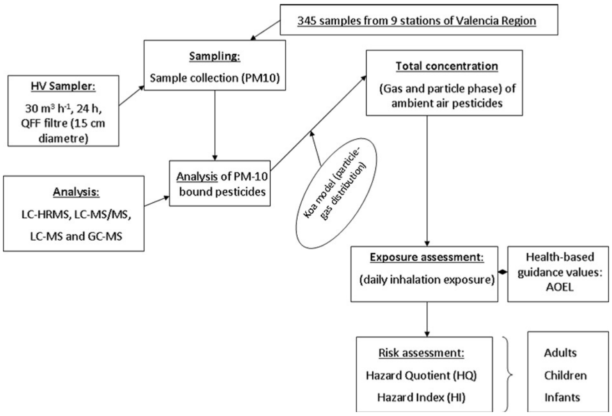
HIGHLIGHTS

- Levels of airborne pesticides ranged from 8 to 30,000 pg m^{-3}.
- Inhalation exposure was estimated for 40 airborne pesticides.
- Hazard Quotient was <1 for all pesticides detected in the three groups of population.
- Hazard Index was less than 1 for the three groups of population.

GRAPHICAL ABSTRACT



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ABSTRACT

A risk assessment strategy based on the quantitative target analysis and semi-quantitative retrospective screening determination of pesticides in PM10 has been developed. The proposed methodology was applied to 345 real samples from nine stations of a Mediterranean area in Spain, and the risk was assessed for adult, children and infants. Forty pesticides were detected with average concentrations ranging from 8 to 30,000 pg m^{-3}. Each station showed its specific pesticide profile, which is linked to the different types of crops around each station. For adults, children and infants the estimated chronic inhalation risk, expressed as Hazard Quotient (HQ), was <1 for all pesticides. The cumulative exposure for organophosphates, neonicotinoids, benzimidazoles, carbamates, micro-organism and triazoles pesticides (HI, Hazard Index) were <1 for the three groups of populations assessed. For infants, the cancer risk estimated for the detected pesticides classified as possible and potential carcinogens were lower than 1.0 E-06, except for carbendazim and hexythiazox.

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1. Introduction

A wide variety of pesticides can be applied in agriculture and their identity depends on a range of factors including the specific pest and crop of interest. During 2013, about 300,000 t of pesticide active ingredients were used in Europe (EU-15) (Eurostat, 2013; ECPA, 2010) and around 500 active substances are nowadays authorised by the European Union for their application on various crops according to the Regulation (EC) 1107/2009 (EU Pesticide Database, 2016). The potentially adverse effects of exposure to pesticides on the general population, and specifically on the more susceptible groups such as infants and children, are a public health concern (Marks et al., 2010; London et al., 2012).

Apart from ingestion of food and drinking water, inhalation of ambient air could be a relevant pathway of exposure to pesticides. To perform an inhalation risk assessment of exposures to atmospheric CUPs (currently used pesticides), it is necessary to know the total concentration (gas + particulate phases) of these compounds in the ambient air. This requires that the air samplers collect both the particle phase and the gas phase (using appropriate adsorbents). At present, there is a lack of consistency in sampling methodologies. Standardization of sampling methods for pesticides in the gas phase is the most difficult part, owing to the wide range of physicochemical properties of the active substance currently in use (Yusà et al., 2009). On the contrary, the methods for collection of pesticides bound to the particulate matter seem to be more homogenous, and in general, pesticides are trapped in glass fibre filters (GFF) or quartz fibre filters (QFFs) (Yusà et al., 2009).

The pesticides applied to crops must have no harmful effects on humans. Although international guidelines on pesticide exposure and risk assessment for operators, workers, bystanders and residents have recently been developed (EFSA, 2014), the methodologies focused on the exposure and risk assessment of airborne pesticides on the general population are scarce. Risk assessment to inhalated pesticides have been studied in rural and urban areas worldwide. In Spain, Yusà et al. (2014) proposed a screening approach for inhalation chronic risk assessment of CUPs present in rural ambient air, based on the concentration of these compounds in the inhalable particulate matter (PM10). In that study, total pesticide concentration was estimated applying theoretical partitioning models. In addition, Li et al. (2014) studied the inhalation exposure of organophosphate pesticides in an urban community of South China and Lee et al. (2002) in rural and urban stations in California region (USA).

In this paper, we have assessed the inhalation risk of pesticides in Valencia Region population based on the quantitative (target) and semi-quantitative (retrospective screening) determination of pesticides in PM10. The strategy was applied to six rural stations, two urban stations and one remote station placed in Valencia Region, and the risk was assessed for three populations (adults, children and infants).

2. Experimental

2.1. Reagents and chemicals

Certified commercial standards were of high purity and purchase from Dr. Ehrenstorfer (Augsburg, Germany) and Sigma Aldrich (Barcelona, Spain). Individual stock standards were prepared weighing 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 (SANCO, 2007). 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 PM10 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 and formic acid 98% were provided by Panreac (Barcelona, Spain). Ammonium formate, solution Ultra (100 mL, 10 M in water) was provided by Fluka (Steinheim, Switzerland).

2.2. Sampling and site characterization

Valencia Region is a Mediterranean area and is situated on the East coast of Spain. This region made up 12.6% of the total national consumption of pesticides in 2014 (AEPLA, 2014). The main irrigated crops are citrus fruit, other fruit trees (mainly peach, apricot and plum trees), rice and garden produce (primarily watermelon, cabbage, artichoke, lettuce, cauliflower, tomatoes, potatoes and onion). The main dry crops are vineyards, olive trees and almonds (CAPA, 2013).

Samples were collected using a high-volume sampler from Digitel (Madrid) and quartz fibre 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 volume of around 720 m^3 was used. A total of 345 samples were collected from 2008 to 2014, following pesticide applications in the Valencia Region between February to November. PM10 samples were collected from six rural sampling stations (Alzira, Burriana, Sant Jordi, Benicarló, Villar del Arzobispo and Benifaió), two urban stations (Viveros and Burjassot) and one remote station (Morella) (Table 1). Rural stations are close to many citrus crops (orange trees), vineyards and cereals.

Prior to exposition, filters were baked for 24 h at 300 °C to eliminate organics. To determine the weight of particulate matter accumulated during 24-h exposition of filters, a Metler Toledo MX5 microbalance (from Bedford, MA, USA) was used. Filters were previously conditioned according to European standard sampling at a temperature of 20 ± 1 °C and at relative humidity of 50 ± 5 °C for at least 48 h, and then weighted.

2.3. Sample preparation

For Alzira, Burriana, Morella, Sant Jordi and Viveros stations, air samples were analyzed by LC-MS/MS (Liquid Chromatography coupled to mass spectrometry in tandem), except for Alzira samples in 2013 and Burriana samples in 2014. In this period and stations, air samples were analyzed by UHPLC-HRMS (Liquid Chromatography coupled to high resolution mass spectrometry). A generic extraction method developed in a previous work using microwave extraction (MAE) with ethyl acetate was employed (Coscollà et al., 2014). MAE of pesticides from PM10 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–MS/MS or LC-HRMS determination.

In the case of Benicarló, Benifaió, Villar del Arzobispo and Burjassot sampling sites, air samples were analyzed by LC-MS (Liquid chromatography mass spectrometry detection) and GC–MS (Gas chromatography mass spectrometry detection). For LC-MS, air samples were ultrasonically extracted (VWR ultrasonic bath, Barcelona, Spain) three times with 10 mL of ethylacetate 15 min each time. The extract was concentrated in a rotavapor system (50 °C, 180 rpm) for 5 min, to total dryness. Then, the extract was dissolved in 500 μL of methanol and reduced to 100 μL under a gentle stream of N_2. Finally, the extract was injected (5 μL) in the LC-MS. In GC–MS, air samples were ultrasonically extracted (VWR ultrasonic bath, Barcelona, Spain) two times with 10 mL of isooctane for 10 min each time. The extract was concentrated in a rotavapor system (40 °C, 180 rpm) for 5 min, avoiding total dryness. Then, the extract was dissolved in 1 mL of isooctane and dried under a gentle stream