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Particle size distributions of currently used pesticides in ambient air of an agricultural Mediterranean area

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HIGHLIGHTS

- Particle size distribution of pesticides in Mediterranean agriculture was studied.
- Pesticides accumulated in the ultrafine-fine and coarse particle size fractions.
- The total concentrations in the particulate phase ranged from 3.5 to 383.1 pg m^{-3}.

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ABSTRACT

This work presents first data on the particle size distribution of 16 pesticides currently used in Mediterranean agriculture in the atmosphere. Particulate matter air samples were collected using a cascade impactor distributed into four size fractions in a rural site of Valencia Region, during July to September in 2012 and from May to July in 2013. A total of 16 pesticides were detected, including six fungicides, seven insecticides and three herbicides. The total concentrations in the particulate phase (TSP: Total Suspended Particulate) ranged from 3.5 to 383.1 pg m^{-3}. Most of the pesticides (such as carbendazim, tebuconazole, chlorpyrifos-ethyl and chlorpyrifos-methyl) were accumulated in the ultrafine-fine (<1 μm) and coarse (2.5–10 μm) particle size fractions. Others like omethoate, dimethoate and malathion were presented only in the ultrafine-fine size fraction (<1 μm). Finally, diuron, diphenylamine and terbuthylazine-desethyl-2-OH also show a bimodal distribution but mainly in the coarse size fractions.

1. Introduction

The particle size distribution affects the particulate matter's transport in air, the dry or wet deposition from the atmosphere onto natural surfaces and the deposition in the human lungs. So, information about the particle size distribution of organic compounds is vital in order to estimate their inputs into the ecosystems and the human health (Wu et al., 2006; Chrysikou et al., 2009) . Small particles penetrate in the respiratory system, and cause direct health impact (Chrysikou and Samara, 2009). Therefore, particle size distribution of organic pollutants such as n-alkanes, polycyclic aromatic hydrocarbons, polychlorinated biphenyls, polychlorinated dibenzo-p-dioxins, dibenzofurans and metals has been repeatedly studied in several areas around the world (Bi et al., 2005; Allen et al., 1996; Duan et al., 2007; Chrysikou et al., 2009; Oh et al., 2002; Chao et al., 2003; Zereini et al., 2005). However, to our knowledge, only one study have been published related with particle size distribution of currently used pesticides (CUPs) (Coscollà et al., 2013a).

Semivolatile organic compounds (SVOCs) can be bound to particles with different particle size distribution. Particles can be divided roughly into modes. The nucleation (or *nuclei*) mode comprises particles with diameters up to 0.01 μm. The *Aitken* mode spans the size range from about 0.01 μm to 0.1 μm diameter. These two modes account for the preponderance of particles by number; because of their small size, these particles rarely account for more than a few percent of the total mass of airborne particles. The *accumulation* mode, extending from 0.1 to 2.5 μm, usually accounts

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for most of the aerosol surface area and a substantial part of the aerosol mass. The accumulation mode is so named because particle removal mechanisms are least efficient in this regime, causing particles to accumulate there. The *coarse* mode, from >2.5 μm in diameter, is formed by mechanical processes and usually consists of human-made and natural dust particles. Coarse particles have sufficiently large sedimentation velocities that they settle out of the atmosphere in a reasonable short time (Seinfeld and Pandis, 2006).

Fig. 1 a shows the emission sources throughout CUPs can reach the atmosphere and the processes that permit their distribution in the different particle size fractions. There are three different emission sources during or after pesticide application in agricultural practices. Firstly, "*spray drift*" occurs during its application. A fraction of the dosage – 20–30% (Van de Berg et al., 1999) – applied to the target area could be deposited onto the adjacent non-target areas and another fraction can be lost in the atmosphere (Hilz and Vermeer, 2013). Secondly, *volatilization* is a post-application emission from soil and plants. It can happen some days or weeks after application (Bedos et al., 2002a). Thirdly, *wind erosion of soil particles* containing sorbed pesticides represent further significant pesticide input into the troposphere for several days or weeks after application (Voutsas et al., 2005). In addition, processes (see Fig. 1b) throughout pesticides are distributed in the three particle size fraction such as ultrafine, fine and coarse basically depend on the following factors: the primary emission, the gas to particle distribution (G/P distribution) of the pesticide and the particle transformation by different pathways (Bedos et al., 2002b; Voutsas et al., 2005).

Transformation in size occurs by different routes. Growth of particles can correspond to an increase of the mean particle size or shifting of parts of the distribution to larger sizes. Pesticides accumulated in ultrafine can shift to fine size fraction. Small pesticide particles and gaseous pesticides originate from emission sources (primary emissions) can be accumulated in ultrafine fraction. They can growth by coagulation or vapour condensation and then move to be associated in the fine particle size fraction (Venkataraman and Friedlander, 1994). Moreover, pesticides accumulated in the fine size fraction can shift to the coarse fraction. Freshly emitted pesticides can be adsorbed mainly to fine aerosol and they can become associated with coarse particles by volatilization from fine particles followed by condensation onto coarse particles (Bi et al., 2005; Duan et al., 2007).

Research concerning the size distribution of particle-bound organochlorine pesticides (OCPs) in the atmosphere of Thessaloniki (Greece) has shown strong accumulation in the submicron size fraction. OCPs are known to be toxic to humans and many organisms, and are considered widespread environmental contaminants (Chrysikou and Samara, 2009). Moreover, currently used pesticides

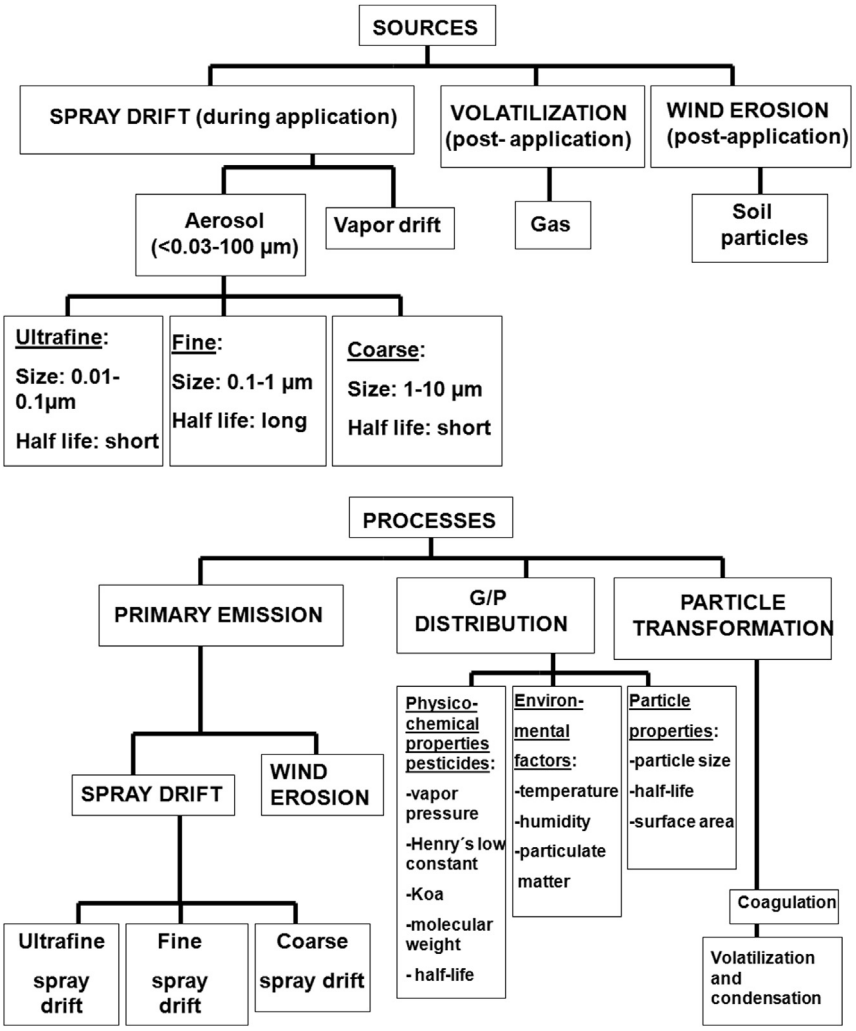

Fig. 1. Sources and processes involved in the distribution of pesticides in the particle size fractions (G/P distribution = gas to particle distribution).