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Particle size distributions of currently used pesticides in a rural atmosphere of France

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HIGHLIGHTS

- Particle size distributions of 49 currently used pesticides were studied in Centre Region, France.
- Pesticides were detected mainly in the fine particle size fractions (frequencies of detections 40–80%).
- Total concentrations ranged from 0.163 to 1.779 ng m^{-3}.

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ABSTRACT

This work presents first data on the particle size distributions of current-used pesticides in the atmosphere. Ambient air samples were collected using a cascade impactor distributed into four size fractions in a rural site of Centre Region (France). Most pesticides were accumulated in the fine (0.1–1 μm) particle size fraction such as cyprodinil, pendimethalin, fenpropidin, fenpropimorph and spiroxamine. Other pesticides such as acetochlor and metolachlor presented a bimodal distribution with maximum concentrations in the ultrafine (0.03–0.1 μm)–coarse (1–10 μm) and in the ultrafine–fine size ranges, respectively. No pesticides were detected in the size fraction >10 μm.

1. Introduction

Air pollution has been considered a hazard to human health. Many studies highlighted the role of ambient airborne particulate matter (PM) as an important environmental pollutant for many different cardiopulmonary diseases and lung cancer. These studies have shown that the size of the airborne particles and their surface area determine the potential to elicit inflammatory injury, oxidative damage, and other biological effects. These effects are stronger for fine and ultrafine particles because they can penetrate deeper into the airways of the respiratory tract and can reach the alveoli in which 50% are retained in the lung parenchyma (Valavandis et al., 2008).

The aerodynamic diameter (a.d.) of aerosol particles span over four orders of magnitude, from a few nanometres to around 100 μm. From the point of view of health effects, the size categories are defined as: *ultrafine* particles, smaller than about 0.1 μm in a.d; *fine* particles, smaller than 1 μm a.d; and *coarse* particles larger than 1 μm a.d. (Health Effects Institute, 2002). Ultrafine particles are generated directly by combustion and photochemical activity. These particles are unstable and persist briefly, aggregating to form

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larger accumulation particles. Fine and ultrafine particles are formed mostly by vehicular exhausts emissions. By contrast, part of coarse particles can be generated by combustion but mostly by mechanical processes that break down material from a variety of non-combustible sources into dust. Most of the suspended PM consists of 90%–95% of coarse particles in mass, whereas smaller particles are only 1%–8% of the total mass. However, ultrafine and fine particles are very high in numbers, have greater total surface area than larger particles, and because of their porous surface, can adsorb and retain toxic substances (Valavandis et al., 2008).

The chemical composition of PM varies greatly and depends on many factors, such as combustion sources, climate, season, and type of rural, urban or industrial pollution. The composition of coarse particles consists mainly of insoluble crust-derived minerals, sea salt, material of biologic origin, and so on. By contrast, the fine and ultrafine particles are mainly carbonaceous aggregates with metals and organic species adsorbed on their surface cavities. Several studies showed that the organic compounds associated to PM such as PAH known for their genotoxicity greatly contribute to various mechanisms of cytotoxicity (Aust et al., 2002; Ramgolam et al., 2009).

Particle size distribution of some pollutants such as *n*-alkanes (Bi et al., 2005), polycyclic aromatic hydrocarbons or PAHs (Allen et al., 1996; Bi et al., 2005; Duan et al., 2007), organochlorine pesticides or OCPs and polychlorinated biphenyls or PCBs (Chrysikou and Samara, 2009), polychlorinated dibenzo-p-dioxins and dibenzofurans (Oh et al., 2002; Chao et al., 2003) and metals (Zereini et al., 2005) has been repeatedly studied in several areas around the world.

The size distribution of *n*-alkanes is affected by a number of parameters such as vapour pressure, absorption and adsorption affinities, emission sources, atmospheric processes. These compounds were mainly distributed in the ultrafine fraction (Chrysikou and Samara, 2009). Polycyclic aromatic hydrocarbons (PAHs) are among the aerosol constituents of greatest concern because some of these compounds are carcinogenic. The partition of PAHs between different sizes of particles depends upon the ambient temperature, the relative humidity, the particle surface available for sorption and the compound properties. The mid-high molecular weight was mainly associated with fine particles, whereas low molecular weight was distributed in both of fine and coarse particle (Wu et al., 2006). Organochlorine pesticides (OCPs) are known to be toxic to humans and many organisms, and are considered widespread environmental contaminants, due to their properties according to chemical stability, lipophilicity and bioaccumulation. Research concerning the size distribution of particle-bound OCPs in the atmosphere has shown strong accumulation in the submicron size fraction (Chrysikou and Samara, 2009).

Currently used pesticides (CUPs) are the newly pesticides which are nowadays applied in the agricultural practices and are approved by EU (CEU, 1991) and other international regulations.

Until now, some studies have analysed CUPs in the particle phase (although not size segregated) in different countries. For instance, in France, Schummer et al. (2010) analysed particle and gaseous phases and detected 38 CUPs in the atmosphere of Strasbourg, in air concentrations ranging from 0.09 to 110.42 ng m^{-3}. Some pesticides such as alachlor, metalochlor or penconazole, were mostly detected in the particulate phase (83.5%; 75.4%; 88.5%). Scheyer et al. (2008) presented the G/P partitioning of six current-use pesticides collected in Alsace region, France. These pesticides were present mainly in the particulate phase (from 50 to 100%) in concentrations from sub to a few ng m^{-3}. Some of our previous recent studies were aimed at assessment of the general pollution levels in urban and rural regions in France and Spain by determination of currently used pesticide concentrations using different size selective inlet PM 2.5, PM 10 and total suspended particle (Coscollà et al., 2010, 2013; Hart et al., 2012). Coscollà et al. (2010) collected total suspended particles (TSP) ambient air samples, during a long period (2006–2008) at three rural and two urban sites in Centre Region (France), which is the same region of the present study, and analysed for 56 pesticides, mainly currently used ones, of which 41 were detected. In Spain, Coscollà et al. (2009) focused their study on 30 airborne CUPs in PM 2.5; they found 19 pesticides with concentrations ranging from 6.5 to 1208 pg m^{-3} in Valencia region. During 2010, in the PM10 fraction 17 pesticides and metabolites were detected overall in the same region (Coscollà et al., 2013).

With the increasing evidence of the contribution of the finest fraction of the aerosol in the adverse health effects there was an urgent need to inform on the distribution of CUPs on such fractions to improve risk assessment.

The main objective of this work is to study the size particle distribution of different currently used pesticides in the ambient air of a rural area in France. To our knowledge, this study represents the first investigation for particle size distribution of CUPs in the ambient air.

1.1. Distribution of pesticides in the size particle fractions

CUPs can reach the atmosphere during or after pesticide application in agricultural practices from three different emission sources. Firstly, "*spray drift*" occurs during its application. A fraction of the dosage applied to the target area could be deposited onto the adjacent non-target areas and another fraction can be lost in the atmosphere. Emissions during application can range from a few percent to 20–30% (Van de Berg et al., 1999) of the dosage applied. Secondly, *volatilization* is a post-application emission from soil and plants. It can happen some days or weeks after application (Bedos et al., 2002). 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).

From these primary sources, pesticides can reach the atmosphere both as gas or aerosols. Moreover, the gas to particle distribution (G/P) and the particle transformation are other two processes than can explain the particle size distribution of pesticides.

Primary emissions during spray application (spray drift) can emit pesticides which can be associated to ultrafine, fine and coarse particle size fraction. The size of spray droplets is influenced by the physico-chemical properties of spray liquids such as surface tension or viscosity, the nozzle design, the orifice size and the operating pressure. Spray droplets of a few microns in size can evaporate before sedimentation. Droplets with diameter <100 μm contributes significantly to drift losses. The smaller a spray droplet is, the longer it remains airborne (Hilz and Vermeer, 2013). Other primary emission is wind erosion of soil particles containing sorbed pesticides. It represents a further significant pesticide input into the troposphere for several days or weeks after application (Bedos et al., 2002; Voutsas et al., 2005). Wind drags pesticides accumulated in the coarse size fraction.

Pesticides emitted as gas from the primary sources could be adsorbed into ultrafine, fine and coarse particles present in the atmosphere. However, the fine particle size fraction (between 0.1 and 1 μm) presents a greater total surface area and organic compounds are more prone to be adsorbed into this fraction (Seinfeld and Pandis, 2006; Valavandis et al., 2008). Consequently pesticides will have a tendency to be accumulated in this fraction.

Another process that can influence the particle size distribution of pesticides is the particle transformation. Growth of particles by coagulation or vapour condensation can produce an increase in the