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Atmospheric degradation of the organothiophosphate insecticide – Pirimiphos-methyl

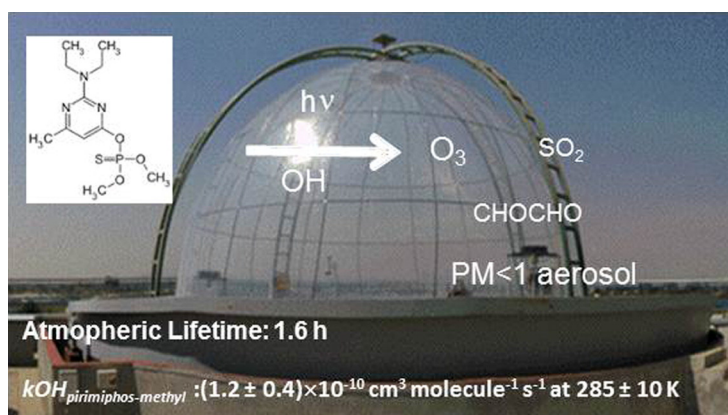
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HIGHLIGHTS

- Atmospheric OH-reaction and photolysis of pirimiphos-methyl
- Reaction profiles and yields of pirimiphos-methyl determined
- Experimental atmospheric life time determined
- Important particulate matter formation from the pirimiphos-methyl degradation

GRAPHICAL ABSTRACT



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ABSTRACT

The gas phase atmospheric degradation of pirimiphos-methyl (a widely used organophosphate insecticide and acaricide in many European regions) has been investigated at the large outdoor European Photoreactor (EUPHORE) in Valencia, Spain. Its photolysis has been studied under sunlight conditions and its reaction rate constant with OH radicals was measured by the relative rate method. The reaction with ozone was also investigated. The tropospheric degradation of pirimiphos-methyl is controlled mainly by the OH radical reaction. The rate coefficient of the OH reaction with pirimiphos-methyl, k , was measured by a conventional relative rate technique, where aniline was taken as a reference. The resulting value of the OH reaction rate constant with pirimiphos-methyl was $k = (1.14 \pm 0.2) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The tropospheric lifetime of pirimiphos-methyl with respect to the reaction with OH radicals was estimated to be around 1.6 h (283 ± 10) K and atmospheric pressure. Significant aerosol formation was observed in the OH reaction with yields that ranged from 25 to 37%, and with particle diameters below 550 nm. This therefore reveals a high human risk due to $PM < 1$, without taking into account the chemical composition of the degradation products. SO_2 , glyoxal and other oxygenated and nitrogenated compounds were the main degradation products detected.

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1. Introduction

Pesticides are extensively used in agriculture, gardening and a variety of other household applications, and are the most widely used chemical compounds. Their intensive use worldwide has led to the ubiquitous contamination of exposed and remote areas, not only water or soil, but also the atmosphere (Atkinson et al., 1999; Coscollá and Yusá, 2016; Reddy and Kim, 2015; Socorro et al., 2016). Pesticides can be released to the atmosphere through dispersion during spraying, which is carried out mainly in spring and autumn, but also through volatilization from ground or leaf surfaces, especially in summer when temperatures, particularly in Southern Europe can reach 40 °C (Muñoz et al., 2011a). Once in the atmosphere, pesticides are distributed among gas, particle and aqueous phases. Partitioning into different phases depends on their physicochemical properties (e.g., equilibrium vapor pressures, Henry's law constants) and on environmental conditions (temperature, wind direction, height of cloud base) (Majewski and Capel, 1995).

Pirimiphos-methyl, (4-dimethoxyphosphinothioxyloxy-*N,N*-diethyl-6-methylpyrimidin-2-amine) is an organophosphorus insecticide used to control insects and mites in stores, animal houses, and domestic and industrial premises (Fleurat-Lessard et al., 2007). It can be released to the atmosphere directly while being sprayed. A vapor pressure of 2.0×10^{-3} Pa (1.5×10^{-5} mm Hg) at 20 °C; 6.9×10^{-3} Pa (5.17×10^{-5} mm Hg) at 30 °C (MacBean, 2010) indicates that pirimiphos-methyl will exist in both gas and particulate phases in the atmosphere. It will be removed from the atmosphere by wet or dry deposition, or will be degraded by a reaction with atmospheric oxidants. Understanding the atmospheric degradation of pirimiphos-methyl is crucial to assess its behavior and potential risk to non-targets. Among occupational workers exposed to pirimiphos-methyl, it may induce DNA damage, decreased acetyl cholinesterase (AChE) activity, hepatotoxicity and nephrotoxicity (Singh et al., 2011). However, current knowledge concerning this field is very limited. Few studies have been recently presented, but only about the heterogeneous reaction on the particulate phase with ozone and nitrate radicals (Wang et al., 2012; Yang et al., 2015).

As for other organic compounds, the gas-phase degradation of pirimiphos-methyl in the atmosphere could be controlled by photolysis and/or reaction with ozone, OH and NO₃ radicals (Finlayson-Pitts and Pitts, 2000). However, studies into the gas-phase degradation of pesticides are problematic because of their low vapor pressures. One advantage of using large simulation chambers, such as those at the European Photoreactor (EUPHORE) to study them, is that compounds with vapor pressures as low as 1×10^{-3} Pa can be introduced into the chamber in the gas-phase. Studies on atmospheric simulation chambers allow assessing chemical transformation processes being isolated from meteorological effects, such as dispersion (Borrás and Tortajada-Genaro, 2012a, 2012b). Due to their design and infrastructure, in which irradiation takes place with natural solar light, studies done in large simulation chambers allow to obtain the behavior of compounds of interest under very close conditions to reality.

In this work, we report the first experimental study on the gas phase chemistry of pirimiphos-methyl (Fig. 1) under atmospheric conditions at ambient temperature at the outdoor European photoreactor (EUPHORE).

The present series of experiments performed in the EUPHORE simulators were carried out to improve the understanding of the degradation of pirimiphos-methyl in the troposphere, to identify the products generated in both the gas and particulate phases, and their contribution to secondary organic aerosol (SOA) production. It should be taken into account that the atmospheric behavior of some pesticides in the gas phase may differ from the particulate phase in reactivity and persistence terms (Al Rashidi et al., 2014; Socorro et al., 2015). The main diurnal process on semi-urban/rural locations, influenced by pesticide emissions, was reproduced. Measurements were taken from a wide range

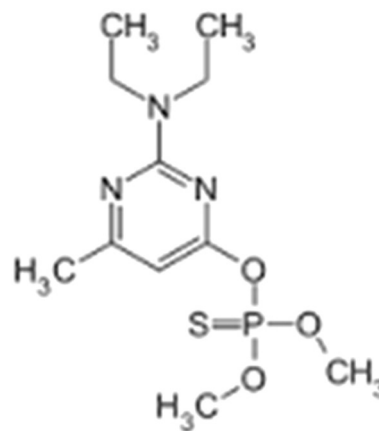


Fig. 1. Pirimiphos-methyl (4-dimethoxyphosphinothioxyloxy-*N,N*-diethyl-6-methylpyrimidin-2-amine) structure.

of specific instruments to monitor parent compound and products, and both gas and particulate phases, and to provide information about chemical composition. Also, a deeper analysis of the results was performed to provide information on the atmospheric lifetime of pirimiphos-methyl in relation to photolysis, and also for the reaction with OH radicals and ozone, the elucidation of the degradation pathway, and the evaluation of its environmental impact.

2. Experimental section

2.1. Photoreactor and online instruments

The experiments were carried out in the EUPHORE high volume outdoor smog chambers (European PHOtoREactor) (Valencia, Spain). This simulation chamber enables reactions to be carried out at realistic atmospheric concentrations, minimizing losses and wall-interactions effects and at solar wavelengths and intensities by following similar procedures to those previously employed in this laboratory to investigate the atmospheric fate of a number of pesticides; i.e., chlorpyrifos-methyl, chlorpyrifos, diazinon, ethalfluralin, lindane, etc. (Borrás et al., 2015a, 2015b; Muñoz et al., 2011a, 2011b; Muñoz et al., 2014a, 2014b; Vera et al., 2015).

These chambers consist in two half spherical fluoropolymeric bags, 200 m³ each, with integrated measuring systems for monitoring pressure, humidity, temperature, precursor species and reaction products (Borrás and Tortajada-Genaro, 2012a; Muñoz et al., 2011a). Pressure, humidity and temperature were measured with a pressure sensor (Air-DB-VOC, Sirsa, Madrid, Spain) and a dew point hydrometer (TS-2, Walz, Effeltrich, Germany). A TAPI NO_x monitor (T200, Teledyne, Sand Diego, USA) was used to measure NO, NO₂ and NO_x. Ozone was measured by an Ecotech ozone analyzer (Serius 10, Ecotech, Knoxfield VIC Australia). SO₂ was measured by a Thermo Electron monitor model 43i. A White-type multi-reflection mirror system (path length of 553.5 m), coupled to a Fourier Transform Infrared spectrometer equipped with an MCT detector (NICOLET Magna 6700, Thermo Scientific, USA) was used to record concentrations of pirimiphos-methyl (760–1225 cm⁻¹), nitrous acid (762–956 cm⁻¹), SO₂ (1050–1200 cm⁻¹), ozone (990–1150 cm⁻¹), formic acid (990–1150 cm⁻¹), nitric acid (762–956 cm⁻¹), SF₆ (762–956 cm⁻¹) and formaldehyde (2710–2900 cm⁻¹). The IR region analysis bands are shown in parentheses. Concentration profiles were calculated by specific software (Ródenas, 2008) which, compared to the classic minimum least square method, improves the analysis of the complex gas mixtures when unknown interfering compounds are present in the sample. Its effectiveness depends on the structure of the absorption bands. The FTIR calibration procedure consisted in several introductions of each compound, using standards, into the EUPHORE simulation chamber at

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