Particulate and gas-phase products from the atmospheric degradation of chlorpyrifos and chlorpyrifos-oxon

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HIGHLIGHTS

- Atmospheric OH-reaction and photolysis of organothiophosphorus.
- Reaction profiles and yields of chlorpyrifos and chlorpyrifos-oxon determined.
- Phosphorothioate derivatives were the main degradation products observed.
- The degradation routes were formulated based on the structurally defined products.

GRAPHICAL ABSTRACT
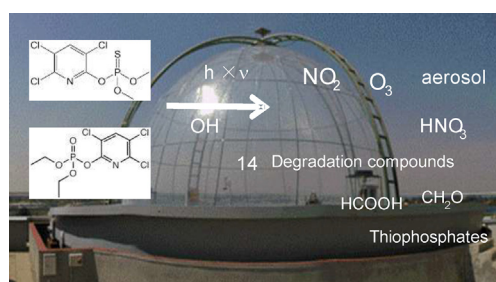
ABSTRACT

The phosphorothioate structure is highly present in several pesticides. However, there is a lack of information about its degradation process in air and the secondary pollutants formed. Herein, the atmospheric reactions of chlorpyrifos, one of the most world-used insecticide, and its main degradation product — chlorpyrifos-oxon — are described. The photo-oxidation under the presence of NO_x was studied in a large outdoor simulation chamber for both chlorpyrifos and chlorpyrifos-oxon, observing a rapid degradation (Half lifetime < 3.5 h for both compounds). Also, the photolysis reactions of both were studied. The formation of particulate matter (aerosol mass yield ranged 6—59%) and gaseous products were monitored. The chemical composition of minor products was studied, identifying 15 multi-oxygenated derivatives. The most abundant products were ring-retaining molecules such as 3,5,6-trichloropyridin-2-ol and ethyl 3,5,6-trichloropyridin-2-yl hydrogen phosphate. An atmospheric degradation mechanism has been amplified based on an oxidation started with OH-nucleophilic attack to P=S bond.

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1. Introduction

Organophosphorus pesticides are extensively world-used in agriculture, horticulture, and a variety of household applications. They include herbicides, acaricides, and insecticides and are chemical or biological products used to prevent diseases, kill, repel, control plagues or interrupt the growth of plants. Once pesticides are applied in the field, they can be partitioned into the soil, water, and atmosphere with a significant environmental impact. Pesticides can be emitted into the atmosphere from ground or leaf surfaces, and the amount emitted is a function of their physical properties and their manner of application (Van den Berg et al., 1999; Unsworth et al., 1999). Moreover, they have a distribution into gas and condensed phases more or less displaced depending

on their physicochemical properties and environmental conditions (Espallardo et al., 2012; Borrás et al., 2015).

Chlorpyrifos (o,o-diethyl o-(3,5,6-trichloropyridin-2-yl) phosphorothioate) is considered as one of the most widely used insecticides in the world. It is applied on an important range of crops, particularly in the fruit-growing crops as well as and in numerous non-agricultural situations (Balinova et al., 2007). It is highly used in south-west Europe countries (France, Italy and Spain) and in USA. For example, this pesticide was detected in the gas phase in 39% of cases and in particulate phase in 18% of cases during 2008–2009 at different rural and agricultural Spanish areas (Borrás et al., 2011). However, despite recent progress on the degradation of chlorpyrifos in atmosphere, soil, water, and heterogeneous reactions (Muñoz et al., 2014a; El Masri et al., 2014; Mackay et al., 2014), little is known about its degradation products in air beyond its transformation in the oxon compound.

As recently published (Muñoz et al., 2014a), after chlorpyrifos is emitted to the atmosphere, it is subjected to oxidation processes as happens to other semi-volatile organic compounds (SVOCs) (Atkinson et al., 1983). A set of new products, called residues or secondary pollutants, is formed. These gaseous and above all condensed products have a different atmospheric residence time, and sometimes exhibit worse toxicity than the original molecule (Hamilton et al., 2005; Mackay et al., 2014). However, the real atmospheric behavior is difficult to evaluate due to their low concentrations. In order to get a comprehensive overview of their atmospheric fate, the use of highly-equipped atmospheric simulation chambers solves some of these limitations (Finlayson-Pitts and Pitts, 2000). These facilities have allowed the examination of pollutant degradations under near-realistic atmospheric conditions (Le Person et al., 2007; Muñoz et al., 2012, 2014b). In fact, a previous study performed at EUPHORE, one of the most high-volume atmospheric simulator chambers, demonstrated the general kinetics of the chlorpyrifos and its oxon towards OH-radicals (Muñoz et al., 2014a).

The present series of experiments performed in the EUPHORE simulators were carried out in order to improve the understanding of the degradation of chlorpyrifos, and its main degradation product – chlorpyrifos-oxon – in the troposphere.

This research was focused on the contribution to particulate matter production and the identification of secondary organic aerosol (SOA) generated, being the novelty, the measurement and the qualitative analysis of SOA from photolysis and OH-degradation as well as a deeper investigation of the mechanism thanks to the detection of new degradation products. For that, measurements from a wide range of specific instruments and techniques such as mainly GC–MS, and also FTIR and several monitors were carried out to determine new products, both particulate and gas phase, providing information about the chemical composition. Some compounds formed were herein firstly detected for photodegradation of chlorpyrifos and chlorpyrifos-oxon. Also, a deeper analysis of results has been performed for the elucidation of the degradation pathway and the evaluation of the atmospheric impact of chlorpyrifos and one of its main degradation products.

2. Experimental section

2.1. Photoreactor and on –line instruments

The experiments were carried out in the high volume outdoor smog chambers EUPHORE (*European PHOtoREactor*) (Valencia, Spain). These simulator photoreactors were designed to work under near-realistic atmospheric conditions minimizing losses and wall-interactions effects. These chambers consist of two half spherical fluoropolymeric bags, each one of 200 m³ 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 using a pressure sensor (Air-DB-VOC, Sirsa, Madrid, Spain) and a dew point hydrometer (TS-2, Walz, Effeltrich, Germany). An Eco Physics AG (AL-ppt-77312, Duernten, Switzerland), an API NO_x monitor (API200AU, Teledyne API, San Diego, USA) and a NO_x analyzer (ML9841A, Teledyne Monitor, Englewood, USA) were used for measuring NO, NO_2 and NO_x. White-type multi-reflection mirror system (path length of 553.5 m) coupled to a Fourier Transform Infrared spectrometer equipped with a MCT detector (NICOLET Magna 550, Thermo Scientific, USA) was used for recording concentrations of chlorpyrifos (760–1225 cm⁻¹), chlorpyrifos-oxone (760–1225 cm⁻¹), nitrous acid (762–956 cm⁻¹), SO_2 (1050–1200 cm⁻¹), ozone (990–1150 cm⁻¹), formic acid (990–1150 cm⁻¹), nitric acid (762–956 cm⁻¹), hydrochloric acid (2710–2900 cm⁻¹), methyl glyoxal (2710–2900 cm⁻¹), pyrimidol (760–1225 cm⁻¹), SF_6 (762–956 cm⁻¹) and formaldehyde (2710–2900 cm⁻¹). IR region bands analysis are included in parentheses. Concentration profiles were calculated by using specific software (Ródenas, 2008) that, compared to the classic minimum least square method, improves the analysis of the complex gas mixtures when unknown compounds are present in the sample absorbing in the same region as the compounds of interest and interfering with them. Its effectiveness depends on the structure of their absorption bands. FTIR calibration procedure consisted on several introductions of each compound, using standards, into the EUPHORE simulation chamber at known concentrations. Moreover, concentration values for chlorpyrifos and chlorpyrifos-oxon were also experimentally determined and validated by off-line GC–MS plus derivatization protocol using C18 cartridges to sample them (see Section 2.2). Aerosol mass concentration was measured with two on-line instruments. One was a scanning mobility particle sizer (SMPS), model 3080 (TSI, Shoreview, USA). This system measured size distributions in the 11–789 nm diameter range in real time with a 5 min scan rate, and provided aerosol concentrations assuming spherical shapes and multi-charge correction for the condensed organic material. Sheath and aerosol sampling flows were 3 L min⁻¹ and 0.30 L min⁻¹, respectively. The other automated instrument was a tapered element oscillating monitor (TEOM) (model 1400a, Ruppercht and Patashnick, Albany, USA) with a 1 min scan rate, PM1 sampling head, and a sampling flow of 3 L min⁻¹.

2.2. Derivatization sample treatment and off-line analysis

For fingerprint analysis, particles were collected at maximum aerosol formation, under a flow rate of 23 L min⁻¹ for 1 h, on quartz fiber filters that had been pre-baked at 500 °C for 12 h. Gaseous products were sampled with C18 cartridges during reaction, under a flow rate of 1 L min⁻¹ for 0.5 h. The analysis of multi-oxygenated compounds was carried out after derivatization by gas chromatography–mass spectrometry (GC–MS) (Borrás and Tortajada-Genaro, 2012b). Briefly, 47 mm quartz fiber filters (Whatman, Brentford, England) were sonicated with 5 mL of CH_2Cl_2/CH_3CN (1:1). C18 cartridges (Waters, Barcelona, Spain) were eluted with 2 mL of CH_2Cl_2/CH_3CN (1:1). Then, a derivatization with o-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine hydrochloride (PFBHA) plus diluted N-methyl-N-trimethylsilyltrifluoroacetamide (MSTFA) – supplied by Sigma Aldrich (Barcelona, Spain) – was carried out. After that, the following reagents were added: 0.5 mL of CH_3CN, 150 μL of PFBHA solution of 1000 mg L⁻¹ in CH_3CN and 50 μL of a 4-fluorobenzaldehyde solution (15 mg L⁻¹) as surrogate of carbonyl derivatization. This mixture was left in darkness at