

Particulate matter formation from photochemical degradation of organophosphorus pesticides

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Abstract. Several experiments were performed in the European Photo-reactor – EUPHORE – for studying aerosol formation from organophosphorus pesticides such as diazinon, chlorpyrifos, chlorpyrifos-methyl and pirimiphos-methyl. The mass concentration yields obtained (Y) were in the range 5 – 44 % for the photo-oxidation reactions in the presence and the absence of NO_x. These results confirm the importance of studying pesticides as significant precursors of atmospheric particulate matter due to the serious risks associated to them.

The studies based on the use of EUPHORE photoreactor provide useful data about atmospheric degradation processes of organophosphorus pesticides to the atmosphere. Knowledge of the specific degradation products, including the formation of secondary particulate matter, could complete the assessment of their potential impact, since the formation of those degradation products plays a significant role in the atmospheric chemistry, global climate change, radiative force, and are related to health effects.

1. Introduction

Pesticides are most widely used chemical compounds and actually, they are emerging chemical pollutants precursors of particulate matter. Today's agriculture involves heavy use of synthetic pesticides, including herbicides, fungicides, acaricides, insecticides and avicides. Their entry into the atmosphere occurs during application or subsequent processes such as volatilization and re-suspension [1]. The number of patented pesticides is very high and many families are authorized, prohibited or banned by regulations – e.g., Regulation (EC) 1107/2009 – due to the restricted regulations about human and environmental safety. As consequence, the scientific knowledge about the behaviour of pesticides in the atmosphere is highly demanded due to their use in Mediterranean agriculture in a broad range of applications. However, there is a relative lack in the scientific knowledge about the behaviour of pesticides in the atmosphere.

Organophosphorus pesticides are extensively used in agriculture, horticulture, and a variety of household applications. They are chemical or biological products used to prevent diseases, kill, repel, control plagues or interrupt the growth of plants, including herbicides, acaricides, and insecticides. Once pesticides are applied in the field, it can be partitioned into the soil, water, and atmosphere and, consequently, they have a significant environmental impact. Pesticides can be emitted into the atmosphere through dispersion during spraying or volatilization from ground or leaf surfaces, and the amount emitted is a function of their physical properties and their manner of application. Associate to their low-volatile or semi-volatile nature, they have a distribution into gas and condensed phases more or less displaced depending on their physicochemical properties and environmental conditions [2]. Around a hundred insecticides with the organophosphorus structure can be classified in chemical families showing a wide range of efficacies and action modes. An important group include esters, amides, or thiol



derivatives from phosphoric acid ($\text{R1OP(=O)(OR2)(OR3)}$) or from phosphorothioic acid ($\text{R1OP(=S)(OR2)(OR3)}$). Some examples of the most used organothiophosphorus pesticides in Europe are chlorpyrifos, chlorpyrifos-methyl, diazinon, and pirimiphos-methyl among others.

The major routes of degradation of pesticides in the troposphere involve photolysis, ozonolysis and reactions with hydroxyl and nitrate radicals. The result is a reduction of their concentration in air. However particulate matter (PM) is formed and it could have a toxicity, residence time and atmospheric chemical stability different than the original molecule. Relevant information for several of the most Mediterranean area world-wide used organophosphorus insecticides has been obtained in a high volume atmospheric simulation chambers – EUPHORE – with an extensive instrumentation for monitoring the particulate matter formed.

2. Experimental Section

2.1 Reactor and 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 [3]. 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 an NO_x analyzer (ML9841A, Teledyne Monitor, Englewood, USA) were used for measuring NO, NO₂ and NO_x. A White-type mirror system (path length of 553.5 m) coupled to a Fourier Transform Infrared spectrometer with MCT detector (NICOLET Magna 550, Thermo Scientific, USA) was used for recording concentrations of selected pesticide, nitrous acid (HONO) and SO₂. Retrieval of concentration profiles were calculated by using specific software [4]. FTIR calibration procedure consisted on several introductions of each quantified compound, using standards, into the EUPHORE simulation chamber at known concentrations. 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 it provides 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, Ruppert and Patashnick, Albany, USA) with a 1 min scan rate and a sampling flow of 3 L min⁻¹.

2.2 Experiments

A blank chamber experiment, described in Borrás and Tortajada-Genaro, 2012, was performed to assure the absence of possible simulator artifacts due to the off-gassing of compounds from reactor walls. The photoreactor was filled with air from a purification system. Non-detectable hydrocarbons and nitrogen oxides were measured and the aerosol background was $0.010 \pm 0.005 \mu\text{g m}^{-3}$ (60 part cm⁻³). Specific experiments were performed for guaranteeing the correct injection of chlorpyrifos-methyl into the reaction chamber, because generally low-vapor pressure hydrophobic compounds present important problems (e.g. electrostatic effects with connections). Pesticide was injected via heated air stream (flow 10 L min⁻¹, temperature 350 °C) through a short PTFE tube connection. Under these conditions, losses or decomposition processes were negligible before photochemical degradation reactions started (by opening doom covers).

The oxidation experiments consisted in the sun exposition under dry conditions (<2% RH, 295-298 K) in the absence of initial inorganic seeds and low concentrations of nitrogen oxides (Table 1). For photo-oxidation activated by NO_x, HONO was generated by a liquid-phase

reaction between a 0.5% NaNO_2 solution and a 30% H_2SO_4 solution and transferred via a stream of purified air. Later, individual pesticides were introduced into the chamber in the range of 50 – 100 ppbV. After the reactants were mixed for 10 min, the chamber was exposed to natural sunlight ($\text{JNO}_2 \approx 6.8 \times 10^{-3} \text{ s}^{-1}$) and the reaction started. The onset of aerosol formation was considered to occur when the first significant particle concentration was registered (signal > 3σ background). The specific dilution process was determined using SF_6 as a tracer ($2.3 \times 10^{-5} \text{ s}^{-1}$). Size-resolved wall-loss corrections were not needed for aerosol measurements, since negligible variations were observed during filter sampling for particle number concentration. Data analysis was performed with the statistical package SPSS for Windows v 16.0.

3. Results

A detectable amount of particulate matter was obtained in all experiments and the aerosol yield (Y), or the capacity of organophosphorus pesticide to produce particles, was calculated from the equation proposed by Odum et al. (1996).

$$Y = \frac{M_0}{\Delta HC} \quad [1]$$

where M_0 ($\mu\text{g m}^{-3}$) is the aerosol mass concentration formed and ΔHC ($\mu\text{g m}^{-3}$) is the mass concentration of pesticide reacted. Yields, reported in Table 1, were thus calculated using the precursor concentration from FTIR data and the aerosol concentration from aerosol wall losses corrected SMPS data between the start and the maximum of aerosol formation.

Table1. Summary of aerosol yields from the different photo-oxidation conditions of organophosphorus selected pesticides.

Pesticide	Type of Experiment	Y (%)
Diazinon	Photolysis	< 0.1
	Photo-oxidation in the presence of NOx	44
Chlorpyrifos	Ozonolysis	< 0.1
	Photolysis	6
	Photo-oxidation in the absence of NOx	-
	Photo-oxidation in the presence of NOx	23
Chlorpyrifos-methyl	Ozonolysis	< 0,1
	Photolysis	< 0,1
	Photo-oxidation in the absence of NOx	8,0
	Photo-oxidation in the presence of NOx	21,0
Pirimiphos-methyl	Ozonolysis	< 0,1
	Photolysis	< 0,1
	Photo-oxidation in the absence of NOx	5
	Photo-oxidation in the presence of NOx	15

The Y-values ranged between $2.1 \pm 0.1 \%$ and $44 \pm 0.3 \%$. The results, obtained in the absence of aerosol seeds and temperatures ranged between 14.5 and 15.6 °C indicated that the atmospheric degradation of organophosphorus pesticides led to a reduced formation of products with a low vapor pressure (particulate products). Nevertheless, a higher aerosol formation is expected (2 or 3 folds) in the atmosphere, associated to an early gas-condensed phase partitioning of semi-volatile products in the ambient particles [5] or under lower ambient temperatures. Compared to other organic aromatic pesticides, the aerosol yields obtained under photo-oxidation conditions were similar to propachlor (15%), a chloride-substituted aromatic

ring [6], and hymexazol (4.8%), a N-heterocycle compound [7] employing higher pesticide and NO_x concentrations, in both cases. The aerosol yields were confirmed by calculating the curves of the aerosol mass concentration (Mo) as a function of the pesticide reacted after the onset aerosol formation (Δ HC). A strong linear correlation (R^2 average > 0.95) and statistical test (t-test) confirmed that calculated Y-values from both methods were comparable (p-value<0.05), confirming that the aerosol formation is a NO_x-dependent process.

4. Atmospheric implications

The extensive use of organophosphorus pesticides presents an important environmental effect, and there is a concern about the subsequent changes of chemical atmosphere dynamics and their toxicological hazards. In recent years, many studies have demonstrated that organophosphorus pesticides and some of their degradation products are mutagenic, carcinogenic, cytotoxic, genotoxic, teratogenic, and immunotoxic [8]. The present study, contributes providing useful data about diurnal pesticide degradation. Knowledge of the specific degradation products, including the formation of secondary particulate matter, could complete the assessment of their potential impact. So, the results have indicated that these pollutants are a relevant source of particulate matter. The formation of PM is important because they play a significant role of atmospheric chemistry since they are related to health effects, climate change and radiative force [9]. Hence, the results of this study can contribute to the selection of environmentally sustainable strategies against plagues. Thus, the understanding of atmosphere reactions should help to estimate the expected formation of gas and/or particulate products in the troposphere for each pesticide. Just then, the design and selection between related molecules will be correctly performed based on criteria of efficient action and low environmental impact of the pesticide and their residues.

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References

- [1] Gil Y and Sinfort C 2005 *Atmos. Environ.* **39** 5183
- [2] SANCO/3061/99 – rev. 1.6. 2005
- [3] Borrás E, Tortajada-Genaro L.A 2012a *Atmos. Environ.* **47** 154
- [4] Ródenas M. Report for ESF-INTROP exchange grants, 2008
<http://www.ceam.es/GVAceam/archivos/MRodenasINTROPreport.pdf>.
- [5] Ng NL, Kroll JH, Chan AWH, Chhabra PS, Flagan RC, Seinfeld JH 2007 *Atmos. Chem. Phys.* **7** 3922
- [6] Muñoz A, Vera T, Sidebottom H, Ródenas M, Borrás E, Vázquez M, Raro M, Mellouki A, 2012 *Atmos. Environ.* **49** 40
- [7] Tortajada-Genaro LA, Borrás E, Muñoz A 2013 *Chemosphere* **92** 1041
- [8] Wang X, Mu Z, Shangguan F, Liu R, Pu Y, Yin L 2013 *www.plosone.org* **8** e66703
- [9] Ramanathan V, Crutzen PJ, Kiehl JT, Rosenfeld D 2001 *Science* **294** 2124