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Gas-Phase and Particulate Products from the Atmospheric Degradation of the Organothiophosphorus Insecticide Chlorpyrifos-methyl

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ABSTRACT

The phosphorothioate structure is highly present in several organophosphorus pesticides. However, there is insufficient information about its degradation process after the release to the atmosphere and the secondary pollutants formed. Herein, the atmospheric reaction of chlorpyrifos-methyl (o,o-dimethyl o-(3,5,6-trichloropyridin-2-yl) phosphorothioate), is described for semi-urban or rural locations. The photo-oxidation under low NO_x conditions (5-55 ppbV) was reproduced in a large outdoor simulation chamber, observing a rapid degradation (lifetime <3.5 h). The formation of gaseous products and particulate matter (aerosol yield 2-8%) was monitored. The chemical composition of minor products (gaseous and particulate) was studied, identifying 15 multi-oxygenated derivatives. The most abundant products were ring-retaining molecules such as o,o-dimethyl o-(3,5,6-trichloropyridin-2-yl) phosphorothioate, dimethyl 3,5,6-trichloropyridin-2-yl phosphate, o-methyl o-(3,5,6-trichloropyridin-2-yl) hydrogen phosphorothioate, 3,5,6-trichloropyridin-2-yl dihydrogen phosphate, 3,5,6-trichloropyridin-2-ol, and 3,5,6-trichloropyridine-2,4-diol. An atmospheric degradation mechanism has been proposed based on an oxidation started with OH-nucleophilic attack to P=S bond. The results have been extrapolated to other organothiophosphorus molecules, such as malathion, parathion, diazinon and methidathion, among many others, to estimate their photo-oxidative degradation and the expected products.

Keywords: chlorpyrifos-methyl, insecticide, SOA, photo-oxidation, multi-oxygenated products, reaction mechanism.

1. INTRODUCTION

Organophosphorus pesticides are extensively used in agriculture, horticulture, and a variety of household applications. They are used to prevent diseases, kill, repel, or control plagues 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, 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 (SANCO, 2005). Around a hundred insecticides with the organophosphorus structure can be classified in chemical families. An important group include esters, amides, or thiol derivatives from phosphoric acid ($R_1OP(=O)(OR_2)(OR_3)$) or from phosphorothioic acid ($R_1OP(=S)(OR_2)(OR_3)$). Examples of the most used organothiophosphorus pesticides in Europe are chlorpyrifos, chlorpyrifos-methyl, malathion, parathion, methyl parathion, diazinon, phenotrothion, chlorthion, pirazinon, and methidation among others.

Chlorpyrifos-methyl (o,o-dimethyl o-3,5,6-trichloro-2-pyridyl phosphorothioate) is one of the most widely used insecticides in the world. It is applied on an important range of crops particularly used in the fruit-growing crops and in numerous non-agricultural situations (Balinova et al., 2007). This phosphorothioate is EU-approved and it is highly applied in south-west Europe countries (France, Italy and Spain) and in USA. However, the information about its atmospheric behavior, as well as other organophosphorus insecticides, is quite scarce.

An oxidative process is produced as other semi-volatile organic compounds (SVOCs), After chlorpyrifos-methyl is emitted to the atmosphere (Atkinson et al., 1983). A set of gaseous or condensed products products, called residues or secondary pollutants, is formed with sometimes worse toxicity than the original molecule. However, the real atmospheric behavior and their specific residues are difficult to evaluate. In order to get a comprehensive overview of their atmospheric fate, the use of atmospheric simulation chambers solves some of these limitations (Finlayson-Pitts and Pitts, 2000; Feigenbrugel et al., 2006). These full-equipped facilities have allowed the examination of pollutant degradations under quasy-realistic atmospheric conditions (Bierbach et al., 1992; LePerson et al., 2007, Muñoz et al., 2012, 2014a, 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-methyl degradation and the specific contribution of the main atmospheric reaction (photo-oxidation, ozonolysis, and photolysis) (Muñoz et al., 2011a). Nevertheless, under the experimental conditions employed high concentrations for both pesticide and NO_x (high polluted area), a lower number of specific products were monitored.

The present series of experiments performed in the EUPHORE simulators were carried out in order to improve the understanding of the degradation of chlorpyrifos-methyl in the troposphere, the identification of products generated and in its contribution to secondary organic aerosol (SOA) production. The main diurnal process, over semi-urban/rural locations influenced by the pesticide emissions, was reproduced. Measurements from a wide range of specific instruments were carried out to monitor products, both gas phase and particulate phase, providing information about the chemical composition. Also, a deeper analysis of results has been performed for the elucidation of the degradation pathway and the evaluation of the environmental impact of chlorpyrifos-methyl and related organophosphorus pesticides.

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 chambers consist of two half spherical fluoropolymeric bags, each one of 200 m^3 with integrated measuring systems for monitoring pressure, humidity, temperature, precursor species, and reaction products (Borrás and Tortajada-Genaro, 2012a). 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, NO_2 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 chlorpyrifos-methyl, nitrous acid (HONO) and SO_2. Retrieval of concentration profiles were calculated by using specific software (Ródenas et al., 2008). 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, Ruppercht and Patashnick, Albany, USA) with a 1 min scan rate and a sampling flow of 3 L min^{-1}. For fingerprint analysis, gaseous products were sampled with C18 cartridges during reaction, under a flow rate of 1 L min^{-1} for 0.5 h along the experiment. Particles were collected at maximum aerosol formation at the end of the experiment, under a flow rate of 80 L min^{-1} for 1 h, on quartz fiber filters that had been pre-baked at 500 ^{o}C for 12 h. The analysis of multi-oxygenated compounds by gas chromatography-mass spectrometry (GC-MS) technique plus derivatization was similar to the described in reference (Borrás and Tortajada-Genaro, 2012b) and detailed at Supplementary Information. Blank controls of cartridges and filters showed the absence of artifacts. The use of standards or the determination of the chemical ionization-spectrum confirmed the assigned structure.

2.2 Experiments.

A blank chamber experiment, described in Borrás and Tortajada-Genaro, 2012a, was performed assuring the absence of artifacts e.g. off-gassing of compounds from reactor walls. Also, 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 ± 0.005 µg 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 show important problems (e.g. electrostatic effects with connections). An injection of chlorpyrifos-methyl – pressure vapor 4.2×10^{-5} mm Hg–(99%, Riedel de Häen, Germany) via heated air stream (flow 10 $Lmin^{-1}$, temperature 350 ºC) through a short PTFE tube connection was selected. Under these conditions, losses or decomposition processes were negligible before photochemical degradation reactions started (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, low concentrations of nitrogen oxides and realized in the homogeneous gas phase (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, chlorpyrifos-methyl was 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 ($J_{NO2} \approx 6.8\times10^{-3}$ s^{-1}) and the reaction started. The onset of aerosol formation was considered to occur when the first significant particle concentration was registered (signal > $3\sigma_{background}$). The specific dilution process was determined using SF_6 as a tracer (2.3×10^{-5} 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

3.1. Chlorpyrifos-methyl consumption

The first step was a theoretical study of general chlorpyrifos-methyl reactivity in the troposphere in the homogeneous gas phase, based upon the structure–activity relationship (SAR) methods developed by Kwok and Atkison (1995). The molecular modeling – using a temperature of 25 ºC and typical semi-urban OH concentration of 1.5×10^{6} cm^{3} $molecule^{-1}$ s^{-1} - indicated that a very low or null degradation rate is expected by photolysis and ozonolysis reactions compared to photo-oxidation by OH radicals. The estimated kinetic rate constant

(k_{OH}) was 5.9×10^{-11}cm^3 molecule^{-1} s^{-1} at 25 ºC. However, the model overestimated the atmospheric reactivity of chlorpyrifos-methyl because a lower rate constant (k_{OH} = (4.1 ± 0.4) ×10^{-12} cm^3 molecule^{-1} s^{-1}) was measured in our previous experiments performed in high-volume reaction chambers (Muñoz et al., 2011a).

The following step was focused on the experimental measurement of atmospheric reactivity simulating rural and semi-urban locations in the high volume reaction chamber in the homogeneous gas phase. The typical profiles of chlorpyrifos-methyl degradation under different initial low-NO$_x$ oxidative conditions (HC:NO$_x$ ratios) are shown in Figure 1. An induction period, a delay between the onset of oxidation after sunlight exposure andpesticide consumption, was not observed. This delay has been observed in other pesticide degradations, until the concentration of some oxidant reagent approaches zero (Ng et al., 2007). There is a small anomaly in the first 20 min - in the HC:NO$_x$ 18 serie -, due to variations of solar radiation by clouds. From the decay curves of chlorpyrifos-methyl, the OH concentrations generated were calculated. The average OH concentrations, present in the smog chamber during the photo-oxidation reactions, were (1.34 ± 0.12)×10^6 radicals cm^{-3}and (1.93 ± 0.17)×10^6 radicals cm^{-3} using theoretical k_{OH} and experimental k_{OH}, respectively. These values agreed with previous reported for semi-urban and rural locations (Parrish and Fehsenfeld., 2000). Half-life times (50 % consumption) varied between 1 h (10 HC:NO$_x$ ratio) and 3.8 h (55 HC:NO$_x$ ratio), indicating the atmospheric residence of chlorpyrifos-methyl is relatively short in the troposphere over semi-urban and rural locations, respectively. The values were compared to those obtained under more polluted conditions (two folds higher pesticide and high NO$_x$,Muñoz et al., 2011a). Statistical test (t-test) showed that the half-life times, simulating semi-urban locations, were significantly lower (p-value > 0.05 at 95%). Finally, the reaction reached the stationary state after 5 – 6 h of solar exposition and the consumption of chlorpyrifos-methyl varied from 79 to 83 %, as HC:NO$_x$ ratio changed from ratios 55:1 to 10:1 (Table 1). In summary, the OH reaction of chlorpyrifos-methyl was weakly favored by the presence of nitrogen oxides as it occurs with other pollutants, since it is a second order reaction where [OH] is higher at the beginning of the reaction (Borrás and Tortajada Genaro., 2012a).

3.2. Analysis of aerosol formation

A detectable amount of particulate matter was obtained in all experiments being 12 – 26 µg m^{-3} the aerosol concentrations at the stationary state (Figure 2). The aerosol yield (Y), or the capacity of chlorpyrifos-methyl to produce particles, was calculated from the equation developed by Odum et al. (1996).

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

where M_o (μg m^{-3}) is the aerosol mass concentration formed and aHC (μg 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. The Y-values ranged between 2.1±0.1 % and 9.2±0.3 %. The results, obtained in the absence of aerosol seeds and temperatures ranged between 14.5 and 15.6 ºC, indicated that the atmospheric degradation of chlorpyrifos-methyl leaded to a reduced formation of compounds 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 (Ng et al., 2007) or under lower ambient temperatures. Compared to other organic aromatic pesticides, the aerosol yields obtained were similar to propachlor (15%), a chloride-substituted aromatic ring (Muñoz et al., 2012), and hymexazol (4.8%), a N-heterocycle compound, (Tortajada-Genaro et al., 2013), employing higher pesticide and NO_x concentrations, in both cases. However, the aerosol yields were lower than those calculated from the degradation of diazinon (40%), an organophosphorus compound, under high NO and HCHO conditions (Muñoz et al., 2011b).

The aerosol yields were confirmed by calculating the curves of the aerosol mass concentration (ΔMo) as a function of the chlorpyrifos-methyl reacted after the onset aerosol formation (ΔHC) (Figure 3). Strong linear correlations ($R^2 > 0.95$) were observed with slopes of 7.9 ± 0.3%, 4.4 ± 0.2%, 3.74 ± 0.12%, 2.0 ± 0.1%, and 1.79 ± 0.11%, for HC:NO_x ratios of 10:1, 15:1, 18:1, 35:1, and 55:1, respectively. Statistical t-test indicated that calculated Y-values from both methods were comparable (p-value<0.05). Different HC:NO_x series confirmed that the aerosol formation is a NO_x-dependent process and that aerosol yield increased in the presence of high NO_x concentrations.

Since particle diameter is associated with aerodynamic properties, residence time, human lung deposition and respiratory diseases, the particle size distributions were determined. The variation of photo-oxidation conditions (HC:NO_x ratios) endorsed changes on the nucleation, coagulation and growth of aerosol processes, consequently promoting different particle sizes. A rapid OH generation from HONO photolysis promoted an immediate particulate matter formation and the aerosol size distribution showed an initial growth controlled by condensation or homogeneous/binary nucleation process. Later, the average particle diameter increased from 23-59 nm to 105-160 nm – see experimental size data on Supplementary Information -, being the highest size detected at lower NO_x concentrations although the number of particles decreased. This observation can be explained by an incessantly condensation process, promoting bigger particles but in lower particle number concentration. Hence, mean particle diameter and particle number concentration were found NO_x dependent, but, in all cases, the particle diameters corresponded to the fine particle fraction (diameters < 550 nm).

3.3. Degradation products

The chemical composition of the degradation products formed during low-NO_x photo-oxidations was studied. The major gaseous products, measured by IR technique, were high oxidized compounds such as ozone (6-19 ppbV), formic acid (0.2–9 ppbV), nitric acid (15-70 ppbv), sulfur oxide (5-20 ppbV), nitrogen monoxide (5-60 ppbV), nitrogen dioxide (3-45 ppbV) and formaldehyde (11-17 ppbV). Also, the degradation by OH radicals of chlorpyrifos-methyl generated multi-oxygenated products as a result of a partial oxidation process. For that, a GC–MS technique with PFBHA-MSTFA derivatization was applied to gas-phase and particulate samples collected. A total of 15 products were identified based on chemical properties and their ion fragments, retention time and expected polarity (Supplementary Information). Products were mostly detected under all OH-photo-oxidant conditions. The most abundant products, 3,5,6-trichloropyridin-2-ol (product II) and chlorpyrifos-methyl, were detected in both gaseous and particulate phases. The rest of degradation compounds were detected in particulate phase and some of them also in the gas phase. They include o,o-dimethyl hydrogen phosphorothioate (product VI), and o-methyl o-(3,5,6-trichloropyridin-2-yl) hydrogen phosphorothioate (product III). In a minor amount, dimethyl hydrogen phosphate (product VII), 3,5,6-trichloropyridine-2,4-diol (product V), methoxyphosphorothioic acid (product VIII), phosphoric acid (product IX), 3,5,6-trichloropyridin-2-yl dihydrogen phosphate (product IV), and dimethyl 3,5,6-trichloropyridin-2-yl phosphate (product I) were identified. Hence, most of the multi-oxygenated degradation products identified were ring-retaining products. That means that the partially oxidized molecules maintained the central skeleton of chlorpyrifos-methyl. The phosphorothioate structure was only modified by replacing one of its atoms (double bond P=S for P=O) or some of the O-CH_3 substituent by OH.

A reaction mechanism for the partial oxidation of chlorpyrifos-methyl under low-NO_x conditions is proposed (Figure 4). The previous reaction scheme, described by our group (Muñoz et al., 2011a), has been reinforced including new reaction routes and degradation products supported by the experimental evidences obtained in the present study and in Zhang et al., 2007, Zhou et al., 2009, Dang et al., 2014, Muñoz et al., 2014b,. So, all of multi-oxygenated molecules proposed have been identified on samples collected during the atmospheric degradation process. The reaction mechanism for organothiophosphorus compounds is based on the initial OH attack directed to P=S bond group of chlorpyrifos-methyl. Molecular models indicated the nucleophilic attack can be performed on both phosphorus atom and sulfur atom. If the OH forms an adduct with S atom, it would imply the formation of dimethyl 3,5,6-trichloropyridin-2-yl phosphate (product I), o-methyl o-(3,5,6-trichloropyridin-2-yl) hydrogen phosphorothioate (product III), 3,5,6-trichloropyridin-2-yl dihydrogen phosphate (product IV), and SO_2. On the other hand, the formation of an adduct with P atom yields products such as o-methyl O-(3,5,6-trichloropyridin-2-yl) hydrogen phosphorothioate (product III), 3,5,6-trichloropyridin-2-yl dihydrogen phosphate (product IV), phosphoric acid (product IX), dimethyl hydrogen phosphate (product VII), 3,5,6-trichloropyridine-2,4-diol (product V), methoxyphosphorothioic acid (product VIII), 3,5,6-trichloropyridin-2-ol (product II), and o,o-dimethyl hydrogen phosphorothioate (product VI). This route of aromatic ring release is quite favored by the stabilization of radical intermediate (π-resonance) during the nucleophilic substitution. In fact, the most abundant product in gas phase (3,5,6-trichloropyridin-2-ol) have been extensively identified as metabolite from the degradation of chlorpyrifos and chlorpyrifos-methyl in soils and waters (Ravindra et al., 2010). Finally, a significant formation of phosphoric acid is expected coming from both degradation routes. This hypothesis is supported by the results from FTIR and GC-MS techniques. The residual left in the infrared spectrum after subtraction could match the P=O stretch band (1210-1140 cm^{-1}), although no pure reference could be found to absolutely confirm it.

4. Extrapolation of atmospheric reactivity to other organophosphorus derivatives

Organophosphorus pesticides are an extended family of compounds with a long and increasing number of applications, but their atmospheric chemical behavior is practically unknown. Using the information generated from the study of chlorpyrifos-methyl, the expected diurnal atmospheric degradation of relevant pesticides was estimated. The targeted organophosphorus compounds were chosen as representative examples in terms of high worldwide production taxes and, consequently, high atmospheric emissions. The studied pesticides consisted oforganophosphorothionates R_2O-(P(-OR_1)=S)-OR_3 and organophosphonates HO-(P(-OH)=O)-OR_3, being R_1 -CH_3 or -CH_2CH_3 substituent; R_2 -CH_3 or -CH_2CH_3 substituent; and R_3 aromatic or cyclic structures.

The first approach was the estimation of atmospheric degradation rates using reactivity models based on SAR methods. The theoretical OH kinetic rate constants, listed in Table 2, ranged from k_{OH} = 1.03×10^{-12} molecules cm^{-3} (fosfomycin) to k_{OH} = 1.50×10^{-10} molecules cm^{-3} (methidation) at 25 ºC. Hence, the expected half-lives varied between 17.3 days and 1.4 h for rural locations and 7.8 days and 0.6 h for semi-urban locations. The lowest reactivity was expected for the molecules with P=O bond (oxone structure), such as fosfomycin and triphenylphosphate. Meanwhile, the pesticides with the P=S bond (phophorothiote structure), would react faster with OH. Also, the most reactive molecules to OH attack (2 order of magnitude, higher k_{OH}) would be those that included a pirymidin (e,g. pirazinon) or azol structure (e.g. methidation), due to the contribution of aromatic substitution.

The second approach was the estimation of the degradation products, following the reaction patterns observed in the degradation of chlorpyrifos-methyl. The generation of the high oxidized gaseous products - carbon oxides, phosphoric acid, and SO_2 -, and multi-oxygenated compounds is expected under semi-urban conditions. Table 2 shows the expected photo-oxidation products. The expect products for malathion, chlorthion, methyl parathion and phenotrothion are o,o-dimethyl hydrogen phosphorothioate, dimethyl hydrogen phosphate and phosphoric acid. The organophosphorus degradation products for parathion and diazinon are o,o-diethyl hydrogen phosphorothioate and diethyl hydrogen phosphate. Obviously, there is no experimental evidence for the described derivatives, due to the difficulty to synthesizing them. Only the experimental atmospheric degradation of diazinonhas been performed in a simulation chamber, being the proposed phosphothioate detected compounds, hydroxydiazinon and hydroxydiazinon (Muñoz et al., 2011b).

5. 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 (Wang et al., 2013). The present study, based on the use of EUPHORE high volume photoreactors, contributes providing useful data about diurnal degradation processesof one of the most released 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(Rathore and Nollet, 2012; Majewski et al., 2014). So, the fingerprint analysis of chemical composition has indicated that organophosphorus pollutants are a relevant source of multi-oxygenated molecules. The formation of those types of degradation products is important because they play a significant role of atmospheric chemistry. Multi-oxygenated compounds are related to health effects, climate change and radiative force (Marnett., 1988; Jaoui et al., 2004; Ramanathan et al., 2001). 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. Hence, these results can contribute to the selection of environmentally sustainable strategies against plagues.

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LIST FIGURES AND TABLES

Table 1. Experimental conditions of atmospheric degradations. Standard error < 5%.

Table 2. Estimation of photo-oxidation rate constants based on SAR method, half-lives, and more abundant multi-oxygenated products for some organophosphorus compounds.

Figure 1. Profiles of chlorpyrifos-methyl under different initial low-NO_x oxidative conditions.

Figure 2. Concentration profiles for particle matter from chlorpyrifos-methyl photo-oxidations under different initial low-NO_x oxidative conditions.

Figure 3. Plot of aerosol mass concentration against the reacted chlorpyrifos-methyl concentration from the onset aerosol formation.

Figure 4. Proposed mechanism for the degradation of chlorpyrifos-methyl photo-oxidation.