Heterogeneous Reactivity of Suspended Pirimiphos-Methyl Particles with Ozone

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Pirimiphos-methyl (PMM) is a widely used pesticide that can be released into the atmosphere in the gas phase and the condensed phase. The reaction of suspended PMM particles with ozone is investigated using an online vacuum ultraviolet photoionization aerosol time-of-flight mass spectrometer (VUV-ATOFMS) and a scanning mobility particle sizer (SMPS). The reactions are conducted in an 180 L reaction chamber. The identification of particulate products detected with VUV-ATOFMS is proposed on the basis of GC-MS analysis of PMM ozonation products in methylene dichloride solution. The heterogeneous reactive rate constant of PMM with azelaic acid as matrix under room temperature (293 ± 2 K) is $(1.97 \pm 0.25) \times 10^{-17} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$. The corresponding lifetime at 100 ppbv of ozone is 5.2 ± 0.66 h, and the reactive uptake coefficient (γ) for ozone on PMM particles is $(8.5 \pm 1.1) \times 10^{-4}$. Additionally, ozonation of PMM vapor is conducted, and the rapid formation of secondary organic aerosol (SOA) is observed in the homogeneous ozonation of gas-phase PMM. The experimental results indicate that ozone is an important atmospheric oxidant for the transformation of PMM in the atmosphere.

1. Introduction

Pesticides are toxic chemical substances which are largely applied to agricultural lands and partly used in urban areas as insecticides, herbicides, and fungicides. Although the pesticides directly contaminate ground and surface water, it is considered that the atmosphere is a major receptacle and transport medium for pesticides through their spraying, volatilization, or wind erosion of soil particles and dusts which are loaded with pesticides (1–5). Most pesticides existing in the atmosphere usually undergo extensive chemical transformations through reactions with hydroxyl radicals, nitrate radicals, and ozone as well as photolysis (6). However, these transformations, especially for particulate pesticides, are not understood well.

There are more than 200 kinds of organophosphorus pesticides available in the marketplace, accounting for ~40% of global pesticide use (7). Pirimiphos-methyl (PMM) is one of the broad spectrum organophosphorus pesticides, which acts as a powerful insecticide and acaricide with activity toward many crop pests. It has also been used broadly as a fumigant against pests in a large number of stored products

(8). The investigations on the toxicological evaluation of PMM indicated that it may have effects on nontarget living organisms such as fish, birds, and mammals, including humans (9–15).

Previous studies involving PMM's transformations in biosphere mainly focused on degradation pathways in the water compartments (7, 16, 17). Eneji et al. investigated the degradation of PMM in two nigerian soil/water slurries using microfiltration-high performance liquid chromatography technique (microfiltration-HPLC). The results showed that the product was 2-dimethylamino-6-methylpyrimidin-4-ol, also called pyrimidinol, deriving from direct hydrolysis of the phosphoric ester function. The first-order rate constants for disappearance of PMM from solution were 6.1×10^{-7} and $9.8 \times 10^{-7} \text{ s}^{-1}$ for the Rhodic and Aquic soils, respectively. Chiron et al. evaluated the degradation products of PMM in industrial water under ozone treatment with gas and liquid chromatography–mass spectrometry (GC-MS and LC-MS). Herrmann et al. studied the photocatalytic degradation of PMM in solution with GC, HPLC, GC-MS, and LC-MS. The main degradation pathways they obtained are the hydrolysis of phosphoric ester function, the N-dealkylation of the N-ethyl group, and the oxidation of the alkyl group into an aldehyde function. The vapor pressure of PMM at 20 °C is $2.0 \times 10^{-3} \text{ Pa}$ (18), which means the compound in the atmosphere should exist in the form of both gas and particle phases. Therefore, heterogeneous reactions of PMM may affect its atmospheric degradation behavior in accompany with homogeneous reactions. However, to the best of our knowledge, the study of the heterogeneous and homogeneous oxidation of PMM by gaseous ozone has not been carried out yet.

This paper reports an experimental investigation on the heterogeneous ozonation of suspended PMM particles and homogeneous ozonation of PMM vapor. The PMM particles and their particle-phase ozonation products are analyzed in real time with a vacuum ultraviolet photoionization aerosol time-of-flight mass spectrometer (VUV-ATOFMS). Formation of SOA resulted from the homogeneous reaction of PMM with ozone is observed by SMPS.

2. Experimental Section

2.1. Experimental Equipment. The diagram of the experimental setup is shown elsewhere (19), which is mainly composed of three parts: an aerosol generator, a reaction chamber, and monitoring instruments.

2.1.1. Aerosol Generator. The aerosol generator consists of two tandem 3 cm (outer diameter) $\times$ 40 cm (length) quartz tubes wrapped with heating tapes and equipped with thermometers. The suspended PMM particles are generated by the homogeneous nucleation method. About 0.1 g azelaic acid used to generate nucleus is put in the center of the first quartz tube. Azelaic acid is chosen as the nucleus because it has little reactivity with ozone (20). Meanwhile, ~0.1 g of PMM used to coat the azelaic acid nucleus is placed in the second quartz tube. The particle size, concentration, and coating thickness are controlled by adjusting the temperature of two quartz tubes and flow rates of carrier gas (nitrogen) during the experiments.

2.1.2. Reaction Chamber. The reaction chamber consists of a thin-walled open head stainless steel drum (50 cm (outer diameter) $\times$ 60 cm (height)) and a thin Tedlar polyvinyl fluoride (PVF) film bag (50 cm (diameter) $\times$ 50 cm (length)). The volume of the chamber is ~180 L. A small fan placed at the bottom of the chamber is used to mix reactants rapidly. The reaction chamber is filled with filtered air before each

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experiment. The relative humidity in the chamber is $\sim 20\%$ estimated by the filtered ambient air, except for the homogeneous reaction experiment. The contrast experiment has been conducted using pure nitrogen as the balance gas in our early preliminary tests, which shows that filtered ambient air has no apparent influence on the PMM's reactivity compared with pure nitrogen. The ozone is produced by an ozone generator (Shandong NIPPON, China) with an oxygen stream of 5.0 L min^{-1} . Experiments are conducted under ambient pressure and room temperature ($293 \pm 2 \text{ K}$).

2.1.3. Analysis. The particles are analyzed in real time with VUV-ATOFMS. The VUV-ATOFMS is home-built and described in detail elsewhere (21). The sample rate of the VUV-ATOFMS is $1.3 \text{ cm}^3 \text{ s}^{-1}$. The particles sampled by VUV-ATOFMS are vaporized by a hot surface, and the nascent vapor is photoionized with VUV light radiated from a RF-powered Krypton lamp. The heater temperature is $\sim 400 \text{ K}$. The photo flux and the wavelength of the main VUV radiation is $5 \times 10^{14} \text{ photon/s}$ and 123.6 nm , respectively. The size and concentration of the particles are measured with the SMPS (TSI 3080) equipped with a long differential mobility analyzer (DMA, TSI 3081) and a condensation particle counter (CPC, TSI 3010). The concentration of ozone is measured with an ozone monitor (Model 202, 2B technologies Inc.). The GC-MS is a commercial instrument (Agilent Technologies), which comprises a Hewlett-Packard (HP) 6890 gas chromatograph equipped with a $30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \mu\text{m}$ HP-5 capillary and a HP-5973 quadrupole mass filter with a 70 eV electron impact ionizer. The capillary column is programmed from 60 to $130 \text{ }^\circ\text{C}$ at $23 \text{ }^\circ\text{C min}^{-1}$ and from 130 to $210 \text{ }^\circ\text{C}$ at $4.7 \text{ }^\circ\text{C min}^{-1}$, up to $280 \text{ }^\circ\text{C}$ at $23 \text{ }^\circ\text{C min}^{-1}$, and introduced into the ion source, the temperature of which is $280 \text{ }^\circ\text{C}$. The injection volume is $2 \mu\text{L}$, and the injection mode is splitless (16). The products are identified by comparing the EI mass spectra with the data reported in the literature (16, 17). The mass of PMM vapor used in the homogeneous reaction is estimated by measuring the same volume of PMM vapor with a gas chromatograph with flame ionization detection (GC-FID, EWI, China). China) is equipped with a coil of $30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \mu\text{m}$ fused silica capillary as a column. The PMM vapor is collected by pumping the gas in the reaction chamber through a filter containing 20 g of resin (Amberlite XAD-2 macroporous resin (Sigma-Aldrich)). Then, the resin is ultrasonic-extracted 3 times by ethanol. The solution is concentrated and quantified by the external standard method.

2.2. Experiment Operation. **2.2.1. Heterogeneous Reaction.** The temperatures of two tubes for generating PMM particles are set at $408 \pm 1 \text{ K}$ (azelaic acid) and $388 \pm 1 \text{ K}$ (PMM), respectively. Pure nitrogen passes through the two tubes sequentially at a volumetric flow of $\sim 0.5 \text{ L min}^{-1}$ and transports the particles into the reaction chamber. The mass concentration of residual particles in the chamber is below $0.5 \mu\text{g m}^{-3}$. The filling time of PMM particles is $\sim 30 \text{ min}$ each reaction. The azelaic acid nucleuses have a mean diameter of $\sim 171 \text{ nm}$. The density of azelaic acid is 1.2 g cm^{-3} (22). The PMM particles with azelaic acid nucleus have a mean diameter of $\sim 283 \text{ nm}$, and the mass concentration is $847 \pm 25 \mu\text{g m}^{-3}$. The density of PMM is 1.2 g cm^{-3} (23). The total mass of PMM coating each reaction is $108 \pm 6 \mu\text{g}$. Then, ozone is introduced into the chamber. The readers of the ozone monitor are stabilized in about half a minute.

2.2.2. Homogeneous Gas-Phase Reaction. PMM vapor is produced by heating $\sim 0.1 \text{ g}$ of PMM in one quartz tube at $365 \pm 1 \text{ K}$. The vapor is introduced into the chamber by flushing nitrogen at a flow rate of 0.7 L min^{-1} . The filling time is $\sim 280 \text{ min}$. The mass concentration of residual particles in the chamber throughout the filling progress is below $0.2 \mu\text{g m}^{-3}$. The mass of PMM vapor is $110.7 \pm 13.1 \mu\text{g}$. The ozone

FIGURE 1. Time-of-flight mass spectra of the PMM particles (A) and its ozonation products (B-D). The mass spectra shown in Figure 1(B-D) are acquired 60, 145, and 400 s after ozone is introduced into the chamber. The acquisition time for each mass spectrum is 20 s. The intensities of all the mass peaks shown in the figure are normalized to that of the mass peak at m/z 305 shown in part A.

concentration is $6 \pm 0.1 \text{ ppmv}$ during the reaction. The size distributions of the produced SOAs are measured with SMPS.

2.2.3. Liquid Phase Reaction. An oxygen stream containing 150 ppm ozone bubbles through a solution of 50 mg of PMM in 50 mL of methylene dichloride. The bubbling takes $\sim 20 \text{ min}$ with a flow rate of 1.5 L min^{-1} . Then, a part of the solution is atomized into suspended droplets, and the generated droplets are directly analyzed with VUV-ATOFMS. Meanwhile, another part of the solution is analyzed with GC-MS.

2.3. Chemicals. Pirimiphos-methyl (Dikma, 99.5%) and azelaic acid (HT, China, 99%) are used in the experiment. Oxygen (99.99%) and nitrogen (99.99%) are purchased from Beijing Huayuan Gas Chemical Industry Co. Ltd.

3. Results and Discussion

3.1. Ozonation Products of PMM Particles. The time-dependent mass spectra of PMM ($\text{C}_{11}\text{H}_{20}\text{O}_3\text{N}_3\text{PS}$, mol wt 305) particles and their ozonation products are shown in Figure 1. The acquisition time for each mass spectrum is 20 s. Figure 1 is zoomed in a small scale to show the small mass peaks. The intensities of mass peaks shown in Figure 1(A-D) are normalized to the intensity of the mass peak at m/z 305 shown in Figure 1A. The mass spectrum of PMM particles shown in Figure 1A is almost fragment-free. The dominant mass peak at m/z 305 corresponds to the molecular ion of PMM. The very weak mass peaks at m/z 180, 262, 276, and 290 with the relative intensities of 0.05, 0.02, 0.01, and 0.04 are daughter ion mass peaks of PMM. The characteristic peak of azelaic acid locates at m/z of 152 and is not discussed in this paper.

As shown in Figure 1, the mass peak of the molecular ions of PMM (m/z 305) decreases with the reaction time after the

FIGURE 2. Time-of-flight mass spectrum (A) and the GC-MS total ion chromatogram (B) of the ozonation products of PMM in the methylene dichloride solution.

ozone introduction. Meanwhile, two new mass peaks at m/z 277 and 319 appear and rise with the reaction time. These new mass peaks should be contributed from the ozonation products of PMM particles. The identification of particulate compounds detected with VUV-ATOFMS is proposed on the basis of the GC-MS analysis of PMM ozonation products in methylene dichloride solution. Figure 2 shows the VUV-TOF mass spectrum (A) and the GC-MS total ion chromatogram (B) of ozone-oxidized PMM in methylene dichloride solution. Two major ozonation products 4-dimethoxyphosphinothioxy-N-ethyl-6-methyl-pyrimidin-2-amine (product I, $C_9H_{16}O_3N_3PS$, mol wt 277) and 4-dimethoxyphosphinothioxy-N-ethyl-N-acetyl-6-methyl-pyrimidin-2-amine (product II, $C_{11}H_{18}O_4N_3PS$, mol wt 319) are identified. Product I was reported as one of PMM ozonation products in industrial water under ozone treatment (16). Product II was reported as one kind of photocatalytic products of PMM (17). The main ions and the relative ion abundances of product I and product II obtained by GC-MS are in accordance with the products reported by Chiron et al. and Herrmann et al., respectively (16, 17). Therefore we assign the mass peaks at 277 and 319 shown in Figure 1(B-D) and Figure 2A to the molecular ions of product I and product II of PMM ozonation. The other ozonation products of PMM in methylene dichloride solution are not identified because their match rates are below 60% compared with the available standard samples in the NIST library. The particulate PMM is almost consumed completely in the end of the reaction, indicating that PMM and its ozonation products can be infiltrated by ozone.

3.2. Ozonation Pathways. The reaction pathways of suspended PMM particles with ozone are suggested in Figure 3. It initiates with ozone attack on one ethyl group adjacent to the N atom, leading to the N-dealkylation and the formation of the carbonyl group, which yields product I and product II. There are discrepancies between the observed pathways of heterogeneous ozonation of PMM particles and reported ozonation pathways of PMM in aqueous solutions. In aqueous solution, Chiron et al. suggested three major

pathways for the degradation of PMM under ozone treatment, including the formation of the N-oxime, the dealkylation of the N-ethyl group, and the oxidation of the methyl group (16). The formation of the N-oxime was the major ozonation route (70%) of PMM which results from hydrolysis of the phosphoric ester function, while the dealkylation of N-ethyl group was just a minor route (5%). Likewise, the main pathways of degradation for PMM in soil/water slurries and the photocatalytic degradation in solution are both hydrolysis of the phosphoric ester function (7, 17). The discrepancies may derive from the different moisture conditions under different circumstances. There may also be some volatile products formed in the experiment (via other pathways) but not be detected using the VUV-ATOFMS.

It is reported that ozone mainly involves the removal processes of the unsaturated hydrocarbons in the atmosphere (24) and reacts slowly with saturated hydrocarbons without the UV light or catalysts. In this case, we think that the ethyl groups may be activated by the adjacent N atom. The formation of product I indicates the C atom of the N-ethyl group directly connecting to the N atom may be more active than another atom of the ethyl group. In addition, the N-dealkylation process occurs mainly through hydrolysis, UV radiations, and microbial activity, being observed in many laboratory studies (25–28) and field monitorings (29, 30). It is interesting that the two products are observed in the ozonation of the PMM particle under dark conditions and ozonation of PMM in methylene dichloride solution without the presence of water. It is the first time that N-dealkylation is reported to occur under dark and dry conditions caused by ozone. And based on our knowledge, the detailed mechanism of this process is unavailable yet. Besides, it is well-known that the main transformation products of organophosphorous pesticides in the atmosphere are oxon derivatives, which results from the oxidation of the thiophosphate bond ($P=S$) to oxon ($P=O$) by various oxidants including ozone (31), but this is not observed in the experiment. We speculate that the N-ethyl group of PMM is

FIGURE 3. Proposed pathways for the ozonation of PMM particles.

much more reactive than the P=S bond. The following oxidation of the P=S bond may occur if the oxidation time is long enough.

3.3. Heterogenous Reactive Rate Studies. The pseudo-first-order reaction rate constant of particle-phase PMM ozonation is obtained by analyzing the time-dependent intensities of the mass peak of PMM particles. Figure 4A shows the decay of PMM particles with ozone concentrations of 10, 20, 30, 40, and 60 ppmv. The data points (solid symbols) shown in Figure 4A are the signal intensities of PMM particles normalized to their initial intensities. The fluctuation of the PMM ion intensities before reaction and the ozone concentration during the reaction period are both $\sim 1\%$. The molar ratio of ozone to particulate PMM is about 227, which is calculated with the particulate PMM concentration averaged in the chamber, ensuring that the reaction is under the pseudo-first-order conditions. The decay rate of the PMM particles is obtained by fitting the data points shown in Figure 4A with exponential decay to a minimum function (32). Since the signal intensity of the particle is linear to their concentration (21), the decay rate of the signal intensity is equal to the decay rate of the concentration of the PMM particles. As a result, the pseudo-first-order rate coefficient obtained by the fitting shows a linear function with the ozone concentration, shown in Figure 4B. The linear dependence suggests a similar bimolecular reaction between the surface-adsorbed reactants and gas-phase ozone (18, 32–34), though there are also some studies on the heterogeneous ozonation reaction showing a nonlinear dependence of the pseudo-first-order rate coefficient as a function of the ozone concentration, typical of reactions that proceed by the Langmuir–Hinshelwood mechanism. Thus, second-order rate constants are calculated by dividing pseudo-first-order rate constants by the gaseous ozone concentration. The corresponding second-order rate constant obtained is $(1.97 \pm 0.25) \times 10^{-17} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$. The uncertainty here is estimated by the standard deviation of five experiments, which is also considered as the primary source of experimental uncertainties for the calculation of the following uptake coefficient and the atmosphere lifetime.

FIGURE 4. Decay curves of PMM particles with different ozone concentrations (A) and the linear regressions of pseudo-first-order rate constants as the function of ozone concentration (B). The data points (solid symbols) shown in Figure 4A respectively are the normalized signal intensities of PMM labeled in the figure.

It is well-known that the complicated gas-particle partitioning process is unavoidable in the studies of heterogeneous reactions. Because the heterogeneous reactive rate is

FIGURE 5. Time-dependent size distributions of the SOAs (A) and the growth curve of mass concentrations of SOAs resulted from the ozonation of PMM vapor (B).

obtained by monitoring the decay process of PMM particles, it is considered that the influence from partitioning to the rate constant mainly includes two processes: (1) the volatilization of PMM from the particle phase to the gas phase and (2) the condensation of PMM from the gas phase to the particle phase. If process (1) predominates the partitioning through reaction, the heterogeneous reactive rate obtained would be overestimated. On the contrary, the predominance of process (2) would cause the measurements undervalued. In order to investigate the maximal evaporation of PMM, the evaporation of PMM particles without the presence of PMM vapor is investigated. The PMM particle is quickly filled in the chamber in ~ 8 min, and the decay of the particulate PMM ion signal is monitored with VUV-ATOFMS. After 300 s, the ion signal intensity of particulate PMM decreases to 58% of its initial value, which indicates 42% particle-phase PMM lost into the gas phase. However, in the heterogeneous reaction experiment, the vapor pressure of PMM is saturated at the beginning of the reaction. In addition, the evaporation process of PMM particles is more complicated than that without the presence of ozone. In several previous heterogeneous ozonation experiments of semivolatile organic particles, we observed the ion signals of the organic particles increasing at the first several seconds after the ozone injection. We speculate that the phenomenon results from the absorption of the gas-phase organics by the particles because the equilibrium of the phases is broken due to the covering of ozone on the surface of particles. The nascent ozonation products on the surface of the PMM particles would also greatly inhibit the volatilization of PMM during the reaction. Therefore, it is considered that the reaction rate of the particles measured mainly results from the heterogeneous ozonation but may be influenced by partitioning at a certain extent.

3.4. SOA Formation in Homogenous Reaction. The SOA formation is observed in the ozonation of gas-phase PMM. The size distributions of the SOAs formed in the homogeneous reaction are measured with SMPS. Figure 5A shows

the time-dependent size distributions of SOAs. The lines with diamonds, dots, up-triangles, squares, and down-triangles show the size distributions of the particles measured 3, 6, 13, 27, and 57 min after the ozone injection. Because of the low sensitivity of VUV-ATOFMS toward the particles with diameters less than 70 nm, only product I is observed with a very weak signal. The growth curve of mass concentrations of SOAs is shown in Figure 5B. The density of the SOA is assumed as 1.2 g cm^{-3} . The mass concentration of the particles increases rapidly after ozone is introduced into the chamber and approach to a plateau in 30 min. By fitting the mass concentration of SOA as a function of time with the method reported (35), the pseudo-first-order growth rate of SOA obtained is 0.002 with the related coefficient (R^2) of 0.996. Because the primary components of SOAs come from reaction products and reaction of gas-phase PMM with ozone is prior to formation of SOAs, it would be reasonable to draw a conclusion that the pseudo-first-order rate constant of PMM vapor with ozone is larger than 0.002. There may be some contributions from the sorbed PMM on the reactor wall to the formation of SOAs, but the amount of the contributions should not be significant.

3.5. Atmospheric Implications. The heterogeneous ozonation process of PMM, which yields no product from the reaction between unsaturated C–C bonds and ozone, also has a comparable rate constant with some heterogeneous ozonations of unsaturated C–C bonds (for example, the rate constants of 13 PAHs with graphite and silica as substrates are between $(0.14\text{--}1.5) \times 10^{-17} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$) (32). The atmosphere lifetime of particle-phase PMM at 100 ppbv of ozone, which is calculated by the obtained rate constant, is $5.2 \pm 0.66 \text{ h}$. It is suggested that ozone oxidation may be an important sink for PMM and 2-dialkylaminopyrimidine derivatives. The reactive uptake coefficient (γ) for ozone on PMM particles is $(8.5 \pm 1.1) \times 10^{-4}$, which is calculated by the method reported (36). The value is in the range of effective uptake coefficients for ozone on oleic acid particles and benzo[a]pyrene coated soot aerosol particles (γ at a range of $(0.2 \times 10^{-5}\text{--}3.7 \times 10^{-3})$) (37–39).

There are two major factors that influence the extrapolation of the present laboratory studies to the real atmospheric environment, respectively the relative high concentration of reactants and the much simpler components of the substrate applied in the experiments. The high-concentration PMM in the limited volume of the reaction chamber will lead to the ratio of gas-particle partitioning different from that under atmospheric situations. As a consequence, the different mass-transfer process on the particle surface makes it difficult to interpret the mutual effect of the condense phase and the gas phase in the real atmosphere (40). Furthermore, the uptake coefficients for the same chemical reaction are affected by the morphology, particle size, and substrate of particles. As for some typical model substrates of atmospheric aerosols, the uptake of ozone onto these different substrates may follow this sequence: elemental carbon > fused silica > nonactivated silica gel > solid organic carbon > inorganic salts (41). The particle substrate used in our experiment is azelaic acid. It is reported that the heterogeneous ozonation reaction with azelaic acid as substrate is not only 2 orders of magnitude lower than soot aerosols but also 1 order of magnitude lower than those with aqueous NaCl droplets as substrates for heterogeneous ozonation of PAHs (20). Because all of these model substrates are dominate components in the atmosphere, the heterogeneous ozonation of PMM on these particles' surface in the atmosphere may be faster than that observed in the experiment. Additionally, the chemical morphology within the particles also influences the heterogeneous reactive rate of the particles in the atmosphere. Pure PMM in particle surfaces reacts rapidly with ozone, whereas the reactivity may slow down at a certain extent when it is

trapped inside solids, or when the solids coexist in the particles (40). Nevertheless, the experimental data of heterogeneous and homogeneous ozonations of PMM might help provide a supplementary knowledge for the atmospheric behavior of PMM.

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Literature Cited

- Risebrough, R. W.; Huggett, R. J.; Griffin, J. J.; Goldberg, E. D. Pesticides: transatlantic movements in the northeast trades. *Science* **1968**, *159* (820), 1233–6.
- Aston, L. S.; Seiber, J. N. Fate of summertime airborne organophosphate pesticide residues in the Sierra Nevada mountains. *J. Environ. Qual.* **1997**, *26* (6), 1483–1492.
- Majewski, M. S.; McChesney, M. M.; Woodrow, J. E.; Prueger, J. H.; Seiber, J. N. Aerodynamic measurements of methylbromide volatilization from tarped and nontarped fields. *J. Environ. Qual.* **1995**, *24* (4), 742–752.
- Wolters, A.; Linnemann, V.; Herbst, M.; Klein, M.; Schaffer, A.; Vereecken, H. Pesticide volatilization from soil: Lysimeter measurements versus predictions of European registration models. *J. Environ. Qual.* **2003**, *32* (4), 1183–1193.
- Van Dijk, H. F. G.; Guicherit, R. Atmospheric dispersion of current-use pesticides: A review of the evidence from monitoring studies. *Water, Air, Soil Pollut.* **1999**, *115* (1–4), 21–70.
- Atkinson, R. *Gas Phase Tropospheric Chemistry of Organic Compounds*; Royal Society of Chemistry: London, 1995; Vol. 4, p 152.
- Eneji, I. S.; Buncel, E.; vanLoon, G. W. Degradation and sorption of pirimiphos-methyl in two Nigerian soils. *J. Agric. Food Chem.* **2002**, *50* (20), 5634–5639.
- Fleurat-Lessard, F.; Chaurand, M.; Marchegay, G.; Abecassis, J. Effects of processing on the distribution of pirimiphos-methyl residues in milling fractions of durum wheat. *J. Stored Prod. Res.* **2007**, *43* (4), 384–395.
- Seiler, J. P. Survey on mutagenicity of various pesticides. *Experientia* **1973**, *29* (5), 622–623.
- Hanna, P. J.; Dyer, K. F. Mutagenicity of organophosphorus compounds in bacteria and drosophila. *Mutat. Res.* **1975**, *28* (3), 405–420.
- Moriya, M.; Ohta, T.; Watanabe, K.; Miyazawa, T.; Kato, K.; Shirasu, Y. Further mutagenicity studies on pesticides in bacterial reversion assay systems. *Mutat. Res.* **1983**, *116* (3–4), 185–216.
- Rajini, P. S.; Muralidhara; Krishnakumari, M. K.; Majumder, S. K. Mutagenic properties of pirimiphos-methyl in male-mice. *Bull. Environ. Contam. Toxicol.* **1986**, *36* (5), 680–684.
- Crane, M.; Attwood, C.; Sheahan, D.; Morris, S. Toxicity and bioavailability of the organophosphorus insecticide pirimiphos methyl to the freshwater amphipod *Gammarus pulex* L-in laboratory and mesocosm systems. *Environ. Toxicol. Chem.* **1999**, *18* (7), 1456–1461.
- Lock, E. A.; Johnson, M. K. Delayed neuropathy and acute toxicity studies with pirimiphos-methyl in the hen. *J. Appl. Toxicol.* **1990**, *10* (1), 17–21.
- Hladka, A.; Valkyova, I.; Chabreck, P. Evaluation of professional exposure to pirimiphos methyl actellic. *Sci. Total Environ.* **1991**, *101* (1–2), 177.
- Chiron, S.; Rodriguez, A.; Fernandez-Alba, A. Application of gas and liquid chromatography mass spectrometry to the evaluation of pirimiphos methyl degradation products in industrial water under ozone treatment. *J. Chromatogr., A* **1998**, *823* (1–2), 97–107.
- Herrmann, J. M.; Guillard, C.; Arguello, M.; Aguer, A.; Tejedor, A.; Piedra, L.; Fernandez-Alba, A. Photocatalytic degradation of pesticide pirimiphos-methyl - Determination of the reaction pathway and identification of intermediate products by various analytical methods. *Catal. Today* **1999**, *54* (2–3), 353–367.
- WHO Specifications and Evaluations for Public Health Pesticides, Pirimiphos-methyl, 19.
- Gao, S. K.; Zhang, Y.; Meng, J. W.; Shu, J. N. Online investigations on ozonation products of pyrene and benz[a]anthracene particles with a vacuum ultraviolet photoionization aerosol time-of-flight mass spectrometer. *Atmos. Environ.* **2009**, *43* (21), 3319–3325.
- Kwamena, N. O. A.; Staikova, M. G.; Donaldson, D. J.; George, I. J.; Abbott, J. P. D. Role of the aerosol substrate in the heterogeneous ozonation reactions of surface-bound PAHs. *J. Phys. Chem. A* **2007**, *111* (43), 11050–11058.
- Shu, J. N.; Gao, S. K.; Li, Y. A VUV photoionization aerosol time-of-flight mass spectrometer with a RF-powered VUV lamp for laboratory-based organic aerosol measurements. *Aerosol Sci. Technol.* **2008**, *42* (2), 110–113.
- Lide, D. R.; Milne, G. W. A. *Handbook of data on Common Organic Compounds*; CRC Press: 1994; Vol. 2, p 1522.
- http://www.who.int/whopes/quality/en/Pirimiphos_methyl_eval_may_06.pdf (accessed April 9, 2010).
- Finlayson-Pitts, B. J.; Pitts, J. N., Jr. *Chemistry of the Upper and Lower Atmosphere: Theory Experiments and Applications*; Academic Press: Toronto, 2000.
- Durand, G.; Barcelo, D. Determination of chlorotriazines and their photolysis products by liquid-chromatography with photodiode-array and thermospray mass-spectrometric detection. *J. Chromatogr.* **1990**, *502* (2), 275–286.
- Adams, C. D.; Thurman, E. M. Formation and transport of deethylatrazine in the soil and vadose zone. *J. Environ. Qual.* **1991**, *20* (3), 540–547.
- Mills, M. S.; Thurman, E. M. Reduction of nonpoint-source contamination of surface-water and groundwater by starch encapsulation of herbicides. *Environ. Sci. Technol.* **1994**, *28* (1), 73–79.
- Durand, G.; Debertrand, N.; Barcelo, D. Applications of Thermospray Liquid-Chromatography Mass-Spectrometry in Photochemical Studies of Pesticides in Water. *J. Chromatogr.* **1991**, *554* (1–2), 233–250.
- Thurman, E. M.; Goolsby, D. A.; Meyer, M. T.; Kolpin, D. W. Herbicides in surface waters of the midwestern united-states - the effect of spring flush. *Environ. Sci. Technol.* **1991**, *25* (10), 1794–1796.
- Hallberg, G. R. Pesticide pollution of groundwater in the humid united-states. *Agric. Ecosyst. Environ.* **1989**, *26* (3–4), 299–367.
- Atkinson, R.; Guicherit, R.; Hites, R. A.; Palm, W. U.; Seiber, J. N.; de Voogt, P. Transformations of pesticides in the atmosphere: A state of the art. *Water, Air, Soil Pollut.* **1999**, *115* (1–4), 219–243.
- Perraudin, E.; Budzinski, H.; Villenave, E. Kinetic study of the reactions of ozone with polycyclic aromatic hydrocarbons adsorbed on atmospheric model particles. *J. Atmos. Chem.* **2007**, *56* (1), 57–82.
- Wu, C. H.; Salmeen, I.; Niki, H. Fluorescence spectroscopic study of reactions between gaseous ozone and surface-adsorbed polycyclic aromatic-hydrocarbons. *Environ. Sci. Technol.* **1984**, *18* (8), 603–607.
- Kamens, R. M.; Perry, J. M.; Saucy, D. A.; Bell, D. A.; Newton, D. L.; Brand, B. Factors which influence polycyclic aromatic hydrocarbon decomposition on wood smoke particles. *Environ. Int.* **1985**, *11* (2–4), 131–136.
- Segal-Rosenheimer, M.; Dubowski, Y. Heterogeneous ozonolysis of cypermethrin using real-time monitoring FTIR techniques. *J. Phys. Chem. C* **2007**, *111* (31), 11682–11691.
- Smith, J. D.; Kroll, J. H.; Cappa, C. D.; Che, D. L.; Liu, C. L.; Ahmed, M.; Leone, S. R.; Worsnop, D. R.; Wilson, K. R. The heterogeneous reaction of hydroxyl radicals with sub-micron squalane particles: a model system for understanding the oxidative aging of ambient aerosols. *Atmos. Chem. Phys.* **2009**, *9* (9), 3209–3222.
- Poschl, U.; Letzel, T.; Schauer, C.; Niessner, R. Interaction of ozone and water vapor with spark discharge soot aerosol particles coated with benzo[a]pyrene: O-3 and H2O adsorption, benzo[a]pyrene degradation, and atmospheric implications. *J. Phys. Chem. A* **2001**, *105* (16), 4029–4041.
- Rosen, E. P.; Garland, E. R.; Baer, T. Ozonolysis of Oleic Acid Adsorbed to Polar and Nonpolar Aerosol Particles. *J. Phys. Chem. A* **2008**, *112* (41), 10315–10324.
- Zahardis, J.; Petrucci, G. A. The oleic acid-ozone heterogeneous reaction system: products, kinetics, secondary chemistry, and atmospheric implications of a model system - a review. *Atmos. Chem. Phys.* **2007**, *7*, 1237–1274.
- Rudich, Y.; Donahue, N. M.; Mentel, T. F. Aging of organic aerosol: Bridging the gap between laboratory and field studies. *Annu. Rev. Phys. Chem.* **2007**, *58*, 321–352.
- Kwamena, N. O. A.; Thornton, J. A.; Abbott, J. P. D. Kinetics of surface-bound benzo[a]pyrene and ozone on solid organic and salt aerosols. *J. Phys. Chem. A* **2004**, *108* (52), 11626–11634.

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