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Heterogeneous atmospheric degradation of pesticides by ozone: influence of relative humidity and particle type

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Abstract

In the atmosphere pesticides can be adsorbed on the surface of particles, depending on their physico-chemical properties. They can react with atmospheric oxidants such as ozone but parameters influencing the degradation kinetics are not clear enough. In this study the heterogeneous ozonolysis of eight commonly used pesticides (i.e., difenoconazole, tetraconazole, cyprodinil, fipronil, oxadiazon, pendimethalin, deltamethrin, and permethrin) adsorbed on hydrophobic and hydrophilic silicas, and Arizona dust at relative humidity ranging from 0% to 80% was investigated. Under experimental conditions, only cyprodinil, deltamethrin, permethrin and pendimethalin were degraded by ozone. Second-order kinetic constants calculated for the pesticides degraded by ozone ranged from $(4.7 \pm 0.4) \times 10^{-20} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (pendimethalin, hydrophobic silica, 55% RH) to $(2.3 \pm 0.4) \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (cyprodinil, Arizona dust, 0% RH). Results obtained can contribute to a better understanding of the atmospheric fate of pesticides in the particulate phase and show the importance of taking humidity and particle type into account for the determination of pesticides atmospheric half-lives.

Keywords: pesticides, heterogeneous reactivity, ozonolysis, kinetics, silica particles, relative humidity

1. Introduction

Pesticides are used worldwide to control pests in agricultural production (e.g., vineyards, orchards, and farming) and in many nonagricultural settings (e.g., home, public spaces, gardens and parks, and industrial areas). The important increase in their utilization and their potentially adverse human health effects make their environmental fate to be a hot topic.

Atmospheric pesticide contamination was observed in urban and rural areas with concentration levels from some picogram per cubic meter (pg m^{-3}) to several nanogram per cubic meter ($\mu\text{g m}^{-3}$) (Coscollà et al., 2013, 2014; Estellano et al., 2015; Zivan et al., 2016, 2017). This contamination can be due to spray drift during pesticide applications (about 15 to 40%; Sinfort et al., 2009; Yates et al., 2015; Zivan et al., 2016, 2017), post-application volatilization from treated plants (Zivan et al., 2016, 2017), soil (White et al., 2006) or aquatic surfaces (Luo et al., 2012) (about 0.1 to several dozen %; Lichiheb et al., 2015), and wind erosion (Glotfelty et al., 1989).

Once in the atmosphere, pesticides partition among the gas, particulate, and liquid phases depending on their physicochemical properties and the environmental conditions (Sanusi et al., 1999; Scheyer et al., 2005; Yao et al., 2008; Vogel et al., 2008). Of importance, Sauret et al. (2008) outlined that pesticides recently placed on the market are less volatile than the older ones (e.g., organochlorine compounds) and are mainly associated to the atmospheric particulate phase. Atmospheric sinks of pesticides include wet or dry deposition (Majewski et al., 2014), and direct (Borras et al., 2017) or indirect (Socorro et al., 2017) photochemical degradation. The indirect photochemical lifetime of pesticides in the particulate phase (i.e., adsorbed on atmospheric particles) is mostly governed by their chemical reactivity toward hydroxyl and nitrate radicals, and ozone as photolytic intermediate by-products.

The atmosphere contains particles with concentrations from few thousands to several hundreds

of thousands of particles per cubic centimeter. Most pesticides are mainly accumulated in the ultrafine-fine (below 1 μm) size fractions (Coscollà et al., 2013, 2014). Particles are also exposed to water vapor in atmosphere (at a typical relative humidity (RH) range from 30% to 100% at ambient temperature) that produces mono or multilayer water film on their surfaces depending on the RH (Keskinen et al., 2011). These water layers can have important consequences for heterogeneous reactivity in the atmosphere as the kinetics of many reactions is strongly dependent on the phase of aerosol particles (Knipping et al., 2000). Atmospheric particles are diverse in origin, size, and chemical composition (Seinfeld and Pandis, 2016). They originate from natural sources such as desert dust, volcanic ashes, and marine aerosols, or from anthropogenic sources as vehicular traffic, biomass burning, and fossil fuel combustion (Salameh et al., 2015).

Several kinetic studies of heterogeneous ozonolysis of pesticides (Table 1; Meng et al., 2010; El Masri et al., 2014; Bouya et al., 2015; Socorro et al., 2015 and reference therein) were carried out under different experimental conditions as ozone mixing ratio (e.g., from 0.4 to 86 ppm), RH (e.g., from 0% to 80% RH and uncontrolled), temperature (e.g., from 19°C to 26°C), and type of particles (e.g., hydrophilic and hydrophobic silicas, quartz surfaces, ZnSe crystals, and azelaic acid aerosols). As a result, literature data is often difficult to compare.

The aim of the present work is to better understand the influence of humidity and particle type on the heterogeneous degradation of pesticides by ozone. The experimental protocol and the eight studied pesticides (i.e., difenoconazole, tetraconazole, cyprodinil, fipronil, oxadiazon, pendimethalin, deltamethrin, and permethrin) are identical as those used in previous studies (Socorro et al., 2015, 2016b). Pesticides are representative of major applications, i.e., herbicides, insecticides, and fungicides, and were chosen for their worldwide utilization but also for their physico-chemical properties. The heterogeneous ozonolysis was carried out at 25°C with a range of relative humidity from 0% to 80% RH. Three kinds of silica particles

(i.e., hydrophilic and hydrophobic silicas, and Arizona dust) were used because silica is regarded as one of the main constituents of atmospheric mineral dust and widely used as the model particles for heterogeneous reactions.

2. Experimental section

2.1 Chemicals

Cyprodinil (purity 99.8%), deltamethrin (99.7%), difenoconazole (97.0%), fipronil (97.5%), oxadiazon (99.9%), pendimethalin (98.8%), permethrin (98.3%), and tetraconazole (99.0%) were purchased from Sigma-Aldrich (PESTANAL®, analytical standard) and were used as received. The chemical structures of the pesticides under study are depicted in Fig. S11 and their physico-chemical properties are given in Table S11.

2.2. Particles

Three commercial silica particles were used to mimick atmospheric mineral aerosols: AEROSIL R812 (purchased from Degussa) thereafter called “hydrophobic silica”, AEROSIL 255 (Evonik Industries) called “hydrophilic silica”, and ISO 12103-1, A1 Ultrafine Test Dust (Powder Technology Inc.) called “Arizona dust”. *Composition:* Hydrophobic and hydrophilic silicas (> 99.8 wt%), and Arizona dust (69-77 wt%) contains mainly SiO₂. Arizona dust is also composed of other various mineral oxides (Al₂O₃ (8-14 wt%), Fe₂O₃ (4-7 wt%), Na₂O (1-4 wt%), CaO (2.5-5.5 wt%), K₂O (2-5 wt%), MgO (1-2 wt%), and TiO₂ (0-1 wt%)) and can be thought of as a model dust that originates from deserts (Welti et al., 2009; Coscollà et al., 2013, 2014). *Particle size:* The mean primary particle size of hydrophobic and hydrophilic silica particles ranges from 5 nm to 50 nm (Evonik, 2015). However, most of them can be arranged as agglomerates with an aggregate size roughly measured mainly around 5 µm, sometimes up to 25 µm (Fig. S12-S14). Arizona dust particles are distributed in all size classes and 95.5-97.5

vol% are less than 11 μm . These size ranges are consistent with field observations that show that pesticides are distributed in the fine (0.1-1 μm), ultrafine (0.03-0.1 μm), and coarse (1-10 μm) particle size fraction, and that no pesticides were detected in the size fraction $>10 \mu\text{m}$ (Xu et al., 2011; Coscollà et al., 2013, 2014). *Specific surface area (SSA; BET method)*: Hydrophobic and hydrophilic silica particles have a specific surface area of $(260 \pm 30) \text{ m}^2 \text{ g}^{-1}$ and $(255 \pm 25) \text{ m}^2 \text{ g}^{-1}$, respectively (Evonik, 2015). Arizona dust has a specific surface area of $(20.6 \pm 0.2) \text{ m}^2 \text{ g}^{-1}$ (measured). *Surface chemistry and hygroscopicity*: Surfaces of hydrophobic and hydrophilic silica particles are mainly covered by silanol and siloxane groups. Silanol groups have a hydrophilic nature (i.e., readily mix with water) whereas the siloxane groups are chemically inert and hydrophobic. Vlasenko et al. (2005) suggest that Arizona dust particles are essentially non-hygroscopic (i.e., hydrophobic) due to the low amount of soluble material.

2.3. Particles coating

Hydrophobic silica, hydrophilic silica, and Arizona dust particles were independently coated with pesticides according to a liquid/solid adsorption. In an amber Pyrex bulb of 500 cm^3 , 600 mg of particles were mixed with 6 mL of a pesticide solution (all 8 pesticides at a concentration of 20 mg L^{-1} in dichloromethane (for HPLC, $\geq 99.8\%$, Sigma-Aldrich)), i.e., the load of pesticides on silica particles was about 0.02% by weight) and 40 mL of dichloromethane. After a 5-min ultrasound treatment, dichloromethane was evaporated by a rotary evaporator (Rotavapor R-114, Büchi) at 40°C and 850 mbar. This process allows a reproducible coating of the pesticides on the particle's surface (Socorro et al., 2015). Assuming a uniform particle surface coverage for the pesticide molecules and a spherical geometry for particles, the percentage of the particle surface coated with individual pesticide was between 0.3% and 0.5% of the monolayer for hydrophobic and hydrophilic silicas (See calculation in supplementary information). Then, the total coated particle surface was 2.8% and 2.9% for hydrophobic silica and hydrophilic silica, respectively, which is much less than a monolayer. Due to their weak

SSA, the percentage of the Arizona dust particle surface coated with individual pesticide was between 3.4% and 5.7%, which corresponds to a larger total coated particle surface (35.9%).

2.4. Ozonolysis experiments

The experimental setup was previously described in detail in Socorro et al. (2015) (Fig. SI5). Briefly, a 500 cm³ amber Pyrex bulb containing about 500 mg of dried particles coated with pesticides was fixed to a modified rotary evaporator and placed in a thermostated water bath (25 ± 1°C). Ozone was generated by passing a flow of purified air through an ozone generator. Particles coated with pesticides were exposed to an air flux containing an ozone mixing ratio of 400 ppb (i.e., 9.85 · 10¹² molecules cm⁻³) continuously monitored with a photometric ozone analyzer. The relative humidity (RH) ranged from 0% to 80%. The required humidity was obtained by mixing at different rate of dry and wet gaseous fluxes of purified air. The resulting humidity was measured with a humidity probe with uncertainties of 2% and the sum of the three air fluxes in the reaction flask was 500 mL min⁻¹. Experiments were all conducted for a duration of 26 h.

2.5. Extraction and pesticides quantification

During ozone exposure, 30 mg aliquots of particles were regularly sampled in order to quantify the remaining adsorbed pesticides on their surface. Each 30 mg aliquot of particles was individually introduced in a 33 mL stainless steel cell with an internal standard solution (Triphenyl phosphate, 99.9%, Sigma-Aldrich) and pesticides were extracted by accelerated solvent extraction (ASE 350, Dionex) with dichloromethane. Afterwards, the extracts were concentrated under a nitrogen flow using a concentration workstation (TurboVap II, Biotage). Analysis of the obtained solutions were realized using gas chromatography coupled to tandem mass spectrometry (GC/MS-MS), with a Trace GC Ultra (Thermo Scientific) coupled to a TSQ Quantum™ Triple Quadrupole (Thermo Scientific) using electron impact ionization (70 eV).

More details about ASE extraction, concentration, and GC/MS-MS analysis are available in Socorro et al. (2015).

2.6. Determination of second-order rate constants and half-lives toward ozone

Considering that ozone was continuously drifting in the reactor and that it was used in excess, a pseudo-first order kinetic constant was assumed:

$$\ln \left(\frac{[Pesticide_{(ads)}]_t}{[Pesticide_{(ads)}]_0} \right) = -(k_{O_3(part)}^I + k_{des(part)}^I + k_{hyd(part)}^I) \times t \quad (1)$$

where $k_{O_3(part)}^I$ (s^{-1}) is the pseudo-first order rate constant of the reaction between ozone and the pesticides, $k_{des(part)}^I$ (s^{-1}) is the first order desorption rate constant, $k_{hyd(part)}^I$ (s^{-1}) is the pseudo-first order hydrolysis rate constant, t (s) is the time of ozone exposure, and $[Pesticide_{(ads)}]_t/[Pesticide_{(ads)}]_0$ is the pesticide concentration normalized to the initial pesticide concentration.

The pseudo-first-order reaction rate constants for the heterogeneous ozonolysis of the particle-phase pesticides were determined by analyzing their corresponding temporal profiles in time frame from 0 to 26 h, for 400 ppb ozone mixing ratio.

In order to determine the second-order rate constants $k_{O_3(part)}^{II}$, the experimental pseudo-first order reaction rate constants $k_{O_3(part)}^I$ were plotted as a function of the ozone concentrations.

To simulate the kinetic mechanisms of the heterogeneous reactions the Langmuir-Rideal (L-R, known also as Eley-Rideal) and Langmuir-Hinshelwood (L-H) models are commonly used. In a previous work (Socorro et al., 2015), it was demonstrated that both L-R and L-H models show comparable reactivity for the same pesticide as the ones used in this study. Fig. 1 shows the pseudo-first order rate constant ($k_{O_3(part)}^I$) determined in this work and reported by Socorro et al. (2015) as a function of ozone concentrations for cyprodinil adsorbed on hydrophilic silica.

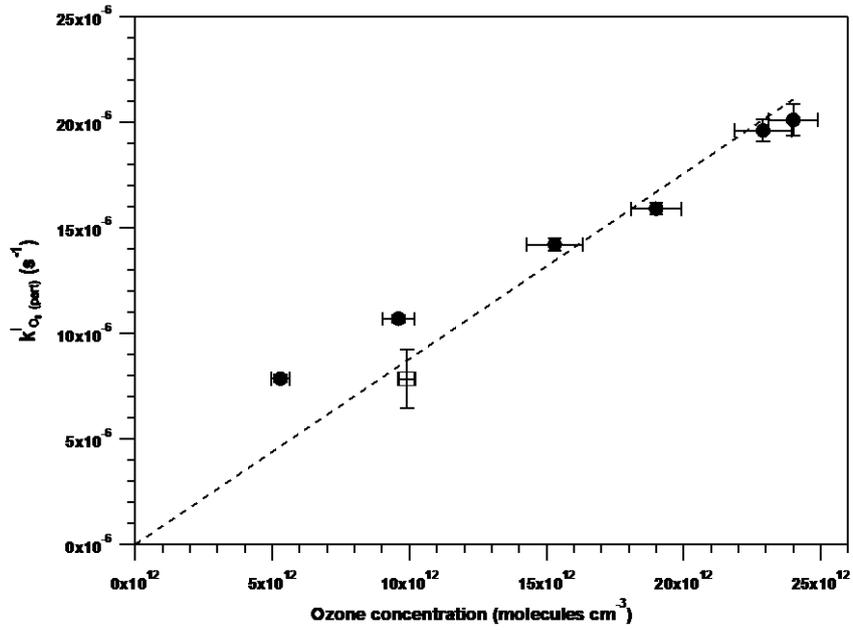


Fig. 1: Observed pseudo-first order rate constants $k_{O_3(part)}^I$ in function of ozone concentrations for cyprodinil adsorbed on hydrophobic silica (● Socorro et al. (2015); □ this work). The dotted line is the linear fitting of Socorro et al. (2015) values, corresponding to a L-R model

The same good agreement between the two studies is observed for the eight pesticides under study. As a result, we assumed to calculate the second-order rate constants $k_{O_3(part)}^{II}$ (cm³ molecule⁻¹ s⁻¹) with only one ozone mixing ratio, i.e., 400 ppb, using a Langmuir-Rideal model. The second-order rate constant was calculated as follows:

$$k_{O_3(part)}^I = k_{O_3(part)}^{II} \times [O_{3(gas)}] \quad (2)$$

where $[O_{3(gas)}]$ is the constant ozone mixing ratio of 400 ppb (i.e., 9.85×10^{12} molecules cm⁻³).

Half-lives corresponding to the heterogeneous atmospheric degradation of pesticides toward ozone were calculated for each specific experimental condition. Ozone mixing ratio used for calculation was 40 ppb (Vingarzan, 2004), and half-lives (s) were obtained with the following

equation:

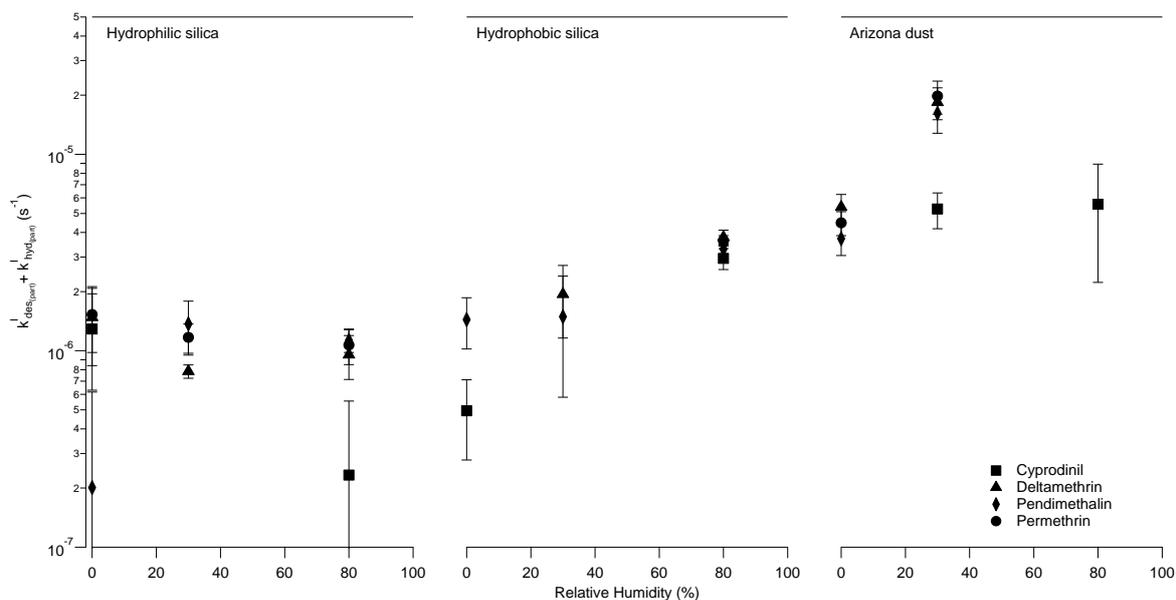
$$t_{1/2 O_3(part)} = \frac{\ln 2}{k_{O_3(part)}^I \times [O_3(gas)]} \quad (3)$$

3. Results and discussion

3.1. Desorption and hydrolysis of pesticides adsorbed on particles

To estimate the loss of pesticide by desorption from particles and by hydrolysis, experiments were carried out for the three kinds of particles, with 500 mL min⁻¹ air flux in the reactor without ozone and light (amber bulb). Experiments were done at various humidities (0%, 30%, 55%, and 80% RH) during 26 h.

Pseudo first-order kinetic constants ($k_{des(part)}^I + k_{hyd(part)}^I$) at different humidity level are presented for each kind of particles in Fig. 2. They ranged from $(2.0 \pm 4.2) \times 10^{-7} \text{ s}^{-1}$ to $(3.4 \pm 1.7) \times 10^{-6} \text{ s}^{-1}$, from $(0.5 \pm 2.2) \times 10^{-7} \text{ s}^{-1}$ to $(3.8 \pm 0.3) \times 10^{-6} \text{ s}^{-1}$, and from $(3.7 \pm 0.7) \times 10^{-6} \text{ s}^{-1}$ to $(2.4 \pm 0.4) \times 10^{-5} \text{ s}^{-1}$, for hydrophilic, hydrophobic, and Arizona dust particles, respectively.



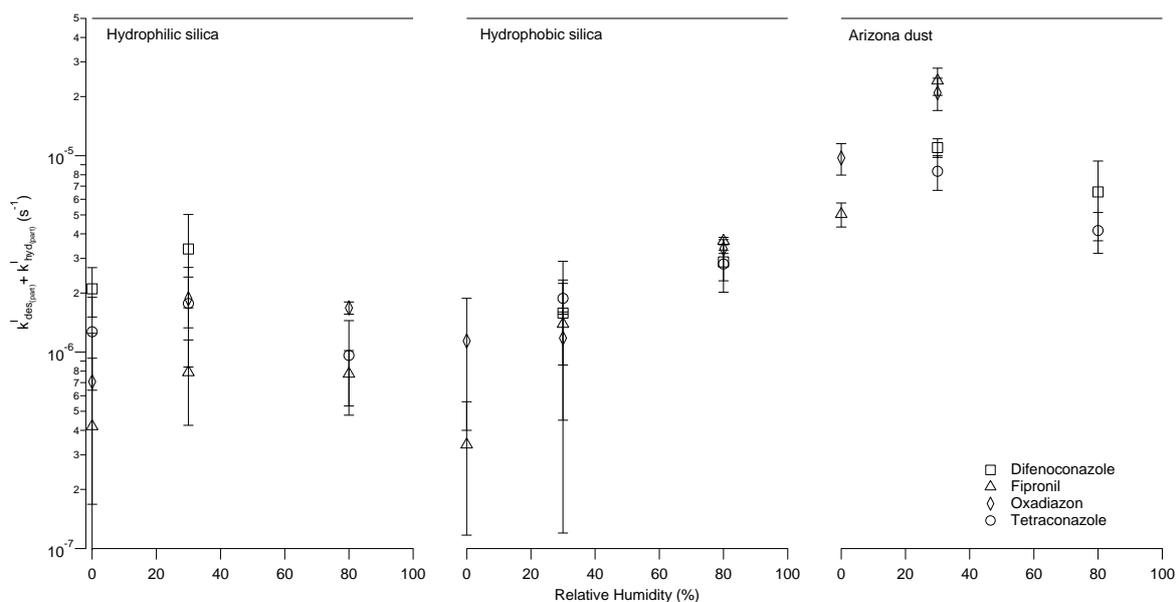


Fig. 2: First order kinetic constants for 8 pesticides adsorbed on hydrophobic silica, hydrophilic silica, and Arizona dust, measured in the absence of ozone and at different RH level

Pesticide losses due to hydrolysis and desorption are not significantly higher for one compound or for a family of compounds. Low losses by hydrolysis is expected for the pesticides under study both because of their low solubility (Table SI1) and their hydrolysis half-lives higher than 30 days (PPDB, 2017). As a result, pesticide losses observed in our experimental conditions are expected to be due to desorption rather than hydrolysis.

Fig. 3 shows that the RH does not significantly influence pesticides desorption when adsorbed on hydrophilic silica and Arizona dust while a slight influence is measured on hydrophobic particles. On the other hand, higher ($k^I_{des(part)} + k^I_{hyd(part)}$) are observed for Arizona dust than for hydrophilic silica particles.

These results are tricky to explain but due to their weak SSA, a larger fraction coated particle surface (35.9%) is expected for the Arizona dust which promotes the formation of pesticide clusters on particle surface. This possibly makes desorption easier and more important than for

the other particles. The nature of the surface (greater proportion of metal oxides) could also play a key role. For hydrophobic silica, the RH dependence could be induced by the expected small amount of adsorbed water. Indeed, at high RH, a competition may take place between water and pesticide which would increase desorption. This hypothesis is contradicted by the results observed for hydrophilic particles, unless it is presumed that a larger amount of adsorbed water (as is the case even for low RH) makes it possible to keep the desorbed pesticides in the liquid phase.

All kinetic constants measured during ozonolysis experiments were corrected using rate constants of desorption and hydrolysis ($k_{des(part)}^I + k_{hyd(part)}^I$), therefore, all values presented below only refer to ozone degradation.

3.2. Heterogeneous ozonolysis

In order to evaluate the influence of humidity on the heterogeneous reaction rates of pesticides, ozonolysis experiments were conducted at relative humidity level between 0% and 80% RH for the three kinds of particles, i.e., hydrophobic silica, hydrophilic silica, and Arizona dust. 0% RH is an unrealistic value as water is always present in the atmosphere. However, most studies of the heterogeneous reactivity of pesticides toward ozone were carried out closer to 0% RH (Pflieger et al., 2009, 2011, 2012; Segal-Rosenheimer et al., 2011). From the analysis of water adsorption on the surface of mineral oxides, Goodman et al. (2001) have shown that the number of water layers is approximately one monolayer at 20% RH, two to three adsorbed water layers at 50% RH, and three to four at 85% RH. 80% RH seems to be a realistic level where the aerosol is close to the state of a deliquescent aerosol.

Under these experimental conditions, tetraconazole, fipronil, oxadiazon, and difenoconazole, were not or slightly degraded ($k_{O_3(part)}^{II} \leq 10^{-20} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$; $t_{1/2} \geq 800 \text{ days}$) whatever the nature of particles. On the other hand, cyprodinil, deltamethrin, permethrin, and pendimethalin,

showed significant losses due to ozone exposure when adsorbed on all three particle types. Second-order rate constants $k_{O_3(part)}^H$ ranged from $(4.7 \pm 0.4) \times 10^{-20} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (pendimethalin, hydrophobic silica, 55% RH) to $(2.3 \pm 0.4) \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (cyprodinil, Arizona dust, 0% RH). The order of magnitude of these constants are in accordance with previous pesticide heterogeneous ozonolysis studies conducted on silica particles (Socorro et al., 2015 and reference therein), quartz surfaces (Al Rashidi et al., 2011, 2013; El Masri et al., 2014; Bouya et al., 2015), ZnSe crystals (Segal-Rosenheimer and Dubowski, 2007), azelaic acid aerosols (Gan et al., 2010; Meng et al., 2010; Yang et al., 2010, 1012), and grape berries (Walse and Karaca, 2011).

It may also be noted that both pyrethroids (deltamethrin and permethrin) are degraded by ozone, probably due to an attack of ozone on the alkene double bond leading to the formation of a primary ozonide (Socorro et al., 2016b), while no significant degradation is observed in our experimental conditions for both triazoles (difenoconazole and tetraconazole). These results show the effect of the chemical structures on pesticide reactivity.

3.3. Influence of humidity

Fig. 3 represents the variation of the second-order rate constants in function of relative humidity for the four pesticides which showed significant losses by ozone exposure, i.e., cyprodinil, deltamethrin, permethrin, and pendimethalin, on all three particles types.

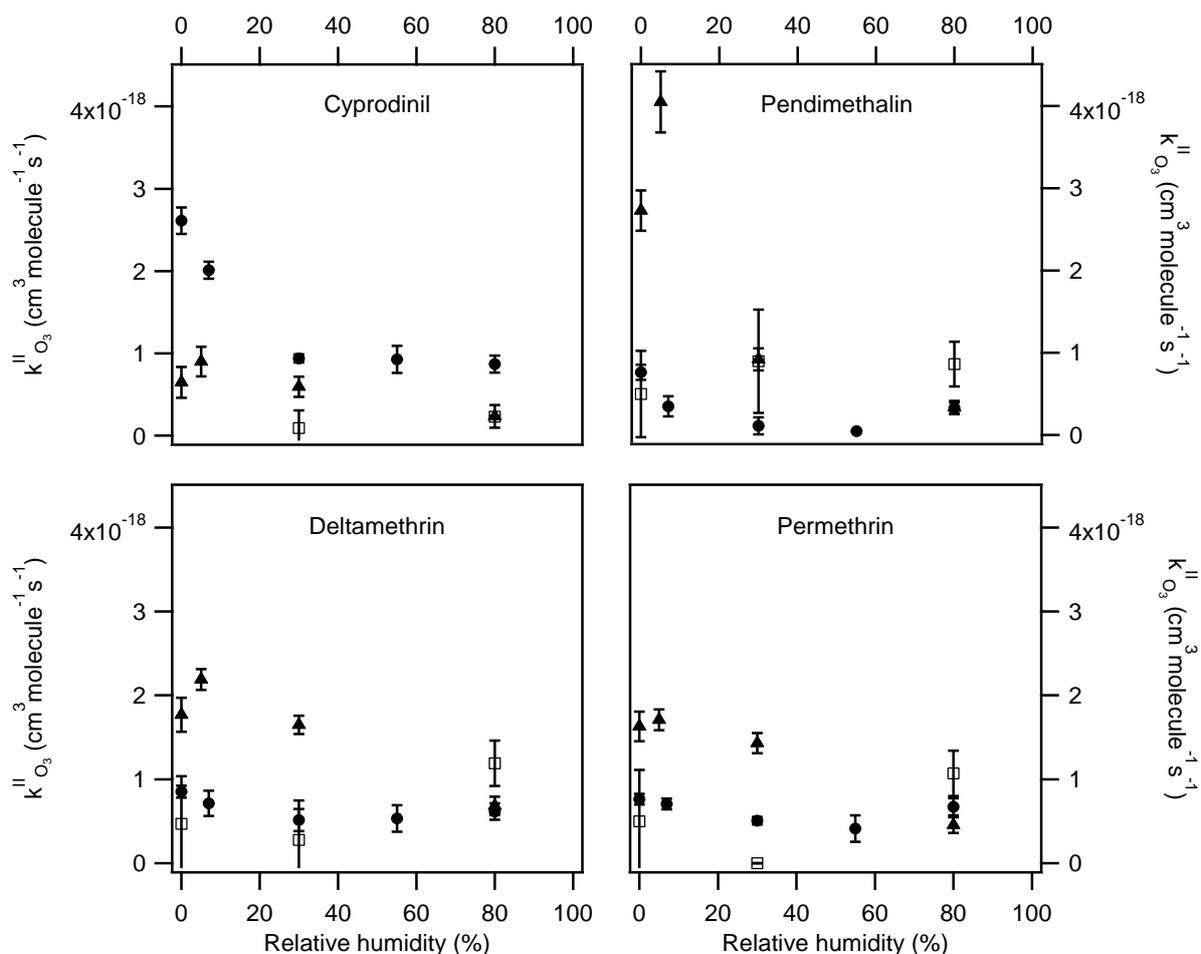


Fig. 3: Second-order rate constants for the ozonolysis of pesticides adsorbed on hydrophobic silica, hydrophilic silica, and Arizona dust at different relative humidity level (▲: Hydrophilic silica; ●: Hydrophobic silica; □: Arizona Dust)

To characterize the influence of RH, the ratio between the lowest and the highest $k_{O_3(part)}^{II}$ obtained at different RH was calculated for each pesticide adsorbed on each particle type.

Hydrophilic silica

Second-order rate constants $k_{O_3(part)}^{II}$ on hydrophilic silica ranged from $(2.3 \pm 1.4) \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (cyprodinil, 80% RH) to $(4.1 \pm 0.4) \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (pendimethalin, 5% RH). The four pesticides exhibit the same trend, characterized by a decrease of their reactivity constant at high relative humidity. For all pesticides, the maximum ratio was obtained

between $k_{O_3(part)}^{II}$ at 80% RH and $k_{O_3(part)}^{II}$ at 5% RH. It should be noted that $k_{O_3(part)}^{II}$ at 0% and 5% RH were not significantly different for all pesticides. Considering these ratios, deltamethrin, permethrin, and cyprodinil reacted 3, 4, and 4 times faster at 5% RH than at 80% RH, respectively. For pendimethalin, $k_{O_3(part)}^{II}$ varied between $(3.3 \pm 0.8) \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (80% RH) and $(4.1 \pm 0.4) \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (5% RH), which corresponds to a degradation 12 times faster when the humidity was low.

Hydrophobic silica

Second-order rate constants $k_{O_3(part)}^{II}$ ranged from $(4.7 \pm 0.4) \times 10^{-20} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (pendimethalin, 55% RH) to $(2.6 \pm 0.2) \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (cyprodinil, 0% RH). For the four pesticides, the highest $k_{O_3(part)}^{II}$ was obtained at 0% RH. As observed for hydrophilic silica particles, pesticides reacted slower when the relative humidity increased. The maximum ratios obtained between the extreme $k_{O_3(part)}^{II}$ were close to those obtained for hydrophilic silica. Deltamethrin, permethrin, cyprodinil, and pendimethalin reacted 2, 2, 3, and 16 times faster at the lowest relative humidity, respectively. For deltamethrin and permethrin, $k_{O_3(part)}^{II}$ were not significantly different between 0% and 80% RH, despite a significant variation with the intermediate RH levels.

Arizona dust

$k_{O_3(part)}^{II}$ measured for Arizona dust were characterized by poor reproducibility, within a range of RSD from 3% to 234%. The difficulty to correctly assess the kinetic constants is potentially due to the ozone degradation on particles surfaces inducing a slow drift of its concentration throughout the experiments. Indeed, during the 26h of experiment, the ozone mixing ratio decreased continuously and could vary up to 33%. This important drift can be compared to those obtained for hydrophobic and hydrophilic silicas that is lower than 4%. This behavior

can be associated to the chemical composition of the particles since silica particles contains mainly SiO₂ (> 99.8wt%) while Arizona dust contains silica but also significant wt% of Al₂O₃ and Fe₂O₃). Those results are in agreement with previous studies (Michel et al., 2003; Usher et al., 2003) which showed that the relative reactivity of ozone followed the trend Fe₂O₃ > Al₂O₃ > SiO₂. Anyway, the important RSD observed for Arizona particles makes it difficult to conclude about the influence of humidity on deltamethrin, permethrin, and pendimethalin for which no significant variation of $k_{O_3(part)}^{II}$ was observed. For cyprodinil, $k_{O_3(part)}^{II}$ varied by two orders of magnitude between dry conditions, i.e., $(2.3 \pm 0.3) \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (0% RH) and humid conditions, i.e., $(0.9 \pm 2.2) \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (30% RH) and $(2.3 \pm 0.1) \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (80% RH).

Overall, whatever the nature of the mineral particles, when an RH effect was observed, the same trend was observed in this work. The more the RH increased, the slowest the heterogeneous ozonolysis was. The influence of humidity on the heterogeneous ozonolysis degradation was already investigated for instance for PAH on many surfaces (Pitts et al., 1986; Pöschl et al., 2001; Kwamena et al., 2004). To our knowledge, only Segal-Rosenheimer and Dubowski (2007) have worked on the heterogeneous ozonolysis of cypermethrin, a pyrethroid insecticide, adsorbed on ZnSe crystals and, to a lesser extent, the influence of the humidification rate on ozonation was investigated for seeds containing pesticides (Bourgin et al., 2013).

In their study, Pitts et al. (1986) exposed five PAH adsorbed on glass fiber (GF) and Teflon impregnated glass fiber (TIGF) filters to 200 ppb of ozone at 1, 25 and 50% RH (ambient temperature). They observed a “humidity effect” with a decrease in reactivity at high RH and concluded to a competition between water and ozone for adsorptive sites. In the same way, Pöschl et al. (2001) observed the decrease of benzo[*a*]pyrene (BaP) decay rates toward ozone (0-1 ppm) on soot aerosols in the presence of water in the range from 0% to 25% RH at 23°C.

In addition, they indicated that an increase of RH beyond 50% may not lead to further reduced reaction rates (Pöschl, 2002). They also suggested a competitive adsorption of ozone and water on the surface. For both studies, this assumption was supported by the nonlinear fits between pseudo first-order rate constants and ozone concentrations, suggesting a L-H mechanism, i.e., the gas-phase ozone is adsorbed on the particle surface prior to the reaction with the adsorbed compounds. Hence, it involves that at high ozone concentration, the relative humidity has less influence on chemical lifetime.

In contrast to the behavior on soot aerosols and GF and TIGF filters, Segal-Rosenheimer and Dubowski (2007) observed no significant difference on the heterogeneous ozonolysis reactivity (30 ppb - 60 ppm) of the insecticide cypermethrin adsorbed on ZnSe crystals at ~7% and ~80% RH. Moreover, Kwamena et al. (2004) mentioned the opposite effect, that is, at high RH (~72% at 25°C) the ozonolysis kinetics were faster than at low RH (<1%) for BaP on azelaic acid aerosols. Even if the influence of the humidity has not the same trend as previous studies, Kwamena et al. (2004) emphasized the role of the surface. Thus, it appears that the influence of the relative humidity on the heterogeneous reactivity should be linked with the nature of particles where pesticides under study were adsorbed.

3.4. Influence of the particle type

Fig. 4 presents the second-order rate constants $k_{O_3(part)}^{II}$ of cyprodinil, deltamethrin, pendimethalin, and permethrin for the three particle types under study in function of relative humidity. Perraudin et al. (2007) have shown no significant kinetic difference during heterogeneous ozonolysis of several PAH adsorbed on various silica particles (same hydrophilic surface chemistry, different particle diameters (5 and 40 μm), pore sizes (70 and 200 \AA), and specific surface areas (200 and 500 $\text{m}^2 \text{g}^{-1}$)). In order to evaluate the influence of the hydrophobicity/hydrophilicity of the surface of particles, both synthetic silicas were chosen

with the same particle size and the same specific surface area. In the present work, only the surface chemistry can be considered to be different as silanol groups have a hydrophilic nature whereas the siloxane groups are chemically inert and hydrophobic. In addition, Arizona dust particles were chosen to be an atmospheric mineral model of particles but, as Saharan sand or Gobi dust (Perraudin et al., 2007), their specific surface area was much lower than both synthetic silicas (one order of magnitude here).

According to their reactivity toward ozone, pesticides under study can be split in two categories whether they were more reactive on hydrophilic or on hydrophobic silica particles.

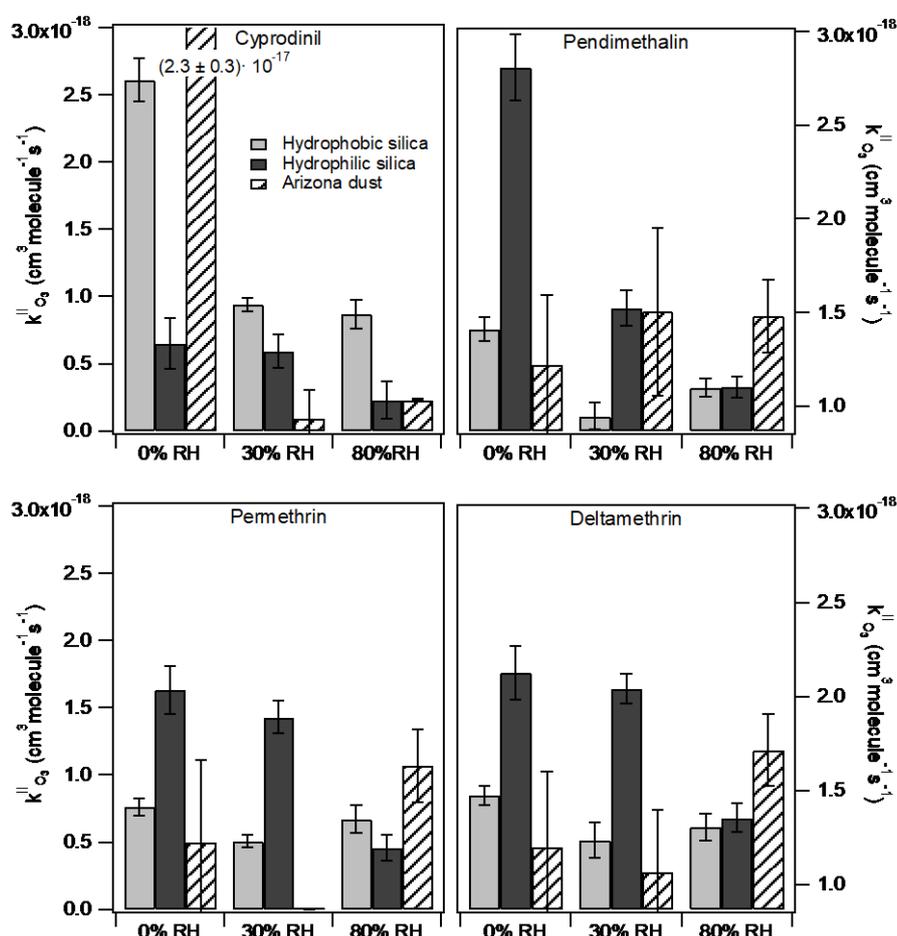


Fig. 4: Second-order rate constant for the degradation of pesticides adsorbed on hydrophobic silica, hydrophilic silica, and Arizona dust by ozone

Pendimethalin, deltamethrin, and permethrin showed the same pattern, that is, at low RH (0% and 30%), the reactivity was from 2 to 8 times faster on hydrophilic particles than on hydrophobic particles whereas at 80% RH, there was no significant difference. The second-order rate constants $k_{O_3(part)}^{II}$ were the same on Arizona dust and hydrophobic silica particles at 0% and 30% RH, partly due to the high RSD of $k_{O_3(part)}^{II}$ for Arizona dust. However, at 80% RH, the reactivity was faster on Arizona dust of a factor of about 2-3 than on synthetic silicas. Thus, the nature of the particle appears to influence the reactivity of pesticides toward ozone. At 0% RH, in the absence of competition between ozone and water for adsorption, the difference in reactivity for pesticides adsorbed on hydrophobic and hydrophilic silica particles suggests a greater affinity of ozone for hydrophilic surface mainly composed by silanol groups. At 30% RH, the amount of water adsorbed on particles increases mainly on hydrophilic particles because of the presence of hydroxyl groups on their surfaces, i.e., silanol groups (Vigil et al., 1994; Muster et al., 2001; Verdaguer et al., 2007). It should be noted that the rehydroxylation of the hydrophobic siloxane surface in presence of wet air is possible, but it is a slow process. Nevertheless, the reactivity on hydrophilic surface remained higher than on hydrophobic surface, suggesting that the amount of water remains too low to induce a competitive adsorption between ozone and water for particle surfaces. At 80% RH, when silica is fully hydrated, all siloxane groups link with water to form silanol groups (Muster et al., 2001), which leads to a similar reactivity on both synthetic silicas.

Unlike the other 3 pesticides (deltamethrin, pendimethalin, and permethrin), cyprodinil was more reactive on hydrophobic silica than on hydrophilic silica of a factor of about 2-4 whatever the RH. Moreover, cyprodinil showed the highest reactivity with $k_{O_3(part)}^{II} = (2.3 \pm 0.3) \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 0% RH when adsorbed on Arizona dust. However, it should be kept in mind that the specific surface area of Arizona dust particles is about one order of magnitude

lower than that of synthetic silicas. Therefore, the percentage of pesticide coating during these ozonolysis exposure was higher for Arizona dust. Complementary experiments will be needed to know the influence of the concentration of adsorbed pesticides on particles.

These differences in kinetic behavior between pendimethalin, deltamethrin, and permethrin on the one hand and cyprodinil on the other, seem to highlight that the chemical nature of the pesticide is also a factor to consider during the heterogeneous ozonolysis.

3.5. Nature of the adsorbed pesticide and comparison with other studies

The different reaction rate constants of heterogeneous ozonolysis and their associated atmospheric half-lives are summarized by chemical family of pesticides under study and compared to literature data (Meylan and Howard, 1993; Pflieger et al., 2009, 2011; Yang et al., 2010, 2012; Walse and Karaca, 2011; Bourgin et al., 2013; Bouya et al., 2015) in Table 1.

Even though no degradation was observed in our conditions for tetraconazole and difenoconazole, two triazole fungicides, several studies were carried out to remove triazole adsorbed on the surface of plants. However, the ozonation process frequently requires high ozone concentration. Heleno et al. (2013) investigated the effect of ozone fumigation on the reduction of difenoconazole residue on strawberries. Difenoconazole was removed up to 95% after 1h when exposed to 400 ppm of ozone. Bourgin et al. (2013) exposed seeds coated by the triazole bitertanol at very high ozone concentration (51,000 ppm). The half-lives calculated from the rate constants reported in literature agree with the present study and confirm that triazole fungicides were not affected by ozonolysis at atmospheric concentrations.

Several ozonolysis studies dealt with the compounds of the pyrimidine family adsorbed on various surfaces without ever specifying the relative humidity. Our results are in accordance with those obtained for pyrimethanil, pirimiphos-methyl, and bupirimate adsorbed on model atmospheric aerosols (Yang et al., 2010; Bouya et al., 2015). However, ozonation studies

performed on surface of grape berries exhibit half-lives much higher (Walse and Karaca, 2011).

The same hydrophobic silica particles were used to study the heterogeneous ozonolysis of dinitroaniline herbicides (Pflieger et al., 2009, 2011; Yang et al., 2012). Half-lives of pendimethalin, trifluralin, and isopropalin were of the same order of magnitude, suggesting that the kinetic data obtained for one pesticide can be extended to the whole chemical family, here, the dinitroaniline family. Moreover, the same results were obtained for both pyrethroid insecticides whatever the particle types, suggesting again a generalization to a whole chemical family. It should also be noted that the kinetic data of the theoretical gas-phase ozonolysis for both pyrethroids under study (Meylan and Howard, 1993) exhibits the same order of magnitude as the experimental ozonolysis kinetics rate constants in the particulate phase.

Table 1: Kinetic data for the ozonolysis of the adsorbed pesticides (in bold) under study and atmospheric half-lives compared to the literature data

Chemical Family	Pesticide	Relative humidity (%)	Temperature (°C)	Ozone mixing ratio (ppm)	Surface	$k_{O_3(part)}^{II}$ (cm ³ molecule ⁻¹ s ⁻¹)	$t_{1/2 O_3(part)}$ (days)	Reference
Triazole	Difenoconazole	(0-80) ± 2	25 ± 1	0.4	Hydrophobic silica Hydrophilic silica Arizona dust	≤ 10⁻²⁰	≥ 800	This work
	Tetraconazole	(0-80) ± 2	25 ± 1	0.4	Hydrophobic silica Hydrophilic silica Arizona dust	≤ 10⁻²⁰	≥ 800	This work
	Bitertanol	Humidification 10% (w/w)	Unknown	51,000	Seeds	~ 1.4 × 10 ⁻²¹	~ 6,000	Bourgin et al. (2013)
Pyrimidine	Cyprodinil	(0-80) ± 2	25 ± 1	0.4	Hydrophobic silica Hydrophilic silica Arizona dust	(0.9 ± 2.2) × 10⁻¹⁹ to (2.3 ± 0.3) × 10⁻¹⁷	0.4 to 91	This work
	Cyprodinil	Uncontrolled	Unknown	150	Glass	~ 7.0 × 10 ⁻²⁰	~ 116	Walse and Karaca (2011)
	Cyprodinil	Uncontrolled	Unknown	150	Grape berries	~ 2.7 × 10 ⁻²¹	~ 3,000	Walse and Karaca (2011)
	Pyrimethanil	Uncontrolled	Unknown	150	Glass	~ 5.3 × 10 ⁻²⁰	~ 154	Walse and Karaca (2011)
	Pyrimethanil	Uncontrolled	Unknown	150	Grape berries	~ 2.5 × 10 ⁻²¹	~ 3,200	Walse and Karaca (2011)
	Pirimiphos-methyl	Unknown	20 ± 2	10 to 60	Azelaic acid	(1.97 ± 0.25) × 10 ⁻¹⁸	4	Yang et al. (2010)
	Bupirimate	Unknown	19 ± 1	12 to 86	Quartz	(5.4 ± 0.3) × 10 ⁻²⁰	151	Bouya et al. (2015)
Dinitroaniline	Pendimethalin	(0-80) ± 2	25 ± 1	0.4	Hydrophobic silica Hydrophilic silica Arizona dust	(4.7 ± 0.4) × 10⁻¹⁹ to (4.0 ± 0.4) × 10⁻¹⁷	0.2 to 17	This work
	Trifluralin	1	25	5 to 41	Hydrophobic silica	(2.9 ± 0.1) × 10 ⁻¹⁹	28	Pflieger et al. (2009)
	Trifluralin	< 1	26 ± 1	1 to 16	Hydrophobic silica	(1.05 ± 0.06) × 10 ⁻¹⁹	78	Pflieger et al. (2011)

	Isopropalin	Unknown	20	0.5 to 25.3	Hydrophobic silica	$(2.70 \pm 0.27) \times 10^{-19}$	30	Yang et al. (2012)
Pyrethroid	Deltamethrin	$(0-80) \pm 2$	25 ± 1	0.4	Hydrophobic silica Hydrophilic silica Arizona dust	$(2.8 \pm 4.7) \times 10^{-19}$ to $(2.2 \pm 0.1) \times 10^{-18}$	4 to 35	This work
	Deltamethrin	0	Theoretical	Theoretical	Gaseous phase	2.2×10^{-19}	37	Meylan and Howard (1993)
	Permethrin	$(0-80) \pm 2$	25 ± 1	0.4	Hydrophobic silica Hydrophilic silica Arizona dust	$(4.1 \pm 1.6) \times 10^{-19}$ to $(1.7 \pm 0.1) \times 10^{-18}$	5 to 20	This work
	Permethrin	0	Theoretical	Theoretical	Gaseous phase	2.3×10^{-19}	35	Meylan and Howard (1993)
Pyrazole	Fipronil	$(0-80) \pm 2$	25 ± 1	0.4	Hydrophobic silica Hydrophilic silica Arizona dust	$\leq 10^{-20}$	≥ 800	This work
Oxadiazole	Oxadiazon	$(0-80) \pm 2$	25 ± 1	0.4	Hydrophobic silica Hydrophilic silica Arizona dust	$\leq 10^{-20}$	≥ 800	This work

^a Atmospheric half-lives calculated for $[O_{3(gas)}] = 40$ ppb (Vingarzan, 2004).

3.6. Atmospheric implications

The heterogeneous ozonolysis yields to deltamethrin, permethrin, cyprodinil, and pendimethalin degradation. However, whatever the atmospheric conditions of humidity and nature of particles, difenoconazole, tetraconazole, fipronil, and oxadiazon will present no degradation towards ozone. Indeed, unlike to deltamethrin and permethrin (alkene double bond) and cyprodinil and pendimethalin (secondary amine group), they have no chemical groups likely to react with ozone. Consequently, the calculated atmospheric half-lives (Table 1) for an ozone mixing ratio of 40 ppb, which is representative of the atmospheric ozone level in mid latitudes of the Northern hemisphere (Vingarzan, 2004), are higher than several years. Moreover, Socorro et al. (2016a) also reported that difenoconazole, tetraconazole, fipronil, and oxadiazon were not degraded by hydroxyl radicals in particulate phase which implies a significant persistence of these pesticides in the atmosphere once adsorbed on particles.

The half-life of cyprodinil can widely range from a few hours to several months, and from a few hours to several weeks for pendimethalin, permethrin, and deltamethrin. These half-lives are also significant enough to involve a transport over long distances prior to be removed and a potential transfer to aquatic and terrestrial ecosystems where they can cause hazard effects.

Hence, from a legislative point of view, according to the Stockholm convention, these pesticides can be considered as persistent organic compounds (POPs) in the atmosphere with respect to the gas-phase ozone (UNEP, 2001).

However, given the complexity of the surfaces of atmospheric particles and the atmospheric variation of relative humidity, the heterogeneous ozonolysis can be considered as a very slow process for the studied pesticides compared with the highly reactive hydroxyl radicals (Socorro et al., 2016a).

4. Conclusions

Kinetic data are dependent on relative humidity, on particles surface chemistry, and chemical nature of the adsorbed pesticides. For the four reactive pesticides (i.e., cyprodinil, deltamethrin, permethrin, and pendimethalin), heterogeneous ozonolysis reactions are slower at high relative humidity suggesting a competitive adsorption of ozone and water on particle surface. Moreover, reactivity on hydrophilic surface are faster than on hydrophobic surface in the absence of water and at low RH for deltamethrin, permethrin, and pendimethalin. When RH increases (i.e., 80% RH), pesticides exhibit comparable reactivity on both synthetic silicas, suggesting a rehydroxylation of the hydrophobic siloxane surface in presence of wet air. However, the opposite kinetic behavior observed for cyprodinil also implies the influence of the chemical nature of pesticide. Pesticides of the same chemical family (deltamethrin/permethrin and difenoconazole/tetraconazole) appear to have the same kinetic behaviour, suggesting a possible generalization of the kinetic results to the whole chemical family.

These results suggest that relative humidity must be taken into account to determine kinetic rate constants and that studies carried out at 0% RH cannot be considered as representative of the atmospheric conditions. Finally, given the chemical structures of pesticides and the complexity of atmospheric particles surface, it is currently difficult to predict degradation kinetics as may be the case for the gas-phase.

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