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# **Heterogeneous degradation of pesticides by OH radicals in the atmosphere: influence of humidity and particle type on the kinetics**

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## Abstract

Pesticides can be adsorbed on the surface of atmospheric aerosol, depending on their physicochemical properties. They can be degraded by atmospheric oxidants such as OH radicals but the influence of some environmental parameters on the degradation kinetics, especially relative humidity and particle surface type, is not well understood. Heterogeneous degradation by OH radicals of eight commonly used pesticides (i.e., difenoconazole, tetraconazole, cyprodinil, fipronil, oxadiazon, pendimethalin, deltamethrin, and permethrin) adsorbed on hydrophobic and hydrophilic silicas at a relative humidity ranging from 0% to 70% was studied. Under experimental conditions, only cyprodinil, deltamethrin, permethrin, and pendimethalin were degraded by OH radical in atmospheric relevant concentration. Second-order kinetic constants calculated for the pesticides degraded by OH radicals ranged from  $(1.93 \pm 0.61) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (permethrin, hydrophobic silica, 30% RH) to  $(4.08 \pm 0.27) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (pendimethalin, hydrophilic silica, 0% RH). Results obtained can contribute to improve the understanding of the atmospheric fate of pesticides and other semi-volatile organic compounds in the particulate phase and they highlight the importance of taking humidity and particle type into account for the determination of pesticides atmospheric half-lives.

## Keywords

Aerosols, atmosphere, degradation, humidity, OH radical, pesticides

## 1. Introduction

Pesticides are of great interest for both the scientific community and the general public due to their worldwide uses and potential adverse health or environmental impacts (Carvalho, 2017; Inserm, 2013). They are present in the atmosphere in concentration levels from some picogram per cubic meter ( $\text{pg m}^{-3}$ ) to several nanograms per cubic meter ( $\text{ng m}^{-3}$ ) (Coscollà et al., 2013, 2014; Désert et al., 2018; Estellano et al., 2015; Lester et al., 2017; Zivan et al., 2016, 2017). Most of the currently used pesticides are semi-volatile organic compounds (SVOC), consequently, they are distributed between the gaseous and particulate phases. In the atmosphere, they can undergo direct photolysis and can react with atmospheric oxidants, whose main representatives are hydroxyl radicals (OH), ozone ( $\text{O}_3$ ), and nitrate radicals ( $\text{NO}_3$ ). On the first hand their gas-phase reactivity has been extensively studied (Borrás et al., 2015; Muñoz et al., 2014; Vera et al., 2015) and numerous kinetic data, especially for the reactivity with OH radicals, is available thanks to modeling (Bahm and Khalil, 2004). On the other hand, very few studies were done on particulate phase reactivity. Moreover, the available heterogeneous degradation kinetics data are subject to large uncertainties because of experimental difficulties to study heterogeneous reactivity and to the numerous atmospheric physicochemical parameters which could influence them (relative humidity (RH), particles hygroscopicity, particle chemical composition...).

The heterogeneous degradation of some pesticides with OH radicals has already been studied (Al Rashidi et al., 2011, 2014; Bouya et al., 2015; Lester et al., 2017; Liu et al., 2005; Palm et al., 1997, 1998, 1999, 2011; Pflieger et al., 2013; Zetzsch, 1991), but conditions employed to determine kinetic constants were very diverse in terms of surface (different silica particles, quartz surface, plant leaves) and humidity (<1% RH to 70% RH). To our knowledge, no study investigated the influence of relative humidity on the degradation kinetics of pesticides with OH radicals, although this factor has an influence on the heterogeneous degradation of organic

compounds by ozone (Kaiser et al., 2011; Mattei et al., 2018; Pöschl et al., 2001). Moreover, no study investigated the influence of the surface on the OH radicals degradation of pesticides while it has been already shown that particle surface influences the OH radicals degradation kinetics of SVOC such as polycyclic aromatic hydrocarbon adsorbed on different diesel particles (Esteve et al., 2006).

As a result, the aim of this study is to investigate the influence of atmospheric relative humidity (RH) and particle physicochemical properties on the heterogeneous degradation of pesticides by OH radicals. To do so, laboratory experiments were performed using two model particles: hydrophobic and hydrophilic silicas at a RH level varying from 0% to 70%. The experiments were done with eight pesticides representative of various chemical classes of pesticides: cyprodinil (pyrimidine), deltamethrin (pyrethroid), difenoconazole (triazole), fipronil (pyrazole), oxadiazon (diazole), pendimethalin (dinitroaniline), permethrin (pyrethroid), and tetraconazole (triazole). The compounds under study were selected based on their distribution between gas and particle phases, their toxicity, and their presence in the atmosphere (Désert et al., 2018). Understanding the influence of these factors on the heterogeneous degradation kinetics of pesticides by OH radicals will help to better understand the atmospheric behavior and the atmospheric transportability of pesticides when they are adsorbed on atmospheric aerosols. This is important to adapt pesticide regulatory policies which, in the atmosphere, concern only gaseous pesticides even though currently used pesticides are often semi-volatile species.

## 2. Material and Methods

### 2.1 Chemicals

Analytical standards (PESTANAL®, analytical standard) of the eight pesticides under study (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%)) as

well as 2,3-dimethyl-2-butene (DMB, 98%) and m-xylene (99.5%) were purchased from Sigma-Aldrich. They were used as received. The chemical structures of the pesticides under study are depicted in Supporting Information (SI) Fig. SI1 and their physicochemical properties are given in Table SI1.

## 2.2 Particles

Two commercial fumed silica particles were used to mimic atmospheric mineral aerosols: AEROSIL R812 (purchased from Degussa) thereafter called “hydrophobic silica” and AEROSIL 255 (Evonik Industries) called “hydrophilic silica”.

*Chemical composition:* Hydrophobic and hydrophilic silicas contain mainly  $\text{SiO}_2$  (> 99.8 wt%). Surfaces of hydrophobic and hydrophilic silica particles are mainly covered by siloxanes and silanols groups, respectively. Siloxane groups are chemically inert and hydrophobic whereas silanol groups have a hydrophilic nature (i.e., readily mix with water). It was shown that 10% to 30% of atmospheric particles are composed of quartz or silica (Finlayson-Pitts and Pitts, 2009; Seinfeld and Pandis, 1998), as a result, our particles are good proxies to simulate the chemical composition of crustal aerosols.

*Particle size:* Very few studies were done on the particle size distribution of pesticides in ambient air. However, the available results showed that most of the pesticides (40% to 80%) are accumulated in the fine (0.1-1  $\mu\text{m}$ ) particle size fraction, while only a small part is adsorbed on the ultrafine (0.03-0.1  $\mu\text{m}$ ) and coarse (1-10  $\mu\text{m}$ ) size ranges. On the other hand, no pesticides were detected in the size fraction > 10  $\mu\text{m}$  (Coscollà et al., 2013, 2014; Xu et al., 2011). In the present study, the individual mean size of hydrophobic and hydrophilic silica particles range from 5 nm to 50 nm (Evonik, 2015) (Fig. SI2-SI3) which is in agreement with the aerosol size observed in the experimental field measurements. However, particles can agglomerate to reach sizes ranging between 5  $\mu\text{m}$  and 25  $\mu\text{m}$  (Fig. SI2-SI3).

*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).

### 2.3 Particle coating

Hydrophobic and hydrophilic silicas were independently coated with pesticides according to a liquid/solid adsorption process. In an amber Pyrex flask of 500 cm<sup>3</sup>, 600 mg of particles were mixed with 6 mL of a solution containing the 8 pesticides under study each at a concentration of 20 mg L<sup>-1</sup> (pesticide solution in dichloromethane for HPLC,  $\geq 99.8\%$ , Sigma-Aldrich). The load of pesticides on silica particles was about 0.02% by weight. After a 5-min ultrasound treatment, dichloromethane was evaporated using a rotary evaporator (Rotavapor R-114, Büchi) at 40 °C and 850 mbar. This process allows a reproducible and realistic 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 a monolayer for hydrophobic and hydrophilic silicas respectively (*SI Silica particles coating*). For the eight pesticides, 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.

### 2.4 Exposition to OH radicals

#### *Experimental set-up:*

The experimental set up to expose pesticide-coated particles to OH radical is presented in Fig. 1. The exposition took place in a 500 mL amber round bottom flask, connected to a modified rotary evaporator (Laborota 4000 efficient, Heidolph) and immersed in a thermostated bath. This device allowed to mix homogeneously and continuously the particles and to maintain a constant temperature ( $25 \pm 1 \text{ }^\circ\text{C}$ ). The reactor was protected against light using an aluminum foil to avoid pesticide photo-degradation. All gas flows were monitored and kept constant

during an experiment, of a duration of 6 hours. The total flow passing the reactor was 500 mL min<sup>-1</sup> to ensure a total renewal of the gases in the reactor every minute.

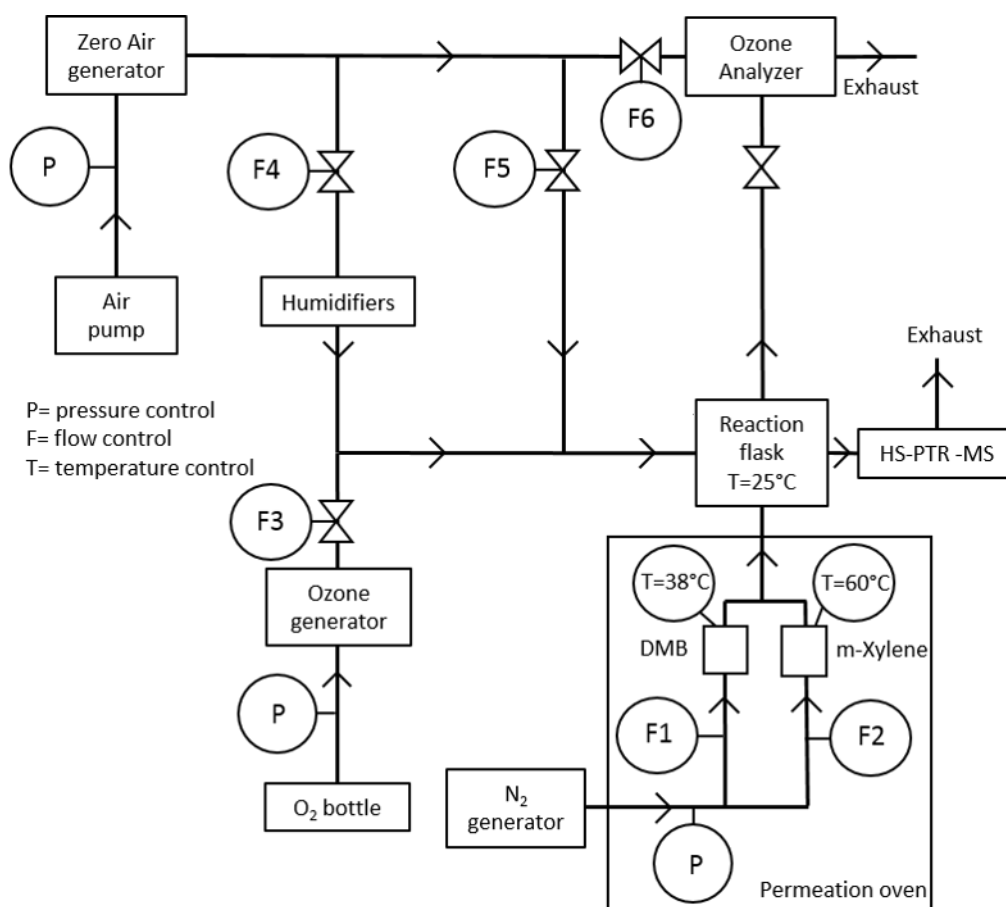
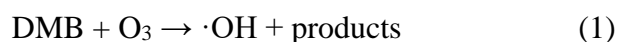


Fig. 1: Experimental setup to study heterogeneous oxidation of pesticides by OH radicals

### ***OH radical generation:***

OH radicals have an atmospheric lifetime inferior to one second (Schlosser et al., 2009) consequently, they need to be generated directly into the reactor. They were generated through the ozonolysis of an alkene, the 2,3-dimethyl-2-butene (DMB), this method is known as the “dark OH radical generation” (Lambe et al., 2007; Le Person et al., 2007; Pflieger et al., 2013; Segal-Rosenheimer et al., 2011). DMB reacts with ozone to give OH radical according to equation 1 with the rate constant  $k_1 = (1.13 \pm 0.01) \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Greene and Atkinson, 1992):

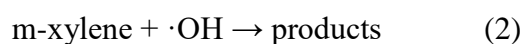




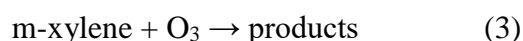
An ozone generator (UVP, LLC Upland, UK) was providing a constant concentration of ozone and an ozone analyzer (O<sub>3</sub> 41M, Environnement S.A) measured its mixing ratio in real time. DMB and m-xylene were constantly flowing in the reactor thanks to two permeation ovens (Pul 200 Calibrage). DMB flow (F1) was set at 109 mL min<sup>-1</sup>. Ozone mixing ratio was kept constant at (3.4 ± 0.3) ppm (i.e., (8.55 ± 0.77) × 10<sup>13</sup> molecules cm<sup>-3</sup>) by changing the exposed surface of the UV light inducing the ozone generation with a constant flow (F3) of 100 mL min<sup>-1</sup>.

#### ***OH radical measurement and concentration calculation:***

The OH radical concentrations were determined using the consumption of a gaseous tracer injected continuously in the reactor. The tracer used was m-xylene (F2, 40 mL min<sup>-1</sup>) because it reacts with OH radical (equation 2) with an accurately known kinetic constant ( $k_2 = (2,2 \pm 0.2) \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> (Atkinson and Aschmann, 1989). This value allowed to observe its degradation during the one-minute residence time of m-xylene in the reactor.



Nevertheless, m-xylene reacts also with ozone according to equation 3 with a rate constant of  $k_3 = 4.10^{-21}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> (Kramp and Paulson, 1998; Papagni et al., 2001).



As a result, the consumption of m-xylene in the reactor can be described according to equation 4.

$$-\frac{d[\text{m-xylene}]}{dt} = k_2 \times [\text{m-xylene}] \times [\text{OH}_{(gas)}] + k_3 \times [\text{m-xylene}] \times [\text{O}_{3(gas)}] \quad (4)$$

According to the experimental conditions used, the reaction between m-xylene and O<sub>3</sub> ( $k_3$ ) is negligible compared to the reaction between m-xylene and OH radical ( $k_2$ ) and equation 4 can be simplified into equation 5:

$$-\frac{d[\text{m-xylene}]}{dt} = k_2 \times [\text{m-xylene}] \times [\text{OH}_{(gas)}] \quad (5)$$

The integration of equation 5 gives the following equation 6:

$$\int_0^t [OH_{(gas)}] \times dt = \ln \left( \frac{[m\text{-xylene}]_0}{[m\text{-xylene}]_t} \right) \times \frac{1}{k_2} \quad (6)$$

Where  $t$  (s) is the residence time of compounds in the gaseous phase in the reactor,  $[m\text{-xylene}]_0$  and  $[m\text{-xylene}]_t$  (molecule  $\text{cm}^{-3}$ ) are the initial and final concentrations of  $m$ -xylene in the reactor,  $k_2$  is the rate constant (equation 2) and  $[OH_{(gas)}]$  is the OH radical concentrations in the reactor during the experiment.

DMB degradation products ( $m/z = 85, 71, 57, 43$ , and  $41$ ) and  $m$ -xylene ( $m/z = 107$ ) (Fig. SI4) concentrations were monitored with a time resolution of 10 seconds using an High-Sensitivity Proton Transfer Reaction Mass Spectrometer (HS-PTR-MS, Ionicon Analytik). A negative shift in the concentration of  $m$ -xylene and a positive shift in DMB degradation products were observed in presence of ozone, corresponding to the loss of  $m$ -xylene due to its consumption by OH radical and the products formed by the ozonolysis of the DMB. *Parameters for HS-PTR-MS analysis* are given in SI.

The atmospheric concentration of OH radicals ranges approximately from  $10^5$  molecule  $\text{cm}^{-3}$  (Hübler et al., 1984) in remote areas to  $10^7$  molecules  $\text{cm}^{-3}$  in heavily polluted areas (Tuazon et al., 1981), during the day as they are formed mainly by photolysis reactions. OH radical concentration in the reactor (average value over the set of experiments:  $(6.61 \pm 0.80) \times 10^7$  molecules  $\text{cm}^{-3}$ ) was set and kept constant prior to experiments. OH radicals concentration was measured for each experiment in order to use its exact value for kinetic constants calculations. Along each experiment, OH radicals concentration remained stable with a variation of the concentration of maximum 4.5% over 6 hours.

### ***Humidity:***

The required humidity level was obtained by mixing a clean and dry air flux with a humid air flux (close to water saturation level, i.e., 85% RH) obtained by bubbling clean dry air into a humidifier containing deionized water. Clean dry air was provided using a zero-air generator (zero air generator ZA-1500, F-DGS). Humid and dry air flow (F4 and F5) were adapted to

reach the relative humidity level wanted in the reactor (0% to 70% RH). Humidity was measured before and after each experiment with a humidity probe (Hydrolog NT, Rotronic, USA, uncertainty 2% RH).

## **2.5 Extraction and pesticides quantification**

During OH radical exposure, 30 mg aliquots of particles were regularly sampled in order to quantify the remaining adsorbed pesticides. Each 30 mg aliquot of particles was 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. Afterward, the extracts were concentrated under a nitrogen flow using a concentration workstation (TurboVap II, Biotage).

Analysis of the obtained solutions was 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) and in SI *Detailed protocol for pesticide extraction and analysis*.

## **2.6 Pseudo-first-order rate constant determination**

Considering that OH radicals were continuously produced in the reactor and that its precursors were used in excess, a pseudo-first order kinetic constant was assumed. In the reactor, pesticides could be degraded by OH radicals, but they could also react with ozone as well as with eventual other oxidative compounds produced in the reactor, and finally, they could be hydrolyzed or desorbed from particles. As a result, the equation leading to the decay of pesticide is the following:

$$\begin{aligned}
& -\frac{d[Pesticide_{ads}]}{dt} = k_{OH(part)}^{II} \times [Pesticide_{ads}] \times [OH_{(gas)}] + k_{des(part)}^I \times [Pesticide_{ads}] + \\
& k_{hydr(part)}^I \times [Pesticide_{ads}] + k_{Y(part)}^{II} \times [Pesticide_{ads}] \times [Y] + k_{O3(part)}^{II} \times \\
& [Pesticide_{ads}] \times [O_3] \quad (7)
\end{aligned}$$

where  $k_{OH(part)}^{II}$ ,  $k_{O3(part)}^{II}$  and  $k_{Y(part)}^{II}$  ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) are respectively the second order rate constants of the pesticide heterogeneous reactions with OH radicals, with ozone and with all the other possible oxidant compounds,  $k_{des(part)}^I$  ( $\text{s}^{-1}$ ) is the first order kinetic desorption rate constant, and  $k_{hydr(part)}^I$  ( $\text{s}^{-1}$ ) is the pseudo-first-order kinetic hydrolysis rate constant.  $k_{O3(part)}^{II}$ ,  $k_{des(part)}^I$  and  $k_{hydr(part)}^I$  were determined experimentally (Mattei et al. 2018) and  $k_{Y(part)}^{II}$  was calculated.

The integration of equation 7 leads to:

$$\begin{aligned}
& \ln \left( \frac{[Pesticide_{ads}]_t}{[Pesticide_{ads}]_0} \right) = -(k_{OH(part)}^{II} \times [OH_{(gas)}] + k_{des(part)}^I + k_{hydr(part)}^I + k_{Y(part)}^{II} \times [Y] + \\
& k_{O3(part)}^{II} \times [O_3]) \times t = -k_{all(part)}^I \times t \quad (8)
\end{aligned}$$

where  $k_{all(part)}^I$  ( $\text{s}^{-1}$ ) is the sum of the pseudo-first-order constants of the heterogeneous reactions with OH radicals and oxidant species as well as the pesticide concentration decay constants induced by hydrolysis and desorption.  $k_{all(part)}^I$  is experimentally determined as the slope of the Napierian logarithm of normalized pesticide concentration's decay versus the exposure time.

Then, the pseudo-first order reaction rate constant  $k_{OH(part)}^I$  is expressed as follows:

$$k_{OH(part)}^I = k_{all(part)}^I - k_{des(part)}^I - k_{hydr(part)}^I - k_{Y(part)}^{II} \times [Y] - k_{O3(part)}^{II} \times [O_3] \quad (9)$$

224  $k_{des(part)}^I$ ,  $k_{hydr(part)}^I$  and  $k_{O3(part)}^{II}$  were determined experimentally (Mattei et al., 2018) while  
 225  $k_{Y(part)}^{II} \times [Y]$  was determined mathematically as the intercept of the slope fitting  $k_{all(part)}^I$  with  
 226  $[OH_{(gas)}]$ .

## 227 **2.7 Second-order rate constant and atmospheric half-lives determination**

228 Second order kinetic constants  $k_{OH(part)}^{II}$  were calculated from the first order kinetics constants  
 229 according to a Langmuir-Rideal kinetic model, as detailed in SI *Second-order rate constant*  
 230 *determination*.

231 The atmospheric pesticide half-lives ( $t_{1/2\ OH(part)}$  in s) resulting from pesticide degradation  
 232 toward OH radicals were calculated for each specific experimental condition according to  
 233 equation 11. For these calculations, OH radical concentration was  $1.5 \times 10^6$  molecule  $cm^{-3}$  and  
 234 the exposure time was 12 hours (Lawrence et al., 2001; Palm et al., 2011; Prinn et al., 2001).

$$235 \quad t_{1/2\ OH(part)} = \frac{\ln 2}{k_{OH(part)}^{II} \times [OH_{(gas)}]} \quad (11)$$

236 Where  $k_{OH(part)}^{II}$  is the second order kinetic constant ( $cm^3$  molecule $^{-1}$  s $^{-1}$ ) and  $[OH_{(gas)}]$  the  
 237 gaseous concentration of OH radicals (molecule  $cm^{-3}$ ).

## 238 **3. Results and discussion**

### 239 **3.1 Heterogeneous degradation by OH radicals**

240 In order to study the heterogeneous degradation by OH radicals of eight pesticides, i.e.,  
 241 cyprodinil, deltamethrin, difenoconazole, fipronil, oxadiazon, pendimethalin, permethrin, and  
 242 tetraconazole, experiments were performed at a relative humidity level between 0% and 70%,  
 243 with pesticides adsorbed on hydrophobic and hydrophilic silica particles. The average OH  
 244 radical concentration was  $(6.61 \pm 0.80) \times 10^7$  molecule  $cm^{-3}$ . All kinetic constants obtained were  
 245 corrected as explained in section 2.6 to subtract the pesticides decay induced by hydrolysis,

desorption, ozonolysis, and by reactivity with possible intermediate species formed into the reactor.

Deltamethrin, permethrin, pendimethalin, and cyprodinil were degraded by OH radicals. Analytical issues concerning cyprodinil are responsible for uncertainties on kinetic constants in average 4 times faster than for deltamethrin, permethrin, and pendimethalin. Therefore, the results are not presented here. Second-order rate constant calculated for deltamethrin, permethrin and pendimethalin ranged from  $(1.93 \pm 0.61) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (obtained for permethrin, hydrophobic silica, 30% RH) to  $(4.08 \pm 0.27) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (obtained for pendimethalin, hydrophilic silica, 0% RH).

### 3.2 Unreactive pesticides

Under our experimental conditions, no degradation was observed for fipronil, difenoconazole, oxadiazon, and tetraconazole ( $k_{OH(part)}^{II} \leq 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , which corresponds to  $t_{1/2 OH(part)} \geq 100$  days) whatever the humidity level or the particle type was. These results are unexpected as these four pesticides are degraded in the gas phase, i.e., half-lives of less than 1 day (according to theoretical calculations from AOPWIN software (Atmospheric Oxidation Program for Microsoft Windows (Meylan and Howard 1993)). Furthermore, according to the usual attack mechanism of OH radicals (i.e., for instance, OH abstraction on the C=C double bond for pyrimidine compounds (Steenken, 1987), and H abstraction on the -NR<sub>2</sub> group which is the most likely mechanism as well as OH addition on the aromatic ring for dinitroaniline compounds (Muñoz et al., 2014)) and to the chemical structure of these pesticides, a chemical degradation should occur (Borrás et al., 2015; George and Abbatt, 2010). However, these experimental results are in agreement with the few studies recently done on these compounds, first, in a previous work done with the same experimental protocol (Socorro et al., 2016a), and second in a study using a different experimental set-up which also demonstrates the non-(or

very low) degradation of difenoconazole by OH radicals when adsorbed on quartz surfaces (this work:  $k_{OH(part)}^{II} \leq 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , literature :  $k_{OH(part)}^{II} = (7.1 \pm 0.8) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Al Rashidi et al., 2011)). Concerning other semi-volatile organic compounds, it was shown that gas phase degradation of polycyclic aromatic hydrocarbons (PAH) might be effective, but the degradation of the same compound can be drastically inhibited when adsorbed on a surface (Esteve et al., 2006). These studies corroborate the fact that a compound can be degraded by OH radicals in the gas phase but have its reactivity drastically slowed down in the heterogeneous phase. As these results cannot be explained by the chemistry it is most probably due to steric hindrance or passivation when those semi-volatile organic compounds are adsorbed on particles.

### 3.3 Comparison with other studies

Table 1 present all kinetic data available in the literature concerning the heterogeneous degradation of pesticides by OH radicals as well as the results of this study.

Table 1: Available data for the heterogeneous degradation of pesticides by OH radicals

Chemical family	Pesticide	Relative Humidity (%)	Temperature (°C)	OH radical concentration (molecule cm <sup>-3</sup> )	Surface	$k_{OH(part)}^{II}$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	$t_{1/2 OH(part)}$ (days) <sup>a</sup>	Reference
Pyrethroid	<b>Deltamethrin</b>	0-70	25	$6.61 \times 10^7$	Hydrophobic / hydrophilic silica	$(5.64 \pm 0.53) \times 10^{-13}$ to $(2.88 \pm 0.27) \times 10^{-12}$	4 to 19	This study
		55		$6.1 \times 10^7$ - $1.45 \times 10^8$	Hydrophobic silica	$(6.9 \pm 0.2) \times 10^{-13}$	33.5	Socorro et al., 2015
	<b>Permethrin</b>	0-70		$6.61 \times 10^7$	Hydrophobic / hydrophilic silica	$\leq 10^{-13}$ to $(2.57 \pm 0.09) \times 10^{-12}$	4 to $\geq 100$	This study
		55		$6.1 \times 10^7$ - $1.45 \times 10^8$	Hydrophobic silica	$(5.5 \pm 0.1) \times 10^{-13}$	42.1	Socorro et al., 2015
Dinitroaniline	<b>Pendimethalin</b>	0-70		$6.61 \times 10^7$	Hydrophobic / hydrophilic silica	$\leq 10^{-13}$ to $(4.08 \pm 0.27) \times 10^{-12}$	3 to $\geq 100$	This study
		55		$6.1 \times 10^7$ - $1.45 \times 10^8$	Hydrophobic silica	$(4.3 \pm 0.3) \times 10^{-13}$	53.8	Socorro et al., 2015
Pyrimidine	<b>Cyprodinil</b>	0-70		$6.61 \times 10^7$	Hydrophobic / hydrophilic silica	$\leq 10^{-13}$ to $(2.50 \pm 0.14) \times 10^{-12}$	4 to $\geq 100$	This study
		55		$6.1 \times 10^7$ - $1.45 \times 10^8$	Hydrophobic silica	$(9.7 \pm 0.2) \times 10^{-13}$	23.9	Socorro et al., 2015
Diazole	<b>Oxadiazon</b>	0-70		$6.61 \times 10^7$	Hydrophobic / hydrophilic silica	$\leq 10^{-13}$	$\geq 100$	This study
		55		$6.1 \times 10^7$ - $1.45 \times 10^8$	Hydrophobic silica	$< (4.3 \pm 0.3) \times 10^{-13}$	$> 53.8$	Socorro et al., 2015
Pyrazole	<b>Fipronil</b>	0-70		$6.61 \times 10^7$	Hydrophobic / hydrophilic silica	$\leq 10^{-13}$	$\geq 100$	This study
		55		$6.1 \times 10^7$ - $1.45 \times 10^8$	Hydrophobic silica	$< (4.3 \pm 0.3) \times 10^{-13}$	$> 53.8$	Socorro et al., 2015
Triazole	<b>Tetraconazole</b>	0-70		$6.61 \times 10^7$	Hydrophobic / hydrophilic silica	$\leq 10^{-13}$	$\geq 100$	This study
		55		$6.1 \times 10^7$ - $1.45 \times 10^8$	Hydrophobic silica	$< (4.3 \pm 0.3) \times 10^{-13}$	$> 53.8$	Socorro et al., 2015
	<b>Difenoconazole</b>	0-70		$6.61 \times 10^7$	Hydrophobic / hydrophilic silica	$\leq 10^{-13}$	$\geq 100$	This study
		55		$6.1 \times 10^7$ - $1.45 \times 10^8$	Hydrophobic silica	$< (4.3 \pm 0.3) \times 10^{-13}$	$> 53.8$	Socorro et al., 2015
		0.7	29	/	quartz	$(7.1 \pm 0.8) \times 10^{-14}$	326	Al Rashidi et al., 2011



Organochloride	Dicofol	/	/	1 x 10 <sup>9</sup>	Hydrophilic silica	2 x 10 <sup>-12</sup>	11.6	Liu et al.,2005
	DDT					5 x 10 <sup>-13</sup>	46	
	Lindane	/	/	/		6 x 10 <sup>-13</sup>	39	Zetsch, 1991
Triazine	Terbuthylazine	42-50	27	5 x 10 <sup>5</sup> - 10 <sup>6</sup>		Hydrophobic silica	(1.1 ± 0.2) x 10 <sup>-11</sup>	2.1
		<1	26	(9.0 ± 4) x 10 <sup>7</sup>	(1.5 ± 0.8) x 10 <sup>-13</sup>		155	Pflieger et al, 2013
	Simazine	25-40	25	10 <sup>5</sup> - 3 x 10 <sup>6</sup>	Hydrophilic silica	1.1 x 10 <sup>-11</sup>	2.1	Palm et al, 1998
Hydroxybenzonitrile	Bromoxynil					≤ 5 x 10 <sup>-13</sup>	≥ 46.3	
Phenylurea	Isoproturon					1.2 x 10 <sup>-11</sup>	1.9	
Pyridine	Pyrifenoх	51	26	10 <sup>5</sup> - 8 x 10 <sup>6</sup>		Quartz	(1.8 ± 0.4) x 10 <sup>-11</sup>	1.3
Sulfonylurea	Primisulfuronmethyl	43-54	/	8 x 10 <sup>7</sup>	6.2 x 10 <sup>-12</sup>		3.7	Palmet al, 2011
Morpholine	Dimethomorph	0.7	29	/	(1.7 ± 1.2) x 10 <sup>-14</sup> to (2.0 ± 1.2) x 10 <sup>-14</sup>		> 1000	Al Rashidi et al, 2014
Dicarboximid	Folpet				(1.6 ± 0.9) x 10 <sup>-13</sup>	145		
Organo-phosphate	Chlorpyriphos	/	25	/	leaves	(5.8 ± 4.0) x 10 <sup>-12</sup>	4	El Masri et al., 2014
		70	/	1.8 x 10 <sup>8</sup>		6 x 10 <sup>-12</sup>	4	Lester et al., 2017
Pyrimidinol	Pyrimidinol	/	25	/	Quartz	(1.1 ± 0.9) x 10 <sup>-12</sup>	21	Bouya et al., 2015

<sup>a</sup>  $t_{1/2 \text{ OH(part)}}$  calculated for OH radical concentration used for the calculation was  $1.5 \times 10^6 \text{ molecule cm}^{-3}$  and the average exposure time was 12 hours

Table 1 shows that available kinetic constants of pesticides in the heterogeneous phase toward OH radicals vary from  $10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (i.e., half-life greater than 1000 days) to  $10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (i.e., half-life of 1.3 days) with the majority of them being around  $10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Values obtained in our study for pesticides degraded by OH radicals are of the order of between  $10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and  $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  which is in accordance with kinetic constants available in the literature calculated for other pesticides of the same or different chemical families on hydrophobic silica (Pflieger et al., 2013), hydrophilic silica (Liu et al., 2005; Palm et al., 2011; Zetzsch, 1991), quartz surfaces (Bouya et al., 2015; Masri et al., 2014), and leaves (Lester et al., 2017). However, our values are of one to two orders of magnitude smaller than values determined by one research team for pesticides adsorbed on silicas (Palm et al., 1997, 1998, 1999).

Generally, great agreement is observed between results obtained with the different experimental set-ups. To our knowledge, only one study using a different set-up shares the same pesticide (difenoconazole) with the present work (Al Rashidi et al., 2011). Regarding this pesticide, results are in accordance, showing a very low reactivity toward OH radicals, even though they studied its degradation on quartz surfaces and in a different experimental set-up. In the same way, similar degradation rates were obtained for chlorpyrifos adsorbed on quartz surface (Masri et al., 2014) and on leaves (Lester et al., 2017). However, terbuthylazine showed different degradation rates according to the surface (i.e., hydrophilic or hydrophobic silica). Kinetic constants were two orders of magnitude higher on hydrophobic silica (Pflieger et al., 2013) than on hydrophilic silica (Palm et al., 1997). The difference could be attributed to mass transport and shielding effect induced by different experimental techniques and conditions (Socorro et al., 2017).

It seems that experimental set-up conditions used can impact the absolute kinetic constants value measured. Given the limited amount of studies concerning OH radical degradation in the

literature, it is complicated to assess which system is the most suitable for this type of work. Nevertheless, comparing values using a given experimental set-up, as it is the case in this study, allows determining which environmental factors are likely to influence the kinetic constants.

### 3.4 Influence of the particle type

Two model particles were chosen to investigate the influence of the particle type on the heterogeneous reactivity of pesticides: hydrophobic and hydrophilic silicas. These two kinds of particles are similar in composition, specific surface area, and size. However, their surface properties are different due to the presence of different surface groups (siloxane vs silanol). Hydrophilic silica is prone to adsorb easily and rapidly water on its surface whereas hydrophobic silica is not.

Fig. 2 presents the second order degradation rate constants of pendimethalin, deltamethrin, and permethrin in absence of water for the two types of particles.

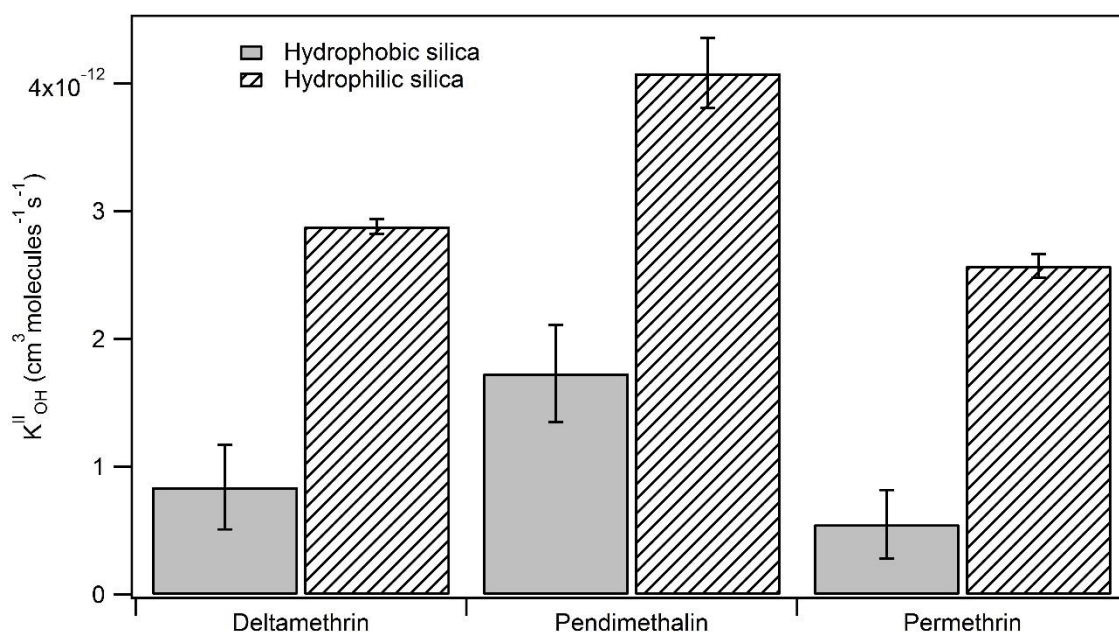


Fig. 2: second-order kinetic constants for deltamethrin, permethrin, and pendimethalin degraded by OH radicals at 0% RH

Deltamethrin, pendimethalin, and permethrin were all degraded on both particle type in absence of water. However, they were degraded 3.3, 2.4, and 4.7 times faster on hydrophilic silica than on hydrophobic silica, respectively (Fig. 2).

The faster degradation on hydrophilic silica than on hydrophobic silica for deltamethrin, pendimethalin, and permethrin suggests an influence of the particle surface properties on the degradation kinetics of the pesticides. Such an observation was already done for the degradation by OH radicals of (PAH) adsorbed on graphite and diesel particles (Esteve et al., 2004, 2006). Authors attributed this influence to the variability of PAH accessibility for OH radicals. This phenomenon is not specific to reactivities with OH radicals since, in a previous work focused on the study of the heterogeneous ozonolysis of cyprodinil, deltamethrin, permethrin, and pendimethalin, a faster degradation was observed when these molecules were adsorbed on hydrophilic silica particles rather than on hydrophobic particles as well (Mattei et al., 2018).

### **3.5 Influence of humidity**

Experiments were conducted at 0% RH, 30% RH, 55% RH, and 70% RH both on hydrophobic and hydrophilic silicas to study the influence of humidity on the degradation of pesticides by OH radicals. 0% RH is a humidity level which does not exist in the atmosphere (relative humidity in the atmosphere commonly ranges from 30% RH to 100% RH), however, several studies were conducted without or almost without water (Al Rashidi et al., 2011, 2014; Pflieger et al., 2013). Experiments in absence of water help to understand the role of water in the degradation processes of pesticides. 55% RH and 70% RH are realistic levels, often reached in the atmosphere. A previous work (Goodman et al., 2001) have shown that the number of water layers on silica particles (hydrophilicity not mentioned) is approximately one monolayer at 20% RH, two to three adsorbed water layers at 50% RH, and three to four at 85% RH. 70% RH, the highest level tested is, therefore, a realistic level where the aerosol is close to the state of a liquid droplet.

Fig.3 a, and b present the degradation rates of deltamethrin, permethrin, and pendimethalin at different relative humidity and adsorbed on the two different particles types.

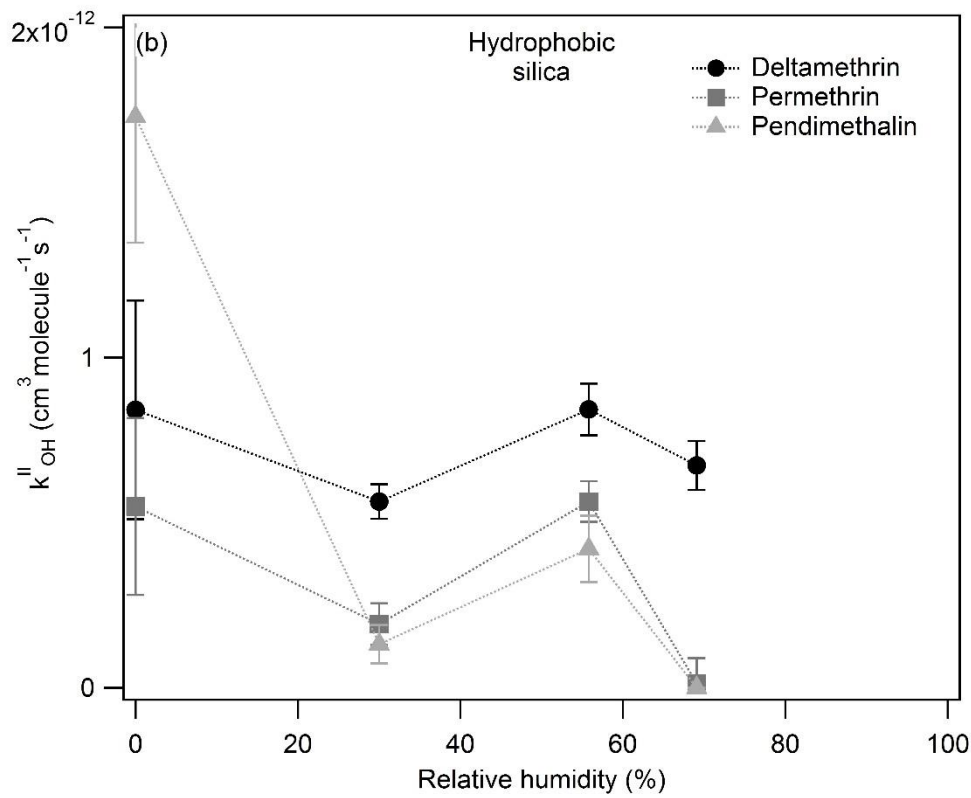
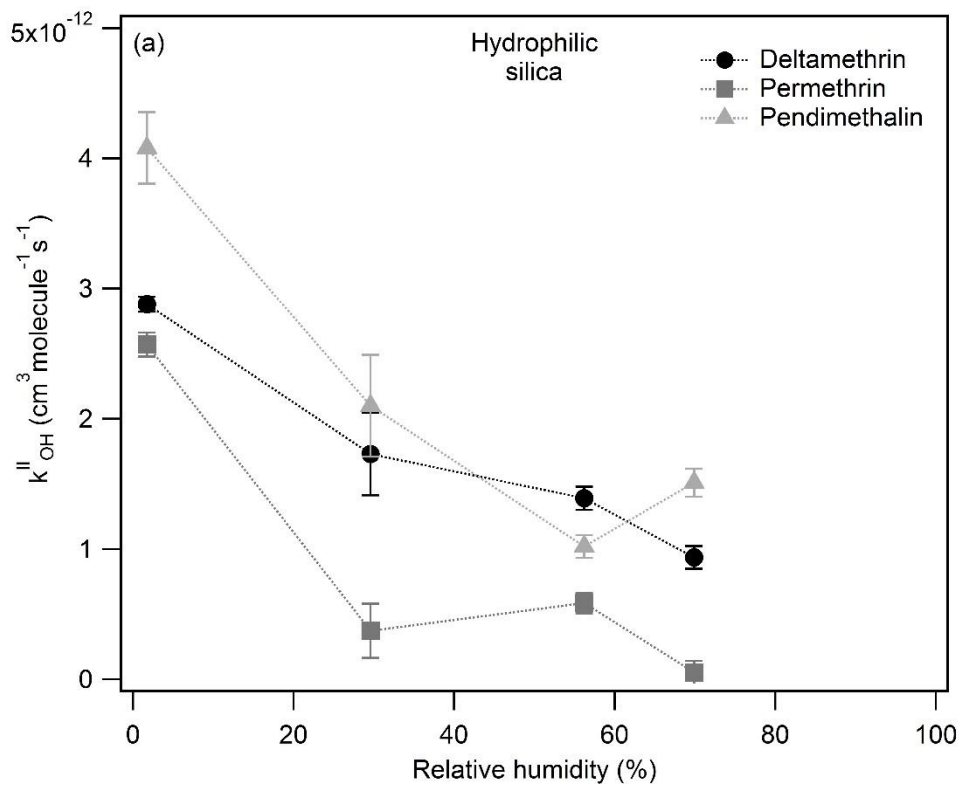


Fig. 3 a, and b: Second-order rate constants for the OH degradation of pesticides adsorbed on hydrophilic silica and hydrophobic silica

When adsorbed on hydrophilic silica, the degradation rate of pesticides by OH radicals ranged from  $\leq 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (unreactive) (permethrin, 70% RH) to  $(4.08 \pm 0.27) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (pendimethalin, 0% RH). Deltamethrin, permethrin, and pendimethalin appeared to be degraded faster when relative humidity was minimized. Deltamethrin and permethrin were degraded respectively 3.1 and 48 times faster in absence of water compared to 70% RH. Pendimethalin was degraded 2.7 faster at 0% RH than at 55% RH but its degradation rate was unexpectedly enhanced by the increase of relative humidity between 55% RH and 70% RH. On hydrophilic silica, relative humidity has, therefore, a strong impact on the degradation rates of pesticides sensitive to OH radical degradation.

Concerning the degradation of pesticides adsorbed on hydrophobic silica, the kinetic constants ranged from  $\leq 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (unreactive) (permethrin and pendimethalin, 70% RH) to  $(1.73 \pm 0.38) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (pendimethalin, 0% RH). Deltamethrin degradation rate was, given the large uncertainties, not influenced by the relative humidity level. Permethrin degradation rates were independent of the relative humidity level between 0% RH and 55% RH but at 70% RH, no degradation was observed. In contrast, pendimethalin reactivity was slowed down by an increase of relative humidity, its degradation rate was 13.1 times faster at 0% RH than at 30% RH and it was close to the detection limit ( $10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) at 70% RH.

Relative humidity appeared to have an influence on the heterogeneous degradation of pesticides under study by OH radicals when adsorbed on hydrophobic silica or hydrophilic silica; the increase of water content induced a decrease in the degradation rates. However, the sensitivity of each pesticide to the influence of relative humidity is different from a compound to another.

The increase of water content on the particle surface could play a shielding effect toward OH radicals. Indeed, in the presence of water, the OH radicals must diffuse through the water layers

to access the pesticide, process which is slower in water than in air. This could be responsible for the slowing down effect at high RH levels when the state of the water droplet is close to being reached. Hydrophilic silica is more prone to adsorb water on its surface than hydrophobic silica for a given relative humidity level. Thereby it is logical that the influence of increasing relative humidity level on the kinetic constants is discernable at a lower relative humidity level on hydrophilic silica than on hydrophobic silica. To our knowledge, there is no study mentioning an influence of humidity on pesticide degradation by OH radicals in the heterogeneous phase. Nevertheless, slower degradation at higher moisture level was already observed in many studies in the case of the heterogeneous degradation of organic compounds by ozone (Kaiser et al., 2011; Mattei et al., 2018; Pöschl et al., 2001), this was often attributed to a competitive adsorption between ozone and water on the surface. Because of the very high OH reactivity, this hypothesis done for ozone, cannot be transposed directly to this work. However, it is possible that the presence of water on the particles surface implies harder pesticide access for OH radicals due to steric constraints or by protecting pesticides under water layers, leading to a competition between OH radicals and water to access the pesticides.

Water could also influence the kinetics additionally if its presence is necessary in the degradation mechanism of the pesticide, in that case, degradation mechanism would take different pathways depending on the presence or absence of water, as it could be the case for pendimethalin which is the most sensitive compound to relative humidity when adsorbed on both particle types.

### **3.6 Influence of pesticide nature**

There is a very large number of pesticides used nowadays (352 in France in 2018 (European Commission, 2018)), they are very diverse in chemical structure and belong to many chemical families. Among the 8 pesticides used in this work, six chemical families are represented: diazole (oxadiazon), dinitroaniline (pendimethalin), pyrazole (fipronil), pyrethroid (permethrin,

deltamethrin), pyrimidine (cyprodinil), and triazole (difenoconazole, tetraconazole). Depending on the pesticide, significant differences are observed in this work on the second-order kinetic constants while the same experimental conditions were used. This was previously observed in other studies concerning heterogeneous degradation of pesticides by OH radicals (Al Rashidi et al., 2014; Masri et al., 2014; Palm et al., 1997).

The chemical structure of pesticides seems to have a significant influence on their reactivity since the two pesticides of the pyrethroid chemical family (deltamethrin and permethrin) were degraded by OH radicals whereas the two pesticides of the triazole chemical family (difenoconazole and tetraconazole) were not (or very slowly) degraded. Indeed, the triazole reactivity toward OH radicals in the gas phase (i.e., an OH-addition onto carbons atoms of the triazole cycle) was considered as a very slow reaction at ambient temperature (Derbel et al., 2018), which might explain our results. The number of pesticides studied in each of these two families is too limited to come to a conclusion, nevertheless, a similar behavior might be extended to other compounds of these families of pesticides.

Deltamethrin and permethrin are both of the pyrethroid family, but reactivity of deltamethrin was influenced by water only when adsorbed on hydrophilic silica, while reactivity of permethrin was influenced by water when absorbed on both particle type. It was previously shown that water plays a role in the heterogeneous degradation mechanism of deltamethrin and permethrin with ozone as well (Socorro et al., 2016b). These results show that the way humidity influences the degradation rate of a pesticide can then hardly be extended to other pesticides even within the same chemical family.

### **3.7 Atmospheric implications**

Fig. 4 shows the extent of particulate half-lives determined in this study regarding OH radicals and the half-lives calculated with the AOPWIN software (Meylan and Howard, 1993) concerning gas-phase OH radical degradation. OH radical concentration used for the calculation



was  $1.5 \times 10^6$  molecule  $\text{cm}^{-3}$  and the average exposure time was 12 hours (Palm et al., 2011; Lawrence et al., 2001; Prinn, 2001). which correspond to OH radical concentration measured in medium polluted areas (Hard et al., 1984; Hübler et al., 1984). Half-lives corresponding to the heterogeneous degradation of the pesticides by OH radicals were calculated using the experimental second order kinetic constants obtained in this study. Finally, half-lives for pesticides in the gaseous phase and particle phase together were calculated using theoretical partitioning of the pesticides between the two phases based on the Junge-Pankow model.

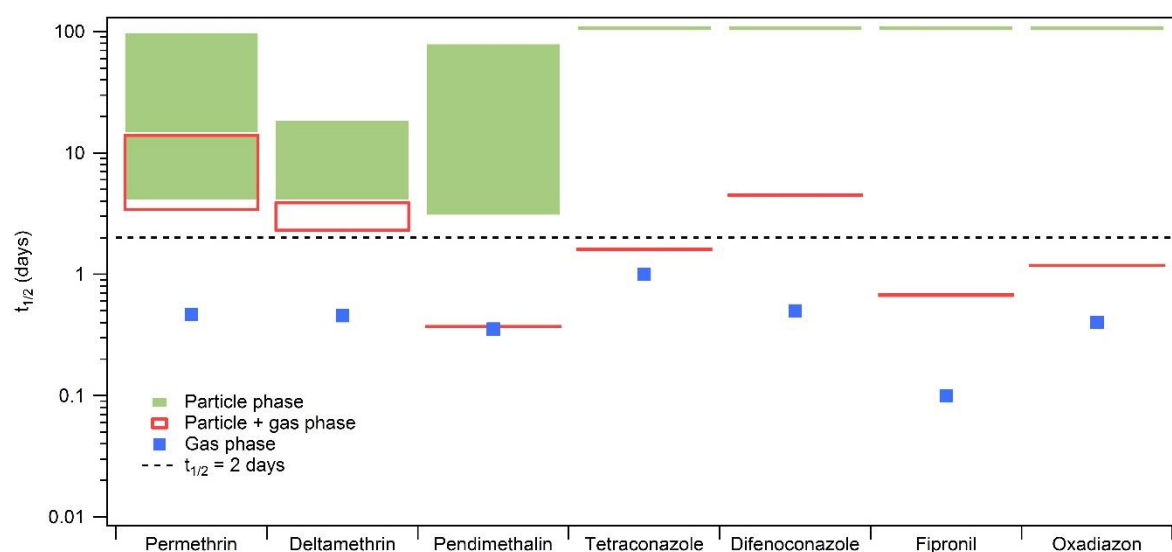


Fig. 4: Half-lives of pesticides in the gas phase, in the particle phase, and in both phases combined and according to their theoretical partitioning between gas and particle phases regarding OH radical reactivity (for an OH radical concentration of  $1.5 \times 10^6$  molecule  $\text{cm}^{-3}$  and an exposure time of 12h)

Heterogeneous half-lives calculated for deltamethrin, pendimethalin, and permethrin ranged from 3 days to more than 100 days. Half-life values were distributed widely, as can be seen in Fig. 4, for permethrin, deltamethrin, and pendimethalin tested in different conditions with OH radicals. This highlight the fact that degradation conditions affect the heterogeneous lifetime of

pesticide in the atmosphere and should, therefore, be chosen carefully when making experiments to determine realistic atmospheric half-lives values.

The software AOPWIN allows the calculation kinetic constants for the degradation of organic molecules by OH radicals in the gas phase. AOPWIN calculations were already proven to give results similar to the experimental ones in the case of the degradation in the gas phase of metolachlor (Chao et al., 2018), as well as of prosulfocarb and S-ethyl N,N244 dipropylthiocarbamate (Munoz et al., 2018), even though disagreement between theory and experimental results were highlighted concerning organonitrogen compounds (Borduas et al., 2015). AOPWIN calculations indicate that in the gas phase the eight pesticides under study should react with OH radicals, with associated half-lives varying from 0.1 days (cyprodinil) to 2.1 days (tetraconazole). Concerning pesticides reacting with OH radicals in the particle phase, half-lives calculated are all superior to 3 days. Also, degradation of tetraconazole, difenoconazole, oxadiazon, and fipronil, which is effective in the gas phase, was hindered in the particle phase. Concerning pesticide under study, heterogeneous degradation by OH radicals is, therefore, slower than homogeneous degradation. Differences in reactivity of pesticides between gas and particle phases were already highlighted in previous studies (El Masri et al., 2014; El Rashidi et al., 2014; Lester et al., 2017; Pflieger et al., 2013; Socorro et al., 2016).

The theoretical partitioning of pesticides between the gas phase and the particle phase allows calculation of half-lives regarding OH radicals in both phases combined. For pesticides present mainly in the gas phase, combined half-lives are close to those concerning the gas phase only, as for instance for pendimethalin and tetraconazole. For other pesticides, taking into account the heterogeneous degradation in the calculation of combined half-lives induces significant differences on the results. For deltamethrin and permethrin, the combined half-lives are therefore widely distributed (2.2 days to 4 days and 3.3 days to 14.4 days, respectively) and are dependent on the conditions (relative humidity and particle type).

Atmospheric half-lives of pesticides help to understand their fate in the atmosphere, for instance, with half-lives of several dozens of days, they might be able to be transported at a global scale, possibly impacting human health and the environment far away from their application location. However, significant half-lives will in fact not be observed in the atmosphere as it is commonly accepted that particles have an atmospheric lifetime of approximately 10 days.

According to the Stockholm convention (UNEP, 2001), the atmospheric half-life in the gas phase is the criteria used to determine if a compound is a persistent organic pollutant ( $t_{1/2} > 2$  days). Therefore, the good determination of atmospheric degradation rates and half-lives is crucial for regulatory purposes. For all pesticides under study half-lives calculated regarding OH radicals in the particle phase only, are all above 2 days and half-lives regarding the gas phase only are all under 2 days. However, taking in account both the particle phase and gas phase, permethrin, deltamethrin, and difenoconazole have halves-lives superior to 2 days regarding OH radicals (2.2 days to 4 days, 3.3 days to 14.4 days, and 4.4 days to 4.5 days, respectively). They should, therefore, be considered as persistent organic pollutants regarding this oxidant, and heterogeneous degradation is thus important to take into account for determining pesticides atmospheric half-lives.

## Conclusion

Heterogeneous degradation of pesticides by OH radicals was investigated, with various relative humidity level and particle type. Cyprodinil, deltamethrin, permethrin, and pendimethalin were reactive with OH radicals, with degradation rates consistent with the literature. OH radical degradation kinetics were dependent on relative humidity, particle surface type, and chemical nature of the adsorbed pesticides. Degradation rates were up to 5 times faster on hydrophilic silica than on hydrophobic silica, suggesting an influence of the surface properties on the

kinetics. Generally, an increase of relative humidity induced a decrease in the degradation kinetics, with diminution factors up to a few dozen times. The influence of the water content might be due mainly to the formation of a water protection layer on the surface lowering the accessibility for OH radicals. These findings imply that relative humidity and particle type must be considered to determine kinetic rate constants and that studies carried out in absence of water cannot be considered as representative of the atmospheric conditions. Also, a significant difference in half-lives values regarding OH radical with only the gas phase (0.1 days to 2.1 days) or the gas phase and the particle phase together (2.2 days to > 100 days) was found. This shows that the heterogeneous degradation should be taken into account when calculating half-lives for regulatory purposes.

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