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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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1 **Abstract**

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

17 **Keywords**

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

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23 **1. Introduction**

24 Pesticides are of great interest for both the scientific community and the general public due to
25 their worldwide uses and potential adverse health or environmental impacts (Carvalho, 2017;
26 Inserm, 2013). They are present in the atmosphere in concentration levels from some picogram
27 per cubic meter (pg m^{-3}) to several nanograms per cubic meter (ng m^{-3}) (Coscollà et al., 2013,
28 2014; Désert et al., 2018; Estellano et al., 2015; Lester et al., 2017; Zivan et al., 2016, 2017).
29 Most of the currently used pesticides are semi-volatile organic compounds (SVOC),
30 consequently, they are distributed between the gaseous and particulate phases. In the
31 atmosphere, they can undergo direct photolysis and can react with atmospheric oxidants, whose
32 main representatives are hydroxyl radicals (OH), ozone (O_3), and nitrate radicals (NO_3). On the
33 first hand their gas-phase reactivity has been extensively studied (Borrás et al., 2015; Muñoz et
34 al., 2014; Vera et al., 2015) and numerous kinetic data, especially for the reactivity with OH
35 radicals, is available thanks to modeling (Bahm and Khalil, 2004). On the other hand, very few
36 studies were done on particulate phase reactivity. Moreover, the available heterogeneous
37 degradation kinetics data are subject to large uncertainties because of experimental difficulties
38 to study heterogeneous reactivity and to the numerous atmospheric physicochemical parameters
39 which could influence them (relative humidity (RH), particles hygroscopicity, particle chemical
40 composition...).

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

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

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

68 **2. Material and Methods**

69 **2.1 Chemicals**

70 Analytical standards (PESTANAL®, analytical standard) of the eight pesticides under study
71 (cyprodinil (purity 99.8%), deltamethrin (99.7%), difenoconazole (97.0%), fipronil (97.5%),
72 oxadiazon (99.9%), pendimethalin (98.8%), permethrin (98.3%), and tetraconazole (99.0%)) as

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

77 **2.2 Particles**

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

81 *Chemical composition:* Hydrophobic and hydrophilic silicas contain mainly SiO₂ (> 99.8 wt%).
82 Surfaces of hydrophobic and hydrophilic silica particles are mainly covered by siloxanes and
83 silanols groups, respectively. Siloxane groups are chemically inert and hydrophobic whereas
84 silanol groups have a hydrophilic nature (i.e., readily mix with water). It was shown that 10%
85 to 30% of atmospheric particles are composed of quartz or silica (Finlayson-Pitts and Pitts,
86 2009; Seinfeld and Pandis, 1998), as a result, our particles are good proxies to simulate the
87 chemical composition of crustal aerosols.

88 *Particle size:* Very few studies were done on the particle size distribution of pesticides in
89 ambient air. However, the available results showed that most of the pesticides (40% to 80%)
90 are accumulated in the fine (0.1-1 μm) particle size fraction, while only a small part is adsorbed
91 on the ultrafine (0.03-0.1 μm) and coarse (1-10 μm) size ranges. On the other hand, no
92 pesticides were detected in the size fraction > 10 μm (Coscollà et al., 2013, 2014; Xu et al.,
93 2011). In the present study, the individual mean size of hydrophobic and hydrophilic silica
94 particles range from 5 nm to 50 nm (Evonik, 2015) (Fig. SI2-SI3) which is in agreement with
95 the aerosol size observed in the experimental field measurements. However, particles can
96 agglomerate to reach sizes ranging between 5 μm and 25 μm (Fig. SI2-SI3).

97 *Specific surface area (SSA; BET method)*: Hydrophobic and hydrophilic silica particles have a
98 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).

99 **2.3 Particle coating**

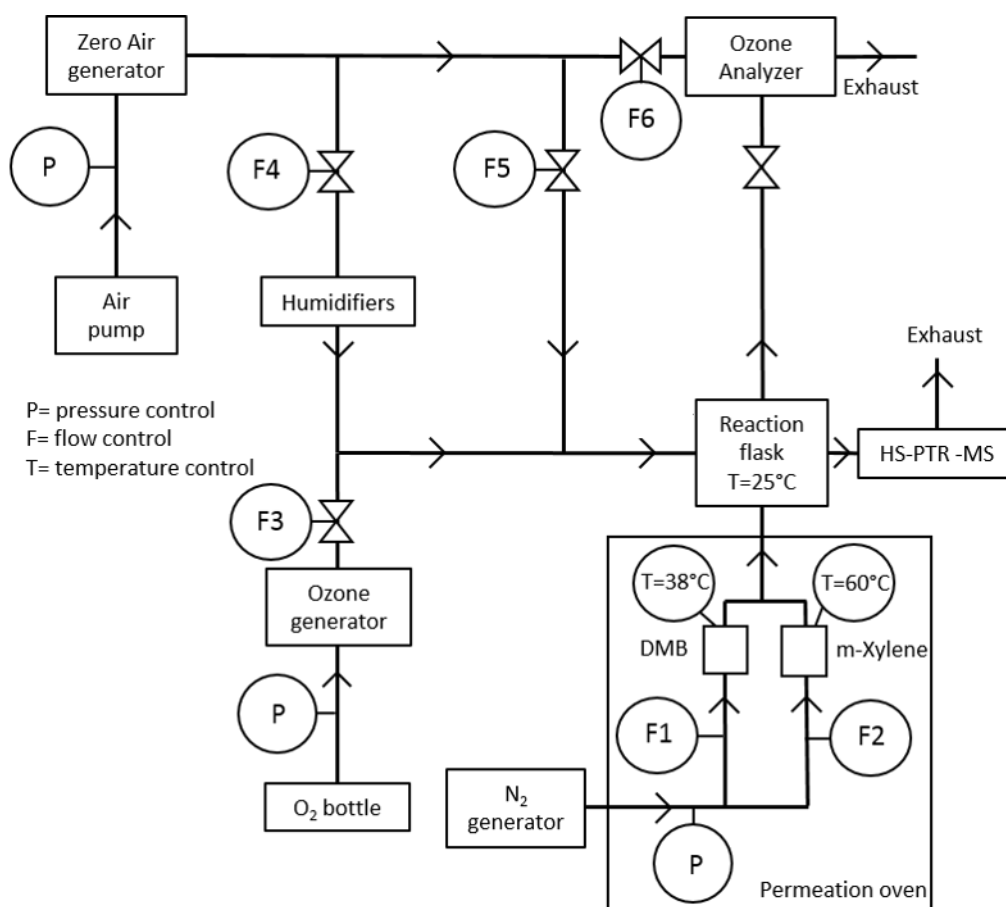
100 Hydrophobic and hydrophilic silicas were independently coated with pesticides according to a
101 liquid/solid adsorption process. In an amber Pyrex flask of 500 cm^3 , 600 mg of particles were
102 mixed with 6 mL of a solution containing the 8 pesticides under study each at a concentration
103 of 20 mg L^{-1} (pesticide solution in dichloromethane for HPLC, $\geq 99.8\%$, Sigma-Aldrich). The
104 load of pesticides on silica particles was about 0.02% by weight. After a 5-min ultrasound
105 treatment, dichloromethane was evaporated using a rotary evaporator (Rotavapor R-114,
106 Büchi) at $40 \text{ }^\circ\text{C}$ and 850 mbar. This process allows a reproducible and realistic coating of the
107 pesticides on the particle's surface (Socorro et al., 2015). Assuming a uniform particle surface
108 coverage for the pesticide molecules and a spherical geometry for particles, the percentage of
109 the particle surface coated with individual pesticide was between 0.3% and 0.5% of a monolayer
110 for hydrophobic and hydrophilic silicas respectively (*SI Silica particles coating*). For the eight
111 pesticides, the total coated particle surface was 2.8% and 2.9% for hydrophobic silica and
112 hydrophilic silica respectively, which is much less than a monolayer.

113 **2.4 Exposition to OH radicals**

114 *Experimental set-up:*

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

121 during an experiment, of a duration of 6 hours. The total flow passing the reactor was 500 mL
 122 min⁻¹ to ensure a total renewal of the gases in the reactor every minute.

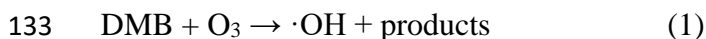


123

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

125 ***OH radical generation:***

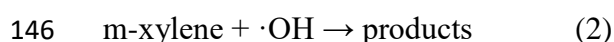
126 OH radicals have an atmospheric lifetime inferior to one second (Schlosser et al., 2009)
 127 consequently, they need to be generated directly into the reactor. They were generated through
 128 the ozonolysis of an alkene, the 2,3-dimethyl-2-butene (DMB), this method is known as the
 129 “dark OH radical generation” (Lambe et al., 2007; Le Person et al., 2007; Pflieger et al., 2013;
 130 Segal-Rosenheimer et al., 2011). DMB reacts with ozone to give OH radical according to
 131 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
 132 Atkinson, 1992):



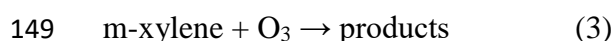
134 An ozone generator (UVP, LLC Upland, UK) was providing a constant concentration of ozone
 135 and an ozone analyzer (O₃ 41M, Environnement S.A) measured its mixing ratio in real time.
 136 DMB and m-xylene were constantly flowing in the reactor thanks to two permeation ovens (Pul
 137 200 Calibrage). DMB flow (F1) was set at 109 mL min⁻¹. Ozone mixing ratio was kept constant
 138 at (3.4 ± 0.3) ppm (i.e., (8.55 ± 0.77) × 10¹³ molecules cm⁻³) by changing the exposed surface
 139 of the UV light inducing the ozone generation with a constant flow (F3) of 100 mL min⁻¹.

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

141 The OH radical concentrations were determined using the consumption of a gaseous tracer
 142 injected continuously in the reactor. The tracer used was m-xylene (F2, 40 mL min⁻¹) because
 143 it reacts with OH radical (equation 2) with an accurately known kinetic constant ($k_2 = (2,2 \pm$
 144 $0.2) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson and Aschmann, 1989). This value allowed to observe
 145 its degradation during the one-minute residence time of m-xylene in the reactor.



147 Nevertheless, m-xylene reacts also with ozone according to equation 3 with a rate constant of
 148 $k_3 = 4.10^{-21} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Kramp and Paulson, 1998; Papagni et al., 2001).



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

152
$$-\frac{d[\text{m-xylene}]}{dt} = k_2 \times [\text{m-xylene}] \times [\text{OH}_{(gas)}] + k_3 \times [\text{m-xylene}] \times [\text{O}_{3(gas)}] \quad (4)$$

153 According to the experimental conditions used, the reaction between m-xylene and O₃ (k₃) is
 154 negligible compared to the reaction between m-xylene and OH radical (k₂) and equation 4 can
 155 be simplified into equation 5:

156
$$-\frac{d[\text{m-xylene}]}{dt} = k_2 \times [\text{m-xylene}] \times [\text{OH}_{(gas)}] \quad (5)$$

157 The integration of equation 5 gives the following equation 6:

158
$$\int_0^t [OH_{(gas)}] \times dt = \ln \left(\frac{[m\text{-xylene}]_0}{[m\text{-xylene}]_t} \right) \times \frac{1}{k_2} \quad (6)$$

159 Where t (s) is the residence time of compounds in the gaseous phase in the reactor, [m-xylene]₀
160 and [m-xylene]_t (molecule cm⁻³) are the initial and final concentrations of m-xylene in the
161 reactor, k₂ is the rate constant (equation 2) and [OH_(gas)] is the OH radical concentrations in the
162 reactor during the experiment.

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

170 The atmospheric concentration of OH radicals ranges approximately from 10⁵ molecule cm⁻³
171 (Hübler et al., 1984) in remote areas to 10⁷ molecules cm⁻³ in heavily polluted areas (Tuazon et
172 al., 1981), during the day as they are formed mainly by photolysis reactions. OH radical
173 concentration in the reactor (average value over the set of experiments: (6.61 ± 0.80) x 10⁷
174 molecules cm⁻³) was set and kept constant prior to experiments. OH radicals concentration was
175 measured for each experiment in order to use its exact value for kinetic constants calculations.
176 Along each experiment, OH radicals concentration remained stable with a variation of the
177 concentration of maximum 4.5% over 6 hours.

178 ***Humidity:***

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

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

186 **2.5 Extraction and pesticides quantification**

187 During OH radical exposure, 30 mg aliquots of particles were regularly sampled in order to
188 quantify the remaining adsorbed pesticides. Each 30 mg aliquot of particles was introduced in
189 a 33 mL stainless steel cell with an internal standard solution (Triphenyl phosphate, 99.9%,
190 Sigma-Aldrich) and pesticides were extracted by accelerated solvent extraction (ASE 350,
191 Dionex) with dichloromethane. Afterward, the extracts were concentrated under a nitrogen flow
192 using a concentration workstation (TurboVap II, Biotage).

193 Analysis of the obtained solutions was realized using gas chromatography coupled to tandem
194 mass spectrometry (GC/MS-MS), with a Trace GC Ultra (Thermo Scientific) coupled to a TSQ
195 Quantum™ Triple Quadrupole (Thermo Scientific) using electron impact ionization (70 eV).
196 More details about ASE extraction, concentration, and GC/MS-MS analysis are available in
197 Socorro et al. (2015) and in *SI Detailed protocol for pesticide extraction and analysis*.

198 **2.6 Pseudo-first-order rate constant determination**

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

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

208 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
209 constants of the pesticide heterogeneous reactions with OH radicals, with ozone and with all
210 the other possible oxidant compounds, $k_{des(part)}^I$ (s^{-1}) is the first order kinetic desorption rate
211 constant, and $k_{hydr(part)}^I$ (s^{-1}) is the pseudo-first-order kinetic hydrolysis rate constant. $k_{O3(part)}^{II}$,
212 $k_{des(part)}^I$ and $k_{hydr(part)}^I$ were determined experimentally (Mattei et al. 2018) and $k_{Y(part)}^{II}$ was
213 calculated.

214 The integration of equation 7 leads to:

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

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

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

$$223 \quad k_{OH(part)}^I = k_{all(part)}^I - k_{des(part)}^I - k_{hydr(part)}^I - k_{Y(part)}^{II} \times [Y] - k_{O3(part)}^{II} \times [O_3] \quad (9)$$

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 1.5×10^6 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,

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

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

255 **3.2 Unreactive pesticides**

256 Under our experimental conditions, no degradation was observed for fipronil, difenoconazole,
257 oxadiazon, and tetraconazole ($k_{OH(part)}^{II} \leq 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, which corresponds
258 to $t_{1/2 OH(part)} \geq 100$ days) whatever the humidity level or the particle type was. These results are
259 unexpected as these four pesticides are degraded in the gas phase, i.e., half-lives of less than 1
260 day (according to theoretical calculations from AOPWIN software (Atmospheric Oxidation
261 Program for Microsoft Windows (Meylan and Howard 1993)). Furthermore, according to the
262 usual attack mechanism of OH radicals (i.e., for instance, OH abstraction on the C=C double
263 bound for pyrimidine compounds (Steenken, 1987), and H abstraction on the -NR₂ group which
264 is the most likely mechanism as well as OH addition on the aromatic ring for dinitroaniline
265 compounds (Muñoz et al., 2014)) and to the chemical structure of these pesticides, a chemical
266 degradation should occur (Borrás et al., 2015; George and Abbatt, 2010). However, these
267 experimental results are in agreement with the few studies recently done on these compounds,
268 first, in a previous work done with the same experimental protocol (Socorro et al., 2016a), and
269 second in a study using a different experimental set-up which also demonstrates the non-(or

270 very low) degradation of difenoconazole by OH radicals when adsorbed on quartz surfaces (this
271 work: $k_{OH(part)}^{II} \leq 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, literature : $k_{OH(part)}^{II} = (7.1 \pm 0.8) \times 10^{-14} \text{ cm}^3$
272 $\text{molecule}^{-1} \text{ s}^{-1}$ (Al Rashidi et al., 2011)). Concerning other semi-volatile organic compounds, it
273 was shown that gas phase degradation of polycyclic aromatic hydrocarbons (PAH) might be
274 effective, but the degradation of the same compound can be drastically inhibited when adsorbed
275 on a surface (Esteve et al., 2006). These studies corroborate the fact that a compound can be
276 degraded by OH radicals in the gas phase but have its reactivity drastically slowed down in the
277 heterogeneous phase. As these results cannot be explained by the chemistry it is most probably
278 due to steric hindrance or passivation when those semi-volatile organic compounds are
279 adsorbed on particles.

280 **3.3 Comparison with other studies**

281 Table 1 present all kinetic data available in the literature concerning the heterogeneous
282 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 ⁻³)	Surface	$k_{OH(part)}^{II}$ (cm ³ molecule ⁻¹ s ⁻¹)	$t_{1/2}$ OH(part) (days) ^a	Reference
Pyrethroid	Deltamethrin	0-70	25	6.61×10^7	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		6.1×10^7 - 1.45×10^8	Hydrophobic silica	$(6.9 \pm 0.2) \times 10^{-13}$	33.5	Socorro et al., 2015
	Permethrin	0-70		6.61×10^7	Hydrophobic / hydrophilic silica	$\leq 10^{-13}$ to $(2.57 \pm 0.09) \times 10^{-12}$	4 to ≥ 100	This study
		55		6.1×10^7 - 1.45×10^8	Hydrophobic silica	$(5.5 \pm 0.1) \times 10^{-13}$	42.1	Socorro et al., 2015
Dinitroaniline	Pendimethalin	0-70		6.61×10^7	Hydrophobic / hydrophilic silica	$\leq 10^{-13}$ to $(4.08 \pm 0.27) \times 10^{-12}$	3 to ≥ 100	This study
		55		6.1×10^7 - 1.45×10^8	Hydrophobic silica	$(4.3 \pm 0.3) \times 10^{-13}$	53.8	Socorro et al., 2015
Pyrimidine	Cyprodinil	0-70		6.61×10^7	Hydrophobic / hydrophilic silica	$\leq 10^{-13}$ to $(2.50 \pm 0.14) \times 10^{-12}$	4 to ≥ 100	This study
		55		6.1×10^7 - 1.45×10^8	Hydrophobic silica	$(9.7 \pm 0.2) \times 10^{-13}$	23.9	Socorro et al., 2015
Diazole	Oxadiazon	0-70		6.61×10^7	Hydrophobic / hydrophilic silica	$\leq 10^{-13}$	≥ 100	This study
		55		6.1×10^7 - 1.45×10^8	Hydrophobic silica	$< (4.3 \pm 0.3) \times 10^{-13}$	> 53.8	Socorro et al., 2015
Pyrazole	Fipronil	0-70		6.61×10^7	Hydrophobic / hydrophilic silica	$\leq 10^{-13}$	≥ 100	This study
		55		6.1×10^7 - 1.45×10^8	Hydrophobic silica	$< (4.3 \pm 0.3) \times 10^{-13}$	> 53.8	Socorro et al., 2015
Triazole	Tetraconazole	0-70	6.61×10^7	Hydrophobic / hydrophilic silica	$\leq 10^{-13}$	≥ 100	This study	
		55	6.1×10^7 - 1.45×10^8	Hydrophobic silica	$< (4.3 \pm 0.3) \times 10^{-13}$	> 53.8	Socorro et al., 2015	
	Difenoconazole	0-70	6.61×10^7	Hydrophobic / hydrophilic silica	$\leq 10^{-13}$	≥ 100	This study	
		55	6.1×10^7 - 1.45×10^8	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	/	/	1×10^9	Hydrophilic silica	2×10^{-12}	11.6	Liu et al., 2005
	DDT	/	/			5×10^{-13}	46	
	Lindane	/	/	/			6×10^{-13}	39
Triazine	Terbuthylazine	42-50	27	$5 \times 10^5 - 10^6$		$(1.1 \pm 0.2) \times 10^{-11}$	2.1	Palm et al., 1997
		<1	26	$(9.0 \pm 4) \times 10^7$	Hydrophobic silica	$(1.5 \pm 0.8) \times 10^{-13}$	155	Pflieger et al, 2013
Hydroxybenzotrile	Bromoxynil	25-40	25	$10^5 - 3 \times 10^6$	Hydrophilic silica	1.1×10^{-11}	2.1	Palm et al, 1998
Phenylurea	Isoproturon					$\leq 5 \times 10^{-13}$	≥ 46.3	
Pyridine	PyrifenoX	51	26	$10^5 - 8 \times 10^6$		1.2×10^{-11}	1.9	
Sulfonylurea	Primisulfuronmethyl	43-54	/	8×10^7		$(1.8 \pm 0.4) \times 10^{-11}$	1.3	Palm et al, 1999
Morpholine	Dimethomorph	0.7	29	/	Quartz	6.2×10^{-12}	3.7	Palmet al, 2011
Dicarboximid	Folpet					$(1.7 \pm 1.2) \times 10^{-14}$ to $(2.0 \pm 1.2) \times 10^{-14}$	> 1000	Al Rashidi et al, 2014
Organo-phosphate	Chlorpyrifos	/	25	/		$(1.6 \pm 0.9) \times 10^{-13}$	145	El Masri et al., 2014
		70	/	1.8×10^8	leaves	$(5.8 \pm 4.0) \times 10^{-12}$	4	Lester et al., 2017
Pyrimidinol	Pyrimidinol	/	25	/	Quartz	6×10^{-12}	4	Bouya et al., 2015
		/	25	/	Quartz	$(1.1 \pm 0.9) \times 10^{-12}$	21	

284

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

285

286 Table 1 shows that available kinetic constants of pesticides in the heterogeneous phase toward
287 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}
288 $\text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (i.e., half-life of 1.3 days) with the majority of them being around 10^{-13} cm^3
289 $\text{ molecule}^{-1} \text{ s}^{-1}$. Values obtained in our study for pesticides degraded by OH radicals are of the
290 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
291 with kinetic constants available in the literature calculated for other pesticides of the same or
292 different chemical families on hydrophobic silica (Pflieger et al., 2013), hydrophilic silica (Liu
293 et al., 2005; Palm et al., 2011; Zetzsch, 1991), quartz surfaces (Bouya et al., 2015; Masri et al.,
294 2014), and leaves (Lester et al., 2017). However, our values are of one to two orders of
295 magnitude smaller than values determined by one research team for pesticides adsorbed on
296 silicas (Palm et al., 1997, 1998, 1999).

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

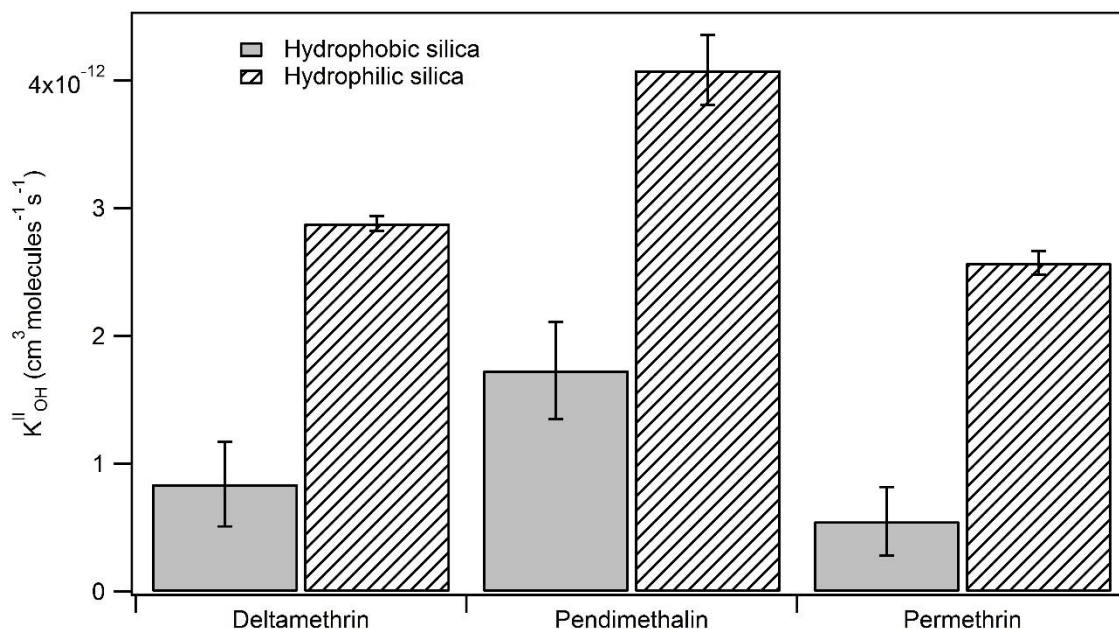
309 It seems that experimental set-up conditions used can impact the absolute kinetic constants
310 value measured. Given the limited amount of studies concerning OH radical degradation in the

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

314 3.4 Influence of the particle type

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

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



323 Fig. 2: second-order kinetic constants for deltamethrin, permethrin, and pendimethalin
324 degraded by OH radicals at 0% RH
325

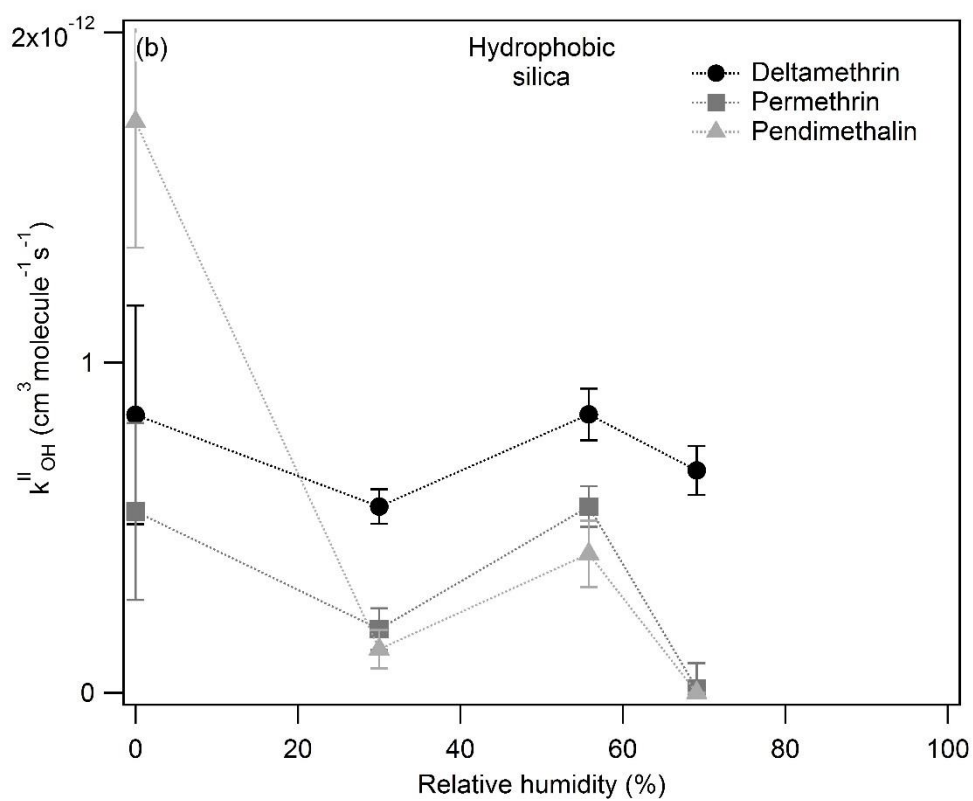
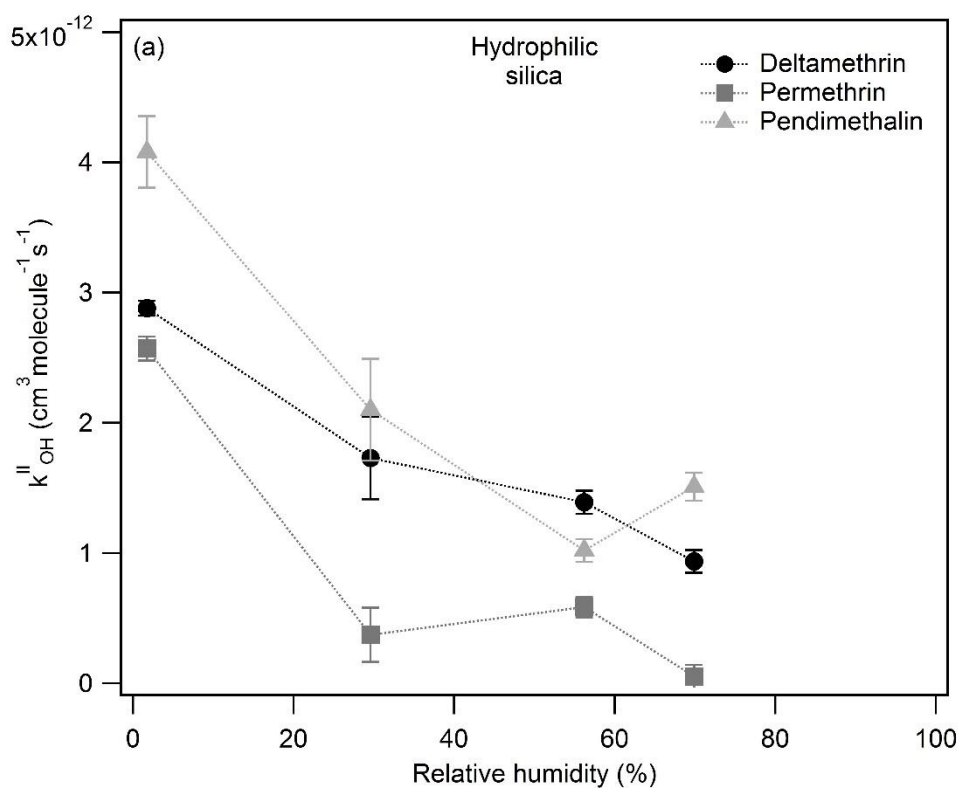
326 Deltamethrin, pendimethalin, and permethrin were all degraded on both particle type in absence
327 of water. However, they were degraded 3.3, 2.4, and 4.7 times faster on hydrophilic silica than
328 on hydrophobic silica, respectively (Fig. 2).

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

338 **3.5 Influence of humidity**

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

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



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

358 When adsorbed on hydrophilic silica, the degradation rate of pesticides by OH radicals ranged
359 from $\leq 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (unreactive) (permethrin, 70% RH) to $(4.08 \pm 0.27) \times 10^{-12} \text{ cm}^3$
360 $\text{ molecule}^{-1} \text{ s}^{-1}$ (pendimethalin, 0% RH). Deltamethrin, permethrin, and pendimethalin appeared
361 to be degraded faster when relative humidity was minimized. Deltamethrin and permethrin were
362 degraded respectively 3.1 and 48 times faster in absence of water compared to 70% RH.
363 Pendimethalin was degraded 2.7 faster at 0% RH than at 55% RH but its degradation rate was
364 unexpectedly enhanced by the increase of relative humidity between 55% RH and 70% RH. On
365 hydrophilic silica, relative humidity has, therefore, a strong impact on the degradation rates of
366 pesticides sensitive to OH radical degradation.

367 Concerning the degradation of pesticides adsorbed on hydrophobic silica, the kinetic constants
368 ranged from $\leq 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (unreactive) (permethrin and pendimethalin, 70% RH)
369 to $(1.73 \pm 0.38) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (pendimethalin, 0% RH). Deltamethrin degradation
370 rate was, given the large uncertainties, not influenced by the relative humidity level. Permethrin
371 degradation rates were independent of the relative humidity level between 0% RH and 55% RH
372 but at 70% RH, no degradation was observed. In contrast, pendimethalin reactivity was slowed
373 down by an increase of relative humidity, its degradation rate was 13.1 times faster at 0% RH
374 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.

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

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

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

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

401 **3.6 Influence of pesticide nature**

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

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

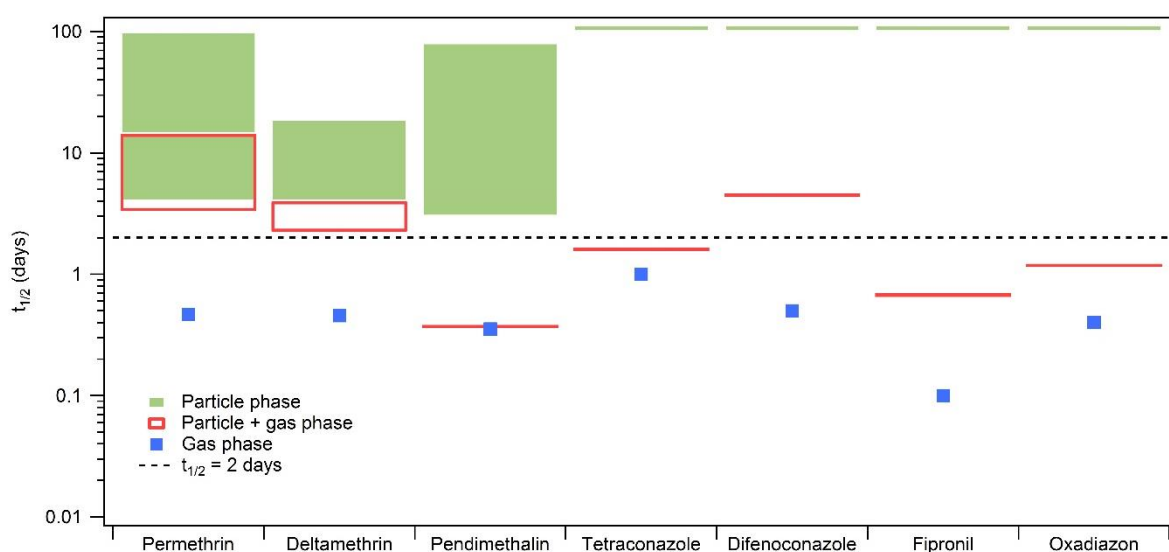
411 The chemical structure of pesticides seems to have a significant influence on their reactivity
412 since the two pesticides of the pyrethroid chemical family (deltamethrin and permethrin) were
413 degraded by OH radicals whereas the two pesticides of the triazole chemical family
414 (difenoconazole and tetraconazole) were not (or very slowly) degraded. Indeed, the triazole
415 reactivity toward OH radicals in the gas phase (i.e., an OH-addition onto carbons atoms of the
416 triazole cycle) was considered as a very slow reaction at ambient temperature (Derbel et al.,
417 2018), which might explain our results. The number of pesticides studied in each of these two
418 families is too limited to come to a conclusion, nevertheless, a similar behavior might be
419 extended to other compounds of these families of pesticides.

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

427 **3.7 Atmospheric implications**

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

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



438
 439 Fig. 4: Half-lives of pesticides in the gas phase, in the particle phase, and in both phases
 440 combined and according to their theoretical partitioning between gas and particle phases
 441 regarding OH radical reactivity (for an OH radical concentration of 1.5×10^6 molecule cm^{-3}
 442 and an exposure time of 12h)

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

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

449 The software AOPWIN allows the calculation kinetic constants for the degradation of organic
450 molecules by OH radicals in the gas phase. AOPWIN calculations were already proven to give
451 results similar to the experimental ones in the case of the degradation in the gas phase of
452 metolachlor (Chao et al., 2018), as well as of prosulfocarb and S-ethyl N,N244
453 dipropylthiocarbamate (Munoz et al., 2018), even though disagreement between theory and
454 experimental results were highlighted concerning organonitrogen compounds (Borduas et al.,
455 2015). AOPWIN calculations indicate that in the gas phase the eight pesticides under study
456 should react with OH radicals, with associated half-lives varying from 0.1 days (cyprodinil) to
457 2.1 days (tetraconazole). Concerning pesticides reacting with OH radicals in the particle phase,
458 half-lives calculated are all superior to 3 days. Also, degradation of tetraconazole,
459 difenoconazole, oxadiazon, and fipronil, which is effective in the gas phase, was hindered in
460 the particle phase. Concerning pesticide under study, heterogeneous degradation by OH radicals
461 is, therefore, slower than homogeneous degradation. Differences in reactivity of pesticides
462 between gas and particle phases were already highlighted in previous studies (El Masri et al.,
463 2014; El Rashidi et al., 2014; Lester et al., 2017; Pflieger et al., 2013; Socorro et al., 2016).

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

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

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

489 **Conclusion**

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

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

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