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## Heterogeneous atmospheric degradation of current-use pesticides by nitrate radicals

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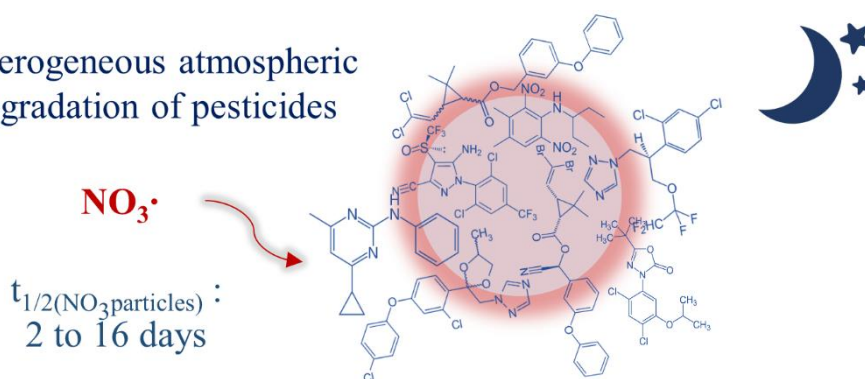
## 22 ABSTRACT

23 In the atmosphere, pesticides are distributed between gaseous and particulate phases  
24 according to their physicochemical properties. In these two phases, they can react with  
25 atmospheric oxidants such as ozone, hydroxyl radical and nitrate radicals. Heterogeneous  
26 kinetics of the degradation by nighttime nitrate radicals are not well described. In this study,  
27 the heterogeneous reactivity with nitrate radicals of eight current-use pesticides (i.e.,  
28 difenoconazole, tetraconazole, cyprodinil, fipronil, oxadiazon, pendimethalin, deltamethrin,  
29 and permethrin) adsorbed on silica model particles was investigated using laboratory  
30 experiments with in-situ nitrate radicals generation and concentration measurement. Under  
31 these experimental conditions, all pesticides were degraded. Atmospheric half-lives calculated  
32 with a Langmuir-Rideal model ranged between 8 days and 16 days and between 2 days to 11  
33 days according to a Langmuir-Hinshelwood model for an atmospheric nitrate radicals  
34 concentration of 20 ppt. Results obtained can contribute to a better understanding of the  
35 atmospheric fate of pesticides in the particulate phase and show the importance of their  
36 degradation by nitrate radical compared to their degradation by other oxidants such as ozone  
37 and hydroxyl radicals.

38

## 39 GRAPHICAL ABSTRACT

Heterogeneous atmospheric  
degradation of pesticides



40

41

42 **KEYWORDS:** pesticides, nitrate radicals, heterogeneous reactivity, kinetics, atmosphere

43

44 **HIGHLIGHTS:**

- 45 • Laboratory experiments at an atmospheric relevant concentration of NO<sub>3</sub> radicals
- 46 • Current-use pesticide studied were degraded by NO<sub>3</sub> radicals in the particle phase
- 47 • Heterogeneous half-lives of pesticides toward NO<sub>3</sub> radicals range from 2 to 16 days
- 48 • NO<sub>3</sub> radicals must be considered for the heterogeneous degradation of pesticides

49

50 **INTRODUCTION**

51 Pesticides are widely used in agriculture and for sanitary purposes. In 2016, they represented  
52 a 50 billion dollar annual market worldwide only concerning crop protection (UIPP, 2017).  
53 However, because of their environmental and health effects (Inserm, 2013; Carvalho, 2017),  
54 they stand for an important topic of interest to both the scientific community and the general  
55 public. When applied, up to 40% of pesticides can be lost to the atmosphere (Sinfort et al.,  
56 2009; Yates et al., 2015; Zivan et al., 2016,2017). They can be dispersed and transported up to  
57 a global scale. As a result, pesticides are found worldwide in the atmosphere, even in  
58 Antarctica where no use of them was ever reported (Khairy et al., 2016). In the atmosphere,  
59 according to their physicochemical properties, pesticides are partitioned between the aqueous,  
60 the gaseous, and the particulate phases, where they can react with atmospheric oxidants.  
61 Current-use pesticides are poorly present in the aqueous phase due to their low water  
62 solubility. In the gas phase, their atmospheric reactivity has been studied and their rate  
63 constant with hydroxyl radicals and, to a lesser extent, with ozone can be estimated

64 (Atmospheric Oxidation Program for Microsoft Windows, AOPWIN<sup>TM</sup> Software, (Meylan  
65 and Howard, 1993)). As semi-volatile compounds, most of them are partly adsorbed on the  
66 surface of atmospheric particles (Sauret et al., 2008) and little is known about their  
67 heterogeneous reactivity.

68 Major atmospheric oxidants are ozone (O<sub>3</sub>), hydroxyl radicals (OH), and nitrate radicals  
69 (NO<sub>3</sub>). Heterogeneous degradation by ozone and OH radicals was already studied for some  
70 pesticides (Borrás et al., 2015; Chen et al., 2016; Socorro et al., 2016; Mattei et al., 2018), but  
71 their degradation by nitrate radicals is poorly described (Yang et al., 2011; Liu et al., 2011,  
72 2012, 2015; Wang et al., 2012, 2013; Li et al., 2014). Nitrate radicals are present during the  
73 night in concentration from a few ppt (Khan et al., 2008; Crowley et al., 2010) up to several  
74 hundreds of ppt (Atkinson et al., 1985; Asaf et al., 2010) and could, therefore, have a  
75 significant impact on the atmospheric half-life of pesticides.

76 Previous studies have shown significant reactivity of nitrate radicals with volatile organic  
77 compounds in the atmosphere (Ng et al., 2017). In particular, studies show that reactivity of  
78 organic compounds with nitrate radicals is generally slower than with hydroxyl radicals.  
79 Nevertheless, the more important atmospheric concentrations of NO<sub>3</sub> radicals compared to  
80 OH radicals leads to a similar or greater oxidation power of NO<sub>3</sub> (Platt et al., 1990; Shiraiwa  
81 et al., 2009; Knopf et al., 2011). Literature concerning the heterogeneous degradation of  
82 pesticides by nitrate radical is very scarce. A few studies (Yang et al., 2011; Liu et al., 2011,  
83 2012, 2015; Wang et al., 2012, 2013; Li et al., 2014) relate the degradation of mainly  
84 organophosphorus pesticides according to degradation rates ranging between of 10<sup>-14</sup> cm<sup>3</sup>  
85 molecule<sup>-1</sup> s<sup>-1</sup> and 10<sup>-12</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, which correspond to heterogeneous half-life  
86 regarding NO<sub>3</sub> radicals of a few hours. This suggests a significant degradation of pesticides by  
87 NO<sub>3</sub> radicals compared to other oxidants. Kinetic studies for the heterogeneous degradation of

88 pesticides by nitrate radicals are therefore highly needed in order to better understand the role  
89 and the importance of this nighttime atmospheric chemistry on pesticide concentrations.

90 The aim of this study is to investigate the heterogeneous reactivity with NO<sub>3</sub> radicals of eight  
91 current-use pesticides (cyprodinil (pyrimidine), deltamethrin (pyrethroid), difenoconazole  
92 (triazole), fipronil (pyrazole), oxadiazon (diazole), pendimethalin (dinitroaniline), permethrin  
93 (pyrethroid), and tetraconazole (triazole)) adsorbed on hydrophobic silica as a model for  
94 mineral atmospheric particles. The compounds under study were selected based on their  
95 distribution between gas and particle phases, their toxicity, their presence in the atmosphere  
96 (Désert et al., 2018). More, their heterogeneous reactivity was extensively investigated toward  
97 OH radicals (Socorro et al., 2016; Mattei et al., 2019a) and ozone (Socorro et al., 2015; Mattei  
98 et al., 2018, 2019b). Nitrate radicals exposure experiments were performed using realistic  
99 NO<sub>3</sub> radicals concentrations (48 ppt to 635 ppt), temperature (25°C) and relative humidity  
100 (40% RH) conditions.

101

## 102 **EXPERIMENTAL SECTION**

### 103 **Chemicals**

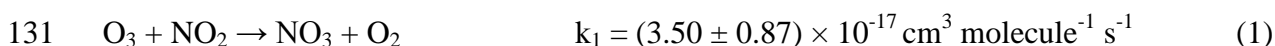
104 Isoprene (purity > 99.5%) and the eight pesticides (PESTANAL®, analytical standard) :  
105 cyprodinil (99.8%), deltamethrin (99.7%), difenoconazole (97.0%), fipronil (97.5%),  
106 oxadiazon (99.9%), pendimethalin (98.8%), permethrin (98.3%), and tetraconazole (99.0%)  
107 were purchased from Sigma-Aldrich and were used as received. The chemical structures of  
108 the pesticides under study are depicted in Supporting Information (SI) Figure S1 and their  
109 physicochemical properties are given in SI Table S1.

### 110 **Silica particles coating**

111 The atmospheric mineral aerosols were mimicked with commercial fumed silica particles  
112 (Mattei et al., 2018). In this study, commercial hydrophobic silica particles (AEROSIL R812,  
113 Degussa, purity SiO<sub>2</sub> content > 99.8 wt%, mean primary particle size ranges from 5 nm to 50  
114 nm, specific surface area (BET method) of (260 ± 30) m<sup>2</sup> g<sup>-1</sup> (Evonik, 2015)) were coated  
115 with pesticides according to a liquid/solid adsorption. In an amber Pyrex bulb of 500 cm<sup>3</sup>, 600  
116 mg of particles were mixed with 6 mL of a pesticide solution (all 8 pesticides at a  
117 concentration of 20 mg L<sup>-1</sup> in dichloromethane (for HPLC, ≥ 99.8%, Sigma-Aldrich)), i.e., a  
118 load of pesticides on silica particles was about 0.02% by weight) and 40 mL of  
119 dichloromethane. After a 5-min ultrasound treatment, dichloromethane was evaporated in a  
120 rotary evaporator (Rotavapor R-114, Büchi) at 40°C and 850 mbar. This process allows a  
121 reproducible coating of the pesticides on the particle's surface (Socorro et al., 2015).  
122 Assuming a uniform particle surface coverage for the pesticide molecules and a spherical  
123 geometry for particles, the percentage of the particle surface coated with individual pesticide  
124 ranged between 0.3% and 0.5% of the monolayer (SI Text S1). Then, the total coated particle  
125 surface was 2.8%, which is much less than a monolayer.

## 126 **Generation of NO<sub>3</sub> radicals and experimental set-up**

127 The gas-phase reaction of ozone in excess with nitrogen dioxide (eq 1) was chosen as the in-  
128 situ method to generate NO<sub>3</sub> radicals (Doussin, 2003; Boyd et al., 2015; Nah et al., 2016),  
129 measurement of NO<sub>3</sub> radicals concentration was made using isoprene as a tracer (Zhang et al.,  
130 2016).



132 where  $k_1$  is the average rate constant for the reaction of ozone with NO<sub>2</sub> at 298 K (Davis et al.,  
133 1974; Graham and Johnston, 1974; Huie and Herron, 1974).

134 The total gas flow in the reactor was maintained constant at 500 mL min<sup>-1</sup>. The reaction  
135 between NO<sub>2</sub> and O<sub>3</sub> occurred inside the bulb where pesticides were exposed to oxidants

136 (Figure 1). A constant NO<sub>2</sub> gaseous flow (F1), (F1 to F8, all Brooks SLA Series mass flow  
137 controller; accuracy, ±1%) was generated from a gas cylinder (a certified mixture of NO<sub>2</sub> (100  
138 ppm) in Helium, Linde gas 5.0). Successive dilutions of NO<sub>2</sub> flux (from 1 mL min<sup>-1</sup> to 10 mL  
139 min<sup>-1</sup>) with purified air (zero air generator ZA-1500, F-DGS; F5, 490-499 mL min<sup>-1</sup>) were  
140 made to provide the specified NO<sub>3</sub> radicals concentration. The NO<sub>2</sub> concentrations were  
141 monitored continuously online by an Eco Physics model (CLD 88p) associated with an Eco  
142 Physics photolytic (metal-halide lamp; 180 W) converter (PLC 860), which allows  
143 simultaneous measurements of NO<sub>x</sub>, NO<sub>2</sub>, and NO concentrations.

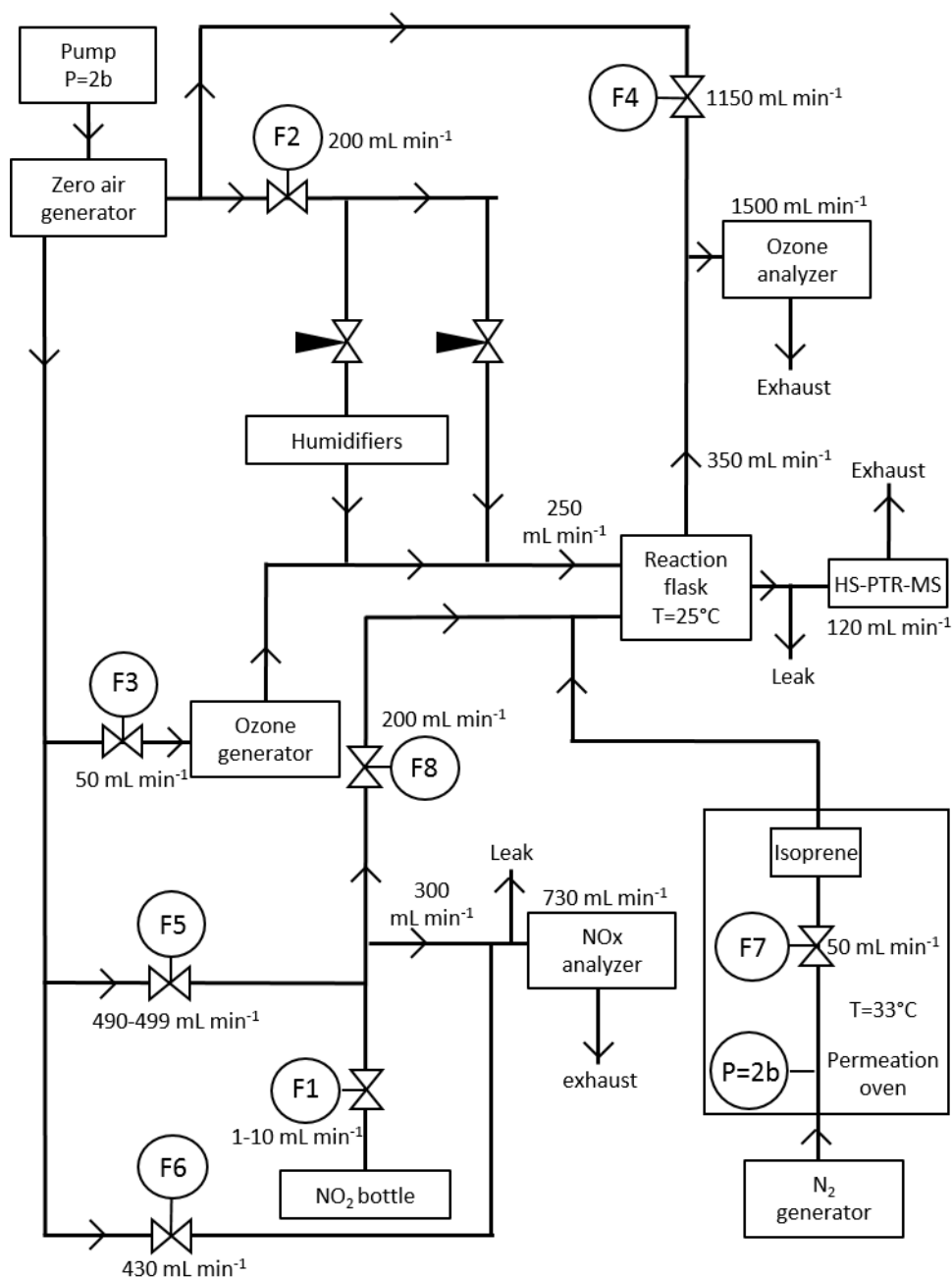
144 Ozone was generated with a constant flow (F3) of 50 mL min<sup>-1</sup> by passing purified air  
145 through an ozone generator (UVP, LLC Upland, UK). Air flow was exposed to ultraviolet  
146 (UV) radiation at 185 nm emitted by a mercury vapor pen ray lamp. Each experiment was  
147 performed at a constant ozone concentration of  $(1.90 \pm 0.15) \times 10^{13}$  molecule cm<sup>-3</sup> (i.e., (760  
148 ± 60) ppb). The ozone concentrations were monitored continuously online by a photometric  
149 ozone analyzer (O<sub>3</sub> 41M, Environnement S.A).

150 A separated humidified air flow was used to avoid a loss of ozone due to its solubility in  
151 water. The relative humidity (RH) was adjusted by purified air, which was split into two  
152 fluxes. The first one consisted of dry air, while the second one was humidified by bubbling  
153 into deionized water. Mixing of these two gas flows (F2, 200 mL min<sup>-1</sup>) generated a carrier  
154 gas at a controlled and constant RH of  $(40 \pm 2)\%$  for all the experiments. 40% RH at 25°C  
155 corresponds to a realistic low atmospheric relative humidity level. RH was measured during  
156 all the experiments by a hygrometer (Hygrolog NT2" (Rotronic) with a "HygroClip SC04"  
157 probe).

158 600 mg of silica particles coated with pesticides were exposed for 5 hours and 30 mg aliquot  
159 of particles were collected at regular intervals during this exposure.



160 Experimental conditions (concentrations and flow rates) were chosen in order to favor the  
161 reactions between  $\text{NO}_2$  and  $\text{O}_3$  and between  $\text{NO}_3$  radicals and isoprene as well as to minimize  
162 all other possible reactions such as  $\text{O}_3$  with isoprene,  $\text{NO}_2$  with isoprene,  $\text{NO}_3$  radicals with  
163  $\text{O}_3$ , or  $\text{NO}_3$  radicals with  $\text{NO}_2$ . Those conditions were chosen with preliminary experiments  
164 and with the calculation of the probability for each reaction to occur compared to other  
165 possible reactions. All kinetic constants of possible reactions (Table SI2) and the measured  
166 concentration of the different species in presence were considered when determining the  
167 appropriate concentration conditions for each compound.



168

169

170 **Figure 1:** Experimental set-up to evaluate the heterogeneous oxidation of adsorbed pesticides

171 under study by NO<sub>3</sub> radicals.

172

173 According to the experimental conditions applied, nitrate radicals concentrations ranged from

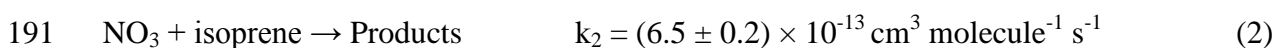
174  $(1.19 \pm 0.06) \times 10^9$  molecule cm<sup>-3</sup> to  $(1.59 \pm 0.11) \times 10^{10}$  molecule cm<sup>-3</sup> (i.e., from 48 to 635

175 ppt). In the atmosphere, NO<sub>3</sub> radicals are predominantly formed by the reaction of nitrogen

176 dioxide (NO<sub>2</sub>) with ozone (O<sub>3</sub>). They are photosensitive because of their strong absorption in  
177 the visible wavelength region (662 nm) and are therefore absent during daytime but they can  
178 greatly accumulate at night. Their nighttime concentration typically ranges between 1 ppt  
179 (Geyer et al., 2001; Khan et al., 2008) and 150 ppt (Stutz et al., 2010) (i.e.,  $2.5 \times 10^7$  molecule  
180 cm<sup>-3</sup> and  $3.75 \times 10^9$  molecule cm<sup>-3</sup>) and can reach up to 420 ppt (Atkinson et al., 1985), or  
181 even 800 ppt (Asaf et al., 2010) (i.e.,  $2 \times 10^{10}$  molecule cm<sup>-3</sup>) in urban polluted areas  
182 (Atkinson et al., 1985). Also, it is important to note that experiments were performed using air  
183 and not inert atmosphere. This makes the oxidant exposure more realistic as it is known that  
184 the presence of O<sub>2</sub> can indirectly influence the degradation mechanism of organic compounds  
185 by NO<sub>3</sub> radicals (Docherty and Ziemann, 2006) and might, therefore, influence the kinetics as  
186 well.

#### 187 **Indirect measurement of NO<sub>3</sub> radicals**

188 Isoprene was used as a gaseous tracer to determine the NO<sub>3</sub> radicals concentrations (Zhang et  
189 al., 2016) (eq 2). It was chosen for its effective and well-described reactivity with NO<sub>3</sub>  
190 radicals.



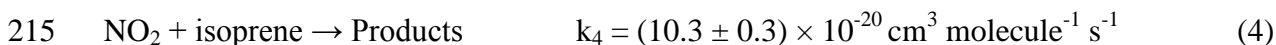
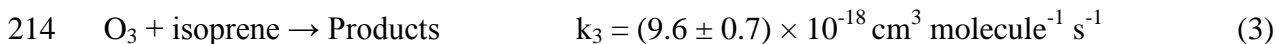
192 where  $k_2$  is the average rate constant for the reaction (Atkinson et al., 1984; Dlugokencky and  
193 Howard, 1989; Wille et al., 1991; Berndt and Böge, 1997; Suh et al., 2001; Stabel et al., 2005;  
194 Zhao et al., 2011).

195 Isoprene was generated using a permeation cell, which consisted of a permeable Teflon tube  
196 (perfluoroalkoxy, 6.4 mm i.d., 8 cm long) filled with pure isoprene (99%, Sigma-Aldrich) and  
197 sealed from both sides. Inside the permeation cell, isoprene was held in liquid/vapor phase  
198 equilibrium at 33°C. The Teflon tube was placed in the permeation chamber, a stainless oven  
199 equipped with an inlet and outlet allowing a carrier gas flow (dried N<sub>2</sub>) to pass through. N<sub>2</sub>  
200 was generated by a Domnick Hunter Nitrox UHPLCMS12 nitrogen generator, at 99.5% purity

201 (0.5% O<sub>2</sub>). A pure N<sub>2</sub> constant flow (F7) continuously passed at a rate of 50 mL min<sup>-1</sup> through  
202 the Teflon porous cell to maintain a constant generation.

203 An HS-PTR-MS (High Sensitivity – Proton Transfer Reaction – Mass Spectrometer, Ionicon  
204 Analytik) was used to monitor isoprene (m/z = 69) and its main degradation products (i.e.,  
205 methacrolein (MACR) and methyl vinyl ketone (MVK), m/z = 71) continuously in gaseous  
206 phase inside the bulb reactor with a time resolution of 10 s (Figure S2). Parameters of the HS-  
207 PTR-MS during the experiments were as follow: E/N = 144 Td, U<sub>drift</sub> = 600 V, T<sub>drift</sub> = 50 °C,  
208 P<sub>drift</sub> = 2.02 mbar. U<sub>drift</sub> is the electric potential applied to the drift tube; T<sub>drift</sub> and P<sub>drift</sub> are the  
209 temperature and the pressure in the drift tube, respectively. E is the strength of the electrical  
210 field in V cm<sup>-1</sup> and N is the gas number density in cm<sup>3</sup>. The ratio E/N in Townsend (1  
211 Townsend = 10<sup>-17</sup> cm<sup>2</sup> V<sup>-1</sup>) is a defining characteristic of the drift tube.

212 Isoprene reacts in the bulb with NO<sub>3</sub> radicals (eq 2), but can also react with O<sub>3</sub> (eq 3), and  
213 NO<sub>2</sub> (eq 4) as follows:



216 where k<sub>3</sub> and k<sub>4</sub> are the rate constants for the reaction of isoprene with O<sub>3</sub> (Karl et al., 2004)  
217 and NO<sub>2</sub> (Atkinson et al., 1984), respectively.

218 The NO<sub>3</sub> radical concentrations were determined using the consumption of the tracer  
219 (isoprene) as follows:

220 
$$-\frac{d[\text{isoprene}]}{dt} = k_2 \times [\text{isoprene}] \times [\text{NO}_3] + k_3 \times [\text{isoprene}] \times [\text{O}_3] + k_4 \times [\text{isoprene}] \times$$
  
221 
$$[\text{NO}_2] \quad (5)$$

222 The integration of eq 5 gives the eq 6 which makes it possible to calculate NO<sub>3</sub> radical  
223 concentrations in the reactor all along with experiments.

224 
$$[\text{NO}_3] = \ln \left( \frac{[\text{isoprene}]_0}{[\text{isoprene}]_t} \right) \times \frac{1}{k_2 \times t} - (k_3 \times [\text{O}_3] - k_4 \times [\text{NO}_2]) \times \frac{1}{k_2} \quad (6)$$

225 Where  $t$  (s) is the residence time of compounds in the gaseous phase in the bulb,  $[\text{isoprene}]_0$   
226 and  $[\text{isoprene}]_t$  (molecule  $\text{cm}^{-3}$ ) are the initial (in absence of oxidants) and the measured  
227 concentrations of isoprene in the bulb reactor at time  $t$ , respectively, finally  $k_2$  is the rate  
228 constant of the reaction between isoprene and  $\text{NO}_3$  radicals (eq 2),  $k_3$  is the rate constant of  
229 the reaction between isoprene and  $\text{O}_3$  (eq 3), and  $k_4$  is the rate constant of the reaction  
230 between isoprene and  $\text{NO}_2$  (eq 4).

### 231 **Extraction and pesticides quantification**

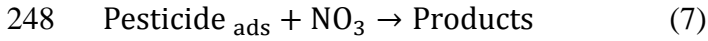
232 During exposure, 30 mg aliquots of particles were regularly sampled in order to quantify the  
233 remaining adsorbed pesticides on their surface. Each 30 mg aliquot of particles was  
234 individually extracted by accelerated solvent extraction (ASE 350, Dionex) with  
235 dichloromethane. For this purpose, particles were introduced in a 33 mL stainless steel cell  
236 with an internal standard solution (Triphenyl phosphate, 99.9%, Sigma-Aldrich). Afterward,  
237 the extracts were concentrated under a nitrogen flow using a concentration workstation  
238 (TurboVap II, Biotage).

239 Analyses of the obtained solutions were realized using gas chromatography coupled to  
240 tandem mass spectrometry (GC/MS-MS), with a Trace GC Ultra (Thermo Scientific) coupled  
241 to a TSQ Quantum™ Triple Quadrupole (Thermo Scientific) using electron impact ionization  
242 (70 eV).

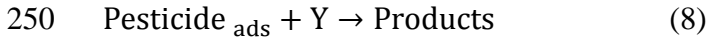
243 More details about ASE extraction, concentration, and GC/MS-MS analysis are available  
244 elsewhere (Socorro et al., 2015).

### 245 **Determination of first-order rate constants**

246 To obtain the first-order rate constants  $k_{\text{NO}_3(\text{part})}^I$  for the heterogeneous reactions of  $\text{NO}_3$   
247 radicals with a pesticide, the following procedure was applied:



249 All degradation reactions of a pesticide not initiated by NO<sub>3</sub> radicals are defined as follows:



251 where Y represent all residual oxidant species. Y species include ozone, nitrogen dioxide but  
 252 also eventual compounds or radicals formed by side reactions. For instance, the reactivity of  
 253 NO<sub>3</sub> radicals with unsaturated volatile organic compounds could lead to the formation of HO<sub>2</sub>  
 254 or OH radicals (Canosa-Mas et al., 1999; Salisbury, 2001). Also the combination of NO<sub>3</sub>  
 255 radical and NO<sub>2</sub> could lead to the formation of N<sub>2</sub>O<sub>5</sub> which is known to be heterogeneously  
 256 reactive with organic compounds (Knopf et al., 2011). However, according to the  
 257 concentrations of NO<sub>2</sub> and NO<sub>3</sub> in the reactor and the kinetic constants (Table SI2) leading to  
 258 the formation of N<sub>2</sub>O<sub>5</sub>, the formation of N<sub>2</sub>O<sub>5</sub> is very unlikely.

259 The reaction rate of the pesticide under study versus time is then defined by Eq 10.

260 
$$-\frac{d[Pesticide_{ads}]}{dt} = k_{NO_3(part)}^{II} \times [Pesticide_{ads}] \times [NO_3] + k_{des(part)}^I \times [Pesticide_{ads}] +$$
  
 261 
$$k_{hydr(part)}^I \times [Pesticide_{ads}] + k_Y^{II} \times [Pesticide_{ads}] \times [Y] \quad (9)$$

262 where  $k_{NO_3(part)}^{II}$  and  $k_Y^{II}$  (cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) are the second-order rate constants of the  
 263 heterogeneous reactions with NO<sub>3</sub> radicals and all other species different than NO<sub>3</sub> radicals,  
 264 respectively.  $k_{des(part)}^I$  (s<sup>-1</sup>) is the first order kinetic desorption rate constant and  $k_{hydr(part)}^I$  (s<sup>-1</sup>)  
 265 is the pseudo-first-order kinetic hydrolysis rate constant.

266 The integration of eq 10 leads to:

267 
$$\ln\left(\frac{[Pesticide_{ads}]_t}{[Pesticide_{ads}]_0}\right) = -(k_{NO_3(part)}^I + k_{des(part)}^I + k_{hydr(part)}^I + k_Y^I) \times t = -k_{all(part)}^I \times t$$
  
 268 (10)

269 where  $k_{all(part)}^I$  ( $s^{-1}$ ) is the pseudo-first-order constant of the heterogeneous reactions with  
 270  $NO_3$  radicals and other species different than  $NO_3$  radicals (Y species), as well as the pesticide  
 271 loss due to hydrolysis or desorption.  $k_{all(part)}^I$  is experimentally determined as the slope of the  
 272 Napierian logarithm of normalized pesticide concentration's decay versus the exposure time.  
 273 Considering that  $NO_3$  radicals are continuously produced in the reactor, a pseudo-first-order  
 274 reaction rate constant  $k_{NO_3(part)}^I$  was assumed and is expressed as follows:

$$275 \quad k_{NO_3(part)}^I = k_{all(part)}^I - k_{des(part)}^I - k_{hydr(part)}^I - k_{Y(part)}^{II} \times [Y] \quad (11)$$

276 ( $k_{des(part)}^I + k_{hydr(part)}^I$ ) were determined experimentally in the absence of oxidants (Mattei et  
 277 al., 2018) while  $k_{Y(part)}^I$  was determined mathematically as the intercept of the slope fitting  
 278  $k_{all(part)}^I$  versus  $[NO_3]$  after correction from the corresponding ozonolysis rate constant.

### 279 **Kinetic mechanism model**

280 In order to determine kinetic constants that are independent of the  $NO_3$  radical concentration,  
 281 pseudo-first-order kinetic constants were plotted against the  $NO_3$  radical concentration. Two  
 282 fitting methods were used: Langmuir–Rideal (L-R, also known as Eley-Rideal) fitting models  
 283 linearly the reaction between a reactant in the gas phase with one adsorbed on the surface of  
 284 the particles whereas Langmuir–Hinshelwood (L-H) models non-linearly the reaction between  
 285 two reactants adsorbed on the surface.

286 The second-order kinetic constant  $k_{NO_3(part)}^{II}$  ( $cm^3 \text{ molecule}^{-1} s^{-1}$ ) determined with L-R fitting  
 287 correspond to the slope of the linear regression line fitting the first order kinetic constant  
 288 according to the oxidant concentration. This correspond to eq 13:

$$289 \quad k_{NO_3(part)}^{II} = \frac{k_{NO_3}^I}{[NO_3]} \quad (12)$$

290 Half-lives corresponding to an L-R model can be calculated as follow:

$$291 \quad t_{\frac{1}{2} NO_3(\text{part})} = \frac{\ln 2}{k_{NO_3(\text{part})}^I \times [NO_3]} \quad (13)$$

292 Where  $t_{\frac{1}{2} NO_3(\text{part})}$  ( $s^{-1}$ ) is the half-life of a pesticide and  $[NO_3]$  (molecules  $cm^{-3}$ ) is the  
293 atmospheric concentration of  $NO_3$  radicals chosen as representative of atmospheric values. In  
294 this work,  $[NO_3]$  used is  $5 \times 10^8$  molecule  $cm^{-3}$  (i.e., 20 ppt) over an exposure time of 12  
295 hours (Atkinson, 1991).

296 With the L-H model, the pseudo-first-order rate coefficient ( $k_{NO_3}^I$ ,  $s^{-1}$ ) is expressed using eq  
297 15:

$$298 \quad k_{NO_3}^I = \frac{(k_{\max} \times k_{NO_3} \times [NO_3])}{(1 + k_{NO_3} \times [NO_3])} \quad (14)$$

299 where  $k_{\max}$  ( $s^{-1}$ ) is the maximum rate constant obtained at high oxidant concentration and  $k_{NO_3}$   
300 (molecule  $cm^{-3}$ ) is the  $NO_3$  radical gas-surface equilibrium constant. These two parameters  
301 can be obtained by fitting the experimental results  $k_{NO_3}^I$  versus  $[NO_3]$  using a non-linear least-  
302 square fit of eq 15. Hence, the second-order rate constant of the reaction follows a non-linear  
303 dependence with respect to the gas-phase oxidant.

304 Uncertainties were determined as the error on the fitting parameters calculated by the software  
305 Igor Pro, taking into account both the uncertainties on the first-order kinetic constants and the  
306 nitrate radical concentration.

307 Half-lives corresponding to an L-H model is calculated as follow:

$$308 \quad t_{\frac{1}{2} NO_3(\text{part})} = \frac{\ln 2}{k_{NO_3}^I} \quad (15)$$

309 Using ( $k_{NO_3}^I$ ,  $s^{-1}$ ) calculated for  $[NO_3]$  of  $5 \times 10^8$  molecule  $cm^{-3}$  and an exposure time of 12 h,  
310 as presented previously.



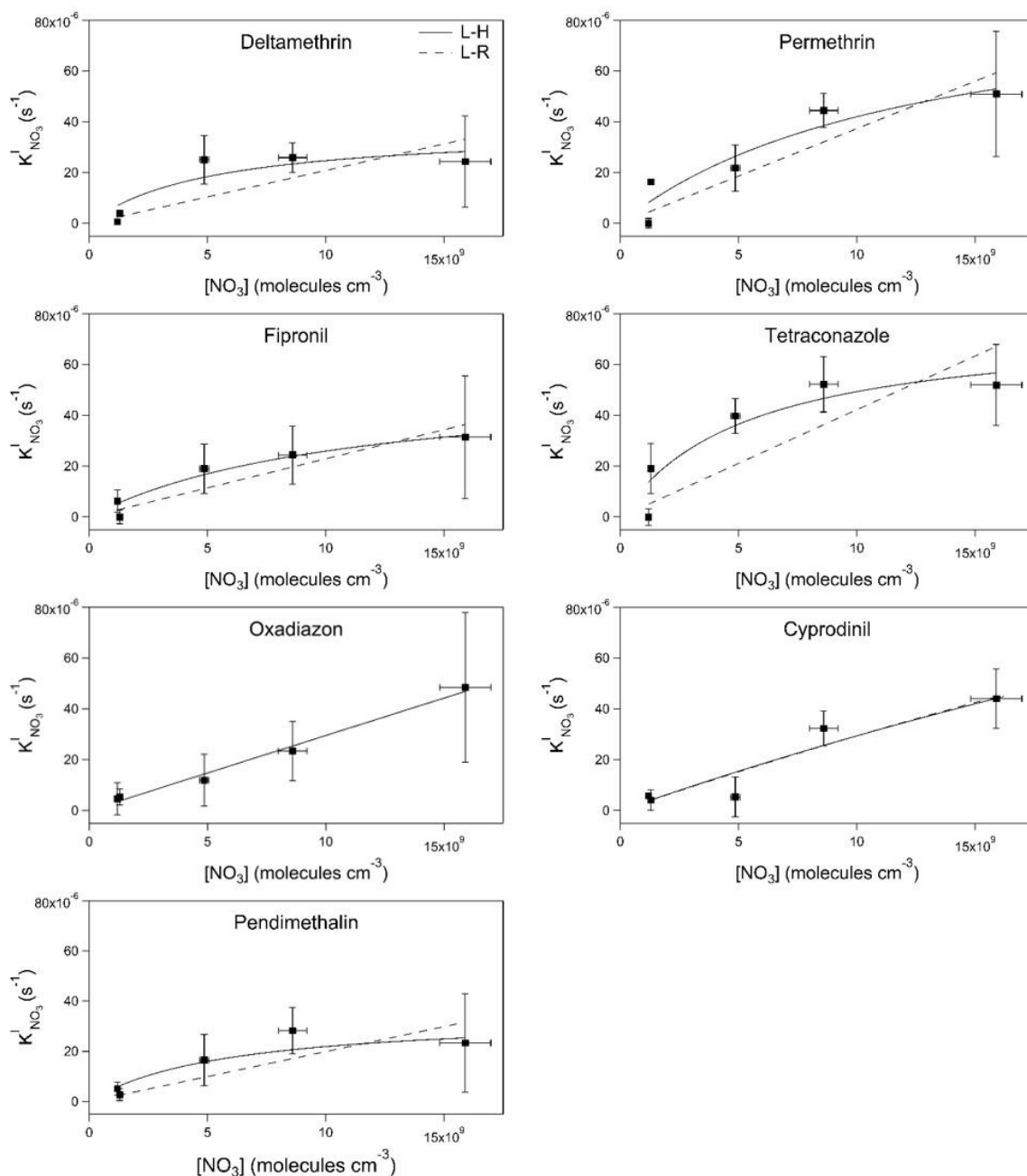
## 311 RESULTS AND DISCUSSION

### 312 Heterogeneous reactivity kinetics

313 Oxidation experiments were conducted for five nitrate radicals concentrations (i.e.,  $(1.2 \pm 0.1)$   
314  $\times 10^9$ ;  $(1.3 \pm 0.1) \times 10^9$ ;  $(4.9 \pm 0.2) \times 10^9$ ;  $(8.6 \pm 0.6) \times 10^9$  and  $(1.6 \pm 0.1) \times 10^{10}$  molecule  
315  $\text{cm}^{-3}$ ) in order to evaluate the heterogeneous degradation rates of 8 pesticides, i.e.,  
316 deltamethrin, permethrin, fipronil, tetraconazole, oxadiazon, cyprodinil, pendimethalin, and  
317 difenoconazole, adsorbed on silica particles.

318 Under these experimental conditions, all pesticides under study showed significant  
319 degradation, in decreasing order of reactivity: tetraconazole ~ permethrin > oxadiazon ~  
320 cyprodinil > fipronil ~ deltamethrin ~ pendimethalin according to an L-R model and  
321 tetraconazole > permethrin ~ deltamethrin > pendimethalin > fipronil > cyprodinil ~  
322 oxadiazon according to an L-H model. Within 5h of exposure to nitrate radicals ranging from  
323  $(1.2 \pm 0.1) \times 10^9$  molecule  $\text{cm}^{-3}$  to  $(1.6 \pm 0.1) \times 10^{10}$  molecule  $\text{cm}^{-3}$ , tetraconazole degradation  
324 ranged from 29% to 61% of the initial concentration. Difenoconazole was also degraded by  
325 nitrate radicals, nevertheless from the noisy data obtained, it is not possible to determine  
326 kinetic constants. Therefore, results regarding difenoconazole degradation are not presented  
327 thereafter.

328 Pseudo-first-order constants corresponding to the degradation of pesticides by nitrate radicals  
329 were plotted against the nitrate radical concentrations (Figure 2). Pseudo-first-order kinetic  
330 constants for all pesticides under study increased as expected with an increase of nitrate  
331 radicals concentrations (Figure 2).



332

333 **Figure 2:** Pseudo-first-order kinetic constants for the degradation of pesticides adsorbed on  
 334 hydrophobic silica by nitrate radicals at 40% RH at five nitrate radicals concentrations from  
 335  $(1.2 \pm 0.1) \times 10^9$  molecule  $cm^{-3}$  to  $(1.6 \pm 0.1) \times 10^{10}$  molecule  $cm^{-3}$ . The solid line  
 336 corresponds to an L-H fitting and the dotted line corresponds to an L-R fitting.

337 **Kinetic mechanism model**

338 The different reaction rate constants of heterogeneous oxidation of the seven adsorbed  
 339 pesticides by nitrate radicals, described by L-R and L-H mechanisms, as well as the

340 corresponding half-lives are summarized in Table 1. For all pesticides, both L-R and L-H  
341 patterns can be applied although, for most compounds, the L-H model seems to better fit the  
342 experimental data. However, the L-H model leads to greater uncertainties on the second order  
343 kinetic constants than the L-R model. According to an L-R model, the slowest degradation  
344 rate is obtained for pendimethalin with  $k_{NO_3(part)}^{II} = (1.99 \pm 0.42) \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and  
345 the fastest degradation rate is obtained for tetraconazole with  $k_{NO_3(part)}^{II} = (4.22 \pm 0.87) \times 10^{-15}$   
346  $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . According to an L-H model, kinetic constants vary from  $k_{\max} = (1.71 \pm$   
347  $1.69) \times 10^{-2} \text{ s}^{-1}$  and  $k_{NO_3} = (1.72 \pm 1.70) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1}$  for oxadiazon to  $k_{\max} = (7.59$   
348  $\pm 2.36) \times 10^{-5} \text{ s}^{-1}$  to  $k_{NO_3} = (1.85 \pm 1.43) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1}$  for tetraconazole.

349 Kinetic data obtained in this study are compared to the literature. Unfortunately, because of  
350 the lack of data, these comparisons are done only with other pesticides. Literature data about  
351 the heterogeneous degradation of pesticides by  $NO_3$  radicals (Yang et al., 2011; Liu et al.,  
352 2012, 2014, 2015; Wang et al., 2012, 2013; Li et al., 2014) only considered the L-R  
353 mechanism. The heterogeneous reactivity of organic compounds with hydroxyl radicals was  
354 described by both L-H mechanism (Bagot et al., 2008; Vlasenko et al., 2008; Enami et al.,  
355 2014) and L-R mechanism (Socorro et al., 2016). However, L-R mechanism was explained  
356 partly because of OH radicals' really short lifetime which does not allow the necessary time to  
357 adsorb on the surface (Socorro et al., 2016).  $NO_3$  radicals have a much longer lifetime than  
358 OH radicals, in the order of magnitude of the minute (Platt et al., 1984) versus the second  
359 (Gligorovski et al., 2015), respectively.  $NO_3$  radicals may be able to adsorb on the particle  
360 surface before reacting with pesticides allowing an L-H mechanism.

### 361 **Comparison with other pesticides in the particle-phase**

362

Table 1: Kinetic data for the heterogeneous reactivity of NO<sub>3</sub> radicals with the adsorbed pesticides under study (in bold) and corresponding

363

atmospheric half-lives, as well as literature data for the degradation of other pesticides by NO<sub>3</sub> radicals

Chemical Family	Pesticide	Relative humidity (%)	Temperature (°C)	NO <sub>3</sub> radical concentration (molecule cm <sup>-3</sup> )	Surface	Langmuir - Rideal model		Langmuir - Hinshelwood model			Reference
						$k_{NO_3(part)}^H$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	t <sub>1/2</sub> NO <sub>3(part)</sub> (d)	k <sub>(max)</sub> (s <sup>-1</sup> )	K <sub>NO3</sub> (cm <sup>3</sup> molecule <sup>-1</sup> )	t <sub>1/2</sub> NO <sub>3(part)</sub> (d)	
Carbamate	Carbaryl	~ 10	25	Unknown	Azelaic acid	$4.4 \times 10^{-13}$	0.7	/			Yang et al. (2011)
Dinitroaniline	<b>Pendimethalin</b>	<b>40 ± 2</b>	<b>25 ± 1</b>	<b>(1.2 – 16.0) × 10<sup>9</sup></b>	<b>Hydrophobic silica</b>	<b>(1.99 ± 0.42) × 10<sup>-15</sup></b>	<b>16.1</b>	<b>(3.47 ± 1.33) × 10<sup>-5</sup></b>	<b>(1.71 ± 1.57) × 10<sup>-10</sup></b>	<b>5.6</b>	<b>This work</b>
Organophosphorus	Chlorpyrifos	~ 40	~ 15	(5.0 ± 0.3) × 10 <sup>10</sup>	Azelaic acid	(3.4 ± 0.2) × 10 <sup>-12</sup>	0.09	/			Li et al. (2014)
	Fenthion	~ 5	~ 20	10 <sup>11</sup> – 10 <sup>12</sup>	Azelaic acid	$3.3 \times 10^{-14} - 3.3 \times 10^{-13}$	0.9 – 9.3	/			Liu et al. (2012)
	Malathion	~ 5	~ 20	10 <sup>11</sup> – 10 <sup>12</sup>	Azelaic acid	$5.6 \times 10^{-14} - 5.6 \times 10^{-13}$	0.6 – 5.5	/			Liu et al. (2012)
	Parathion	~ 5	~ 20	10 <sup>11</sup> – 10 <sup>12</sup>	Azelaic acid	$5.5 \times 10^{-15} - 5.5 \times 10^{-14}$	5.6 – 56	/			Liu et al. (2012)
	Parathion	~ 5	~ 20	(2.7 – 8.5) × 10 <sup>9</sup>	Azelaic acid	$(2.97 \pm 0.13) \times 10^{-12}$	0.1	/			Liu et al. (2015)
	Phosmet	~ 5	~ 20	10 <sup>11</sup> – 10 <sup>12</sup>	Azelaic acid	$(1.92 \pm 0.09) \times 10^{-12}$	0.2	/			Liu et al. (2011)
	Phosmet	~ 5	~ 20	(2.7 – 8.5) × 10 <sup>9</sup>	Azelaic acid	$(2.80 \pm 0.16) \times 10^{-12}$	0.1	/			Liu et al. (2015)
Oxadiazole	<b>Oxadiazon</b>	<b>40 ± 2</b>	<b>25 ± 1</b>	<b>(1.2 – 16.0) × 10<sup>9</sup></b>	<b>Hydrophobic silica</b>	<b>(2.95 ± 0.12) × 10<sup>-15</sup></b>	<b>10.9</b>	<b>(1.71 ± 1.69) × 10<sup>-2</sup></b>	<b>(1.72 ± 1.70) × 10<sup>-13</sup></b>	<b>10.9</b>	<b>This work</b>
Pyrazole	<b>Fipronil</b>	<b>40 ± 2</b>	<b>25 ± 1</b>	<b>(1.2 – 16.0) × 10<sup>9</sup></b>	<b>Hydrophobic silica</b>	<b>(2.29 ± 0.31) × 10<sup>-15</sup></b>	<b>14</b>	<b>(5.45 ± 1.89) × 10<sup>-5</sup></b>	<b>(9.05 ± 5.97) × 10<sup>-11</sup></b>	<b>6.7</b>	<b>This work</b>

Pyrethroid	<b>Deltamethrin</b>	<b>40 ± 2</b>	<b>25 ± 1</b>	<b>(1.2 – 16.0) × 10<sup>9</sup></b>	<b>Hydrophobic silica</b>	<b>(2.08 ± 0.51) × 10<sup>-15</sup></b>	<b>15.4</b>	<b>(3.75 ± 1.52) × 10<sup>-5</sup></b>	<b>(1.93 ± 1.98) × 10<sup>-10</sup></b>	<b>4.6</b>	<b>This work</b>
	Fenvalerate	~ 5	~ 25	(1.5 – 10.2) × 10 <sup>9</sup>	Azelaic acid	(1.86 ± 0.04) × 10 <sup>-12</sup>	0.2	/			Wang et al. (2013)
	<b>Permethrin</b>	<b>40 ± 2</b>	<b>25 ± 1</b>	<b>(1.2 – 16.0) × 10<sup>9</sup></b>	<b>Hydrophobic silica</b>	<b>(3.73 ± 0.52) × 10<sup>-15</sup></b>	<b>8.6</b>	<b>(9.48 ± 4.75) × 10<sup>-5</sup></b>	<b>(7.93 ± 7.21) × 10<sup>-11</sup></b>	<b>4.4</b>	<b>This work</b>
	Phenothrin	~ 5	~ 25	(1.5 – 10.2) × 10 <sup>9</sup>	Azelaic acid	(1.61 ± 0.03) × 10 <sup>-12</sup>	0.2	/			Wang et al. (2013)
	Resmethrin	~ 5	~ 25	(1.5 – 10.2) × 10 <sup>9</sup>	Azelaic acid	(5.54 ± 0.14) × 10 <sup>-12</sup>	0.1	/			Wang et al. (2013)
Pyrimidine	<b>Cyprodinil</b>	<b>(0-80) ± 2</b>	<b>25 ± 1</b>	<b>(1.2 – 16.0) × 10<sup>9</sup></b>	<b>Hydrophobic silica</b>	<b>(2.87 ± 0.32) × 10<sup>-15</sup></b>	<b>11.2</b>	<b>(0.39 ± 1.62) × 10<sup>-3</sup></b>	<b>(0.81 ± 3.70) × 10<sup>-11</sup></b>	<b>10.1</b>	<b>This work</b>
	Pyrimicarb	~ 10	~ 25	(0.6 – 7.0) × 10 <sup>9</sup>	Azelaic acid	(7.5 ± 0.3) × 10 <sup>-13</sup>	0.4	/			Wang et al. (2012)
	Pirimophos-methyl	~ 10	~ 25	(0.6 – 7.0) × 10 <sup>9</sup>	Azelaic acid	(9.9 ± 0.3) × 10 <sup>-12</sup>	0.03	/			Wang et al. (2012)
Triazine	Ametryn	~ 5	~ 25	(0.7 – 7.9) × 10 <sup>10</sup>	Azelaic acid	8.4 × 10 <sup>-13</sup>	0.4	/			Liu et al. (2014)
Triazole	<b>Difenoconazole</b>	<b>40 ± 2</b>	<b>25 ± 1</b>	<b>(1.2 – 16.0) × 10<sup>9</sup></b>	<b>Hydrophobic silica</b>	/	/	/			<b>This work</b>
	<b>Tetraconazole</b>	<b>40 ± 2</b>	<b>25 ± 1</b>	<b>(1.2 – 16.0) × 10<sup>9</sup></b>	<b>Hydrophobic silica</b>	<b>(4.22 ± 0.69) × 10<sup>-15</sup></b>	<b>7.6</b>	<b>(7.59 ± 2.36) × 10<sup>-5</sup></b>	<b>(1.85 ± 1.43) × 10<sup>-10</sup></b>	<b>2.4</b>	<b>This work</b>

364 Atmospheric half-lives calculated for an average concentration  $[NO_3]_{(gas)} = 5 \times 10^8$  molecule  $cm^{-3}$  and for an exposure of 12 h per day (Atkinson, 1991).

365

366 Some studies about heterogeneous NO<sub>3</sub> radicals oxidation of pesticides exist, in which kinetic  
367 data were obtained with pesticides suspended with azelaic acid as nucleation cores to form  
368 aerosols exposed to NO<sub>3</sub> radicals give second-order rate constants ranged between 10<sup>-14</sup> cm<sup>3</sup>  
369 molecule<sup>-1</sup> s<sup>-1</sup> and 10<sup>-12</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> ( Yang et al., 2011; Liu et al., 2012, 2014, 2015;  
370 Wang et al., 2012, 2013; Li et al., 2014). These values are higher than the second-order rate  
371 constants obtained in this study (about 10<sup>-15</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>). Beyond the nature of the  
372 pesticides under study, the relative humidity could explain this difference. Literature data  
373 were obtained at low relative humidity (5-10% RH, except one at 60% RH) (Yang et al.,  
374 2011; Liu et al., 2012, 2014; Wang et al., 2012, 2013; Li et al., 2014) giving second-order rate  
375 constants ranging between 10<sup>-14</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> and 10<sup>-12</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. Previous  
376 work highlighted that the heterogeneous reactivity of organic compounds including pesticides  
377 with ozone was fastest when the relative humidity decreased ( Pöschl et al., 2001; Kaiser et  
378 al., 2011; Mattei et al., 2018). This phenomenon was attributed to the absence or low  
379 competition between water and pesticide molecules to react with the oxidant at low relative  
380 humidity. As this present work was conducted at 40% RH, it is possible that part of the  
381 differences in the degradation rates obtained is due to this difference in experimental  
382 conditions.

383 However, an other experimental condition should lead to opposite results. According to the  
384 experimental process described in the literature (Yang et al., 2011; Liu et al., 2012, 2014,  
385 2015; Wang et al., 2012, 2013; Li et al., 2014), pesticides were suspended on an azelaic  
386 nucleation core which leads to particles highly concentrated in pesticides whereas, in the  
387 present study, the total coated surface of silica particles was less than a monolayer (3% of a  
388 monolayer). The high pesticide concentrations in the aerosols used by the authors previously  
389 cited should lead to slower reactivity than in the case of pesticides adsorbed on the aerosol  
390 surface. Indeed, it was previously demonstrated that NO<sub>3</sub> radicals only react with the top few

391 molecular surface layers of a substrate (Moise et al., 2002). In addition, heterogeneous  
392 reactivity was shown to be slowed down by particle's surface coating increase due to the  
393 decrease of accessibility of pesticides for the oxidant. This phenomenon was demonstrated for  
394 heterogeneous degradation of pesticides by ozone (El Masri et al., 2016).

### 395 **Reaction pathways**

396 All pesticides under study were degraded by NO<sub>3</sub> radicals. From a mechanistic point of view,  
397 the nitration of a double bond (electrophilic addition of NO<sub>3</sub> radical, followed by an addition  
398 of NO<sub>2</sub> molecule and an elimination of HNO<sub>3</sub> molecule, leading to the formation of a NO<sub>2</sub>  
399 moiety), which is favored on the aromatic ring (Wang et al., 2013), is a common reaction  
400 pathway. As all the pesticides under study are aromatic organic compounds (Figure S1), they  
401 could all react in this way. Other studies on the heterogeneous reactivity between NO<sub>3</sub>  
402 radicals and pesticides of the pyrethroid family, as deltamethrin and permethrin, also  
403 suggested the ester cleavage, as shown for resmethrin (Wang et al., 2013) and the NO<sub>3</sub>  
404 radicals addition to an aliphatic double bond, as shown for phenothrin (Wang et al., 2013).  
405 Liu et al., (2014) also proposed the oxidation by NO<sub>3</sub> radicals of the sulfur atom on a methyl  
406 sulfoxide group for fenthion and ametryn. The trifluoro sulfoxide group available on fipronil  
407 could be similarly oxidized.

### 408 **Comparison with pesticide's degradation in the gas-phase**

409 In the literature, some kinetic data are available for the degradation of pesticides in the gas  
410 phase, even if no data concerns the chemical families of compounds under study.

411 Table 2: Kinetic data available in the literature for the gaseous reactivity of NO<sub>3</sub> radicals of  
412 pesticides and corresponding atmospheric half-lives. None of the references provided RH  
413 data.

Chemical Family	Pesticide	Temperature (°C)	$k_{NO_3(part)}^H$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	$t_{1/2} NO_3(part)$ (d)	Reference
-----------------	-----------	---------------------	---	-----------------------------	-----------

Carbamate	Carbaryl <sup>a</sup>	25	$3.37 \times 10^{-13}$	0.1	Cheng et al. (2017)
Organochlorine	DDT <sup>a</sup>	25	$4.01 \times 10^{-15}$	8.0	Liu et al. (2014)
Organophosphorus	DEEP <sup>b</sup>	$25 \pm 2$	$(3.4 \pm 1.4) \times 10^{-16}$	94.4	Aschmann et al. (2005a)
	DEMP <sup>b</sup>	$25 \pm 2$	$(3.7 \pm 1.1) \times 10^{-16}$	86.7	Aschmann et al. (2005a)
	DEMPT <sup>b</sup>	$23 \pm 2$	$(2.01 \pm 0.20) \times 10^{-15}$	16.0	Aschmann et al. (2006)
	DMEP <sup>b</sup>	$25 \pm 2$	$(3.4 \pm 1.4) \times 10^{-16}$	94.4	Aschmann et al. (2005b)
	DMHP <sup>b</sup>	$25 \pm 2$	$< 1.4 \times 10^{-16}$	$> 229.2$	Aschmann et al. (2005b)
	DMMP <sup>b</sup>	$25 \pm 2$	$(2.0 \pm 1.0) \times 10^{-16}$	160.5	Aschmann et al. (2005b)
	IMMP <sup>b</sup>	$23 \pm 2$	$(4.8 \pm 2.1) \times 10^{-16}$	66.9	Aschmann et al. (2010)
	TEP <sup>b</sup>	$25 \pm 2$	$(2.4 \pm 1.4) \times 10^{-16}$	133.7	Aschmann et al. (2005a)
	TEPT <sup>b</sup>	$23 \pm 2$	$(1.03 \pm 0.10) \times 10^{-15}$	31.2	Aschmann et al. (2006)
	TMP <sup>b</sup>	$25 \pm 2$	$< 3 \times 10^{-14}$	$> 1.1$	Goodman et al. (1988)

414

415 DDT : 1,1'-(2,2,2-trichloroethylidene)bis[4-chlorobenzene] ; DEEP : DiEthyl EthylPhosponate ; Demp : DiEthyl  
416 MethylPhosponate ; DEMPT : *O,O*-DiEthyl MethylPhosphonoThioate ; DMEP : DiMethyl EthylPhosponate ; DMHP :  
417 DiMethyl Phosponate ; DMMP : DiMethyl MethylPhosponate ; IMMP : Isopropyl Methyl Methylphosponate ; TEP :  
418 TriEthyl Phosphate ; TEPT : *O,O,O*-TriEthyl PhosphonoThioate ; TMP : Trimethyl Phosphorothioates

419 <sup>a</sup> NO<sub>3</sub> radicals concentration calculated theoretically, <sup>b</sup> NO<sub>3</sub> radicals concentration unknown

420 Atmospheric half-lives calculated for an average concentration  $[NO_3]_{(gas)} = 5 \times 10^8$  molecule cm<sup>-3</sup> and for an exposure of 12  
421 h per day (Atkinson, 1991)

422 Degradation rate constants measured or modeled for pesticides in the gas-phase exposed to  
423 NO<sub>3</sub> radicals range from  $10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> to  $10^{-16}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> (Table 2) (  
424 Goodman et al., 1988; Aschmann et al., 2005a, 2005b; Aschmann and Atkinson, 2006; Liu et  
425 al., 2014; Cheng et al., 2017). Heterogeneous reactivity showed degradation rate constants of  
426 about  $10^{-15}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> (this study). These differences in degradation rates between  
427 gas-phase and particle-phase were expected. Indeed, pesticide's degradation has been  
428 demonstrated to be different in the particle-phase and in the gas-phase in case of their  
429 degradation by OH radicals (Socorro et al., 2016), as well as by ozone (Socorro et al., 2015).

430 **Comparison with the degradation mechanism by OH radicals**



431 NO<sub>3</sub> radicals typically react with organic compounds by electrophilic addition onto aliphatic  
432 or aromatic double bond (Knopf et al., 2011; Liu et al., 2012; Lauraguais et al., 2016; Zhang  
433 et al., 2016) or via an H-abstraction although this second mechanism is generally less favored  
434 ( Wayne et al., 1991; Finlayson-Pitts and Pitts, 2009). Those mechanisms are the same as  
435 those governing the reactivity with OH radicals ( George and Abbatt, 2010; Borrás et al.,  
436 2015). Both of those mechanisms are likely to happen on the pesticides under study,  
437 considering their molecular structure (Figure S1). Yet, while this work shows the effective  
438 heterogeneous degradation of all pesticides under study by nitrate radicals, only four of them  
439 (cyprodinil, deltamethrin, permethrin, and pendimethalin) were heterogeneously degraded by  
440 OH radicals in similar experimental conditions (i.e., RH and hydrophobic silica particles)  
441 (Socorro et al., 2016). This difference in reactivity despite the similarity of the mechanisms  
442 could be the result of the longer life time of nitrate radicals compared to the hydroxyl radicals,  
443 leading to differences in diffusion velocity of radicals, which allows some pesticides to be  
444 accessible to nitrate radicals. Additionally, even though the mechanism is similar in theory,  
445 their probability to occur on a given molecular function might differ according to the oxidant.  
446 For instance, triazole reactivity toward OH radicals in the gas phase is considered as a very  
447 slow reaction at ambient temperature (Derbel et al., 2018), which might explain the non-  
448 degradation of tetraconazole and difenoconazole with OH radicals, however, tetraconazole is  
449 the fastest degraded pesticide by NO<sub>3</sub> radicals, showing that the probability of reactions are  
450 different between OH and NO<sub>3</sub> radicals.

### 451 **Atmospheric implications**

452 Second-order rate constants calculated for the heterogeneous reactivity of pesticides under  
453 study with NO<sub>3</sub> radicals were of the order of magnitude of 10<sup>-15</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, which is  
454 faster than those obtained for the heterogeneous reactivity of the same pesticides with ozone  
455 (i.e.,  $k_{NO_3(part)}^{II} \sim 10^{-18}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) (Mattei et al., 2018) but slower than those obtained

456 for the heterogeneous reactivity with OH radicals (i.e.,  $k_{OH(part)}^{II} \sim 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )  
457 (Socorro et al., 2016). Thus, NO<sub>3</sub> radicals can have a significant influence on the atmospheric  
458 fate of pesticides in particle-phase.

459 Considering an average NO<sub>3</sub> radicals concentration of 20 ppt over 12 hours (Atkinson, 1991),  
460 the half-lives in particle-phase regarding NO<sub>3</sub> radical oxidation calculated for the pesticides  
461 under study vary from 7.6 days (tetraconazole) to 16.1 days (pendimethalin) for an L-R  
462 mechanism, and from 2.4 day (tetraconazole) to 10.9 days (oxadiazon) for an L-H mechanism  
463 (Table 1). Half-lives previously measured for the same pesticides varied from 0.4 days to 91  
464 days for ozone (40 ppb, 24/24 h exposure) (Mattei et al., 2018) and from 0.1 days to 9 days  
465 for OH radicals (0.06 ppt, 12/24 h exposure) (Socorro et al., 2016). The comparison of those  
466 order of magnitude is in accordance with the literature available on the reactivity of other  
467 volatile organic compounds, such as polycyclic aromatic compounds, assessing that the  
468 heterogeneous reactivity with NO<sub>3</sub> radicals is at least as important as the heterogeneous  
469 reactivity with OH radicals or ozone (Shiraiwa et al., 2009; Kaiser et al., 2011).

470 These half-lives in particle-phase of difenoconazole, tetraconazole, fipronil, oxadiazon,  
471 deltamethrin, cyprodinil, permethrin, and pendimethalin, imply that these pesticides can be  
472 transported over long distances, reaching remote regions all over the world. Obtained values  
473 show that atmospheric heterogeneous degradation of pesticides, and in a greater extent of  
474 semi-volatile organic compounds, is of significant importance for nighttime atmospheric  
475 chemistry processes.

476 In this study, the heterogeneous reactivity of pesticides was investigated on model silica  
477 particles. However, NO<sub>3</sub> radicals uptake on surfaces depend on the substrate nature (Moise et  
478 al., 2002; Karagulian and J. Rossi, 2005; Gross et al., 2009) and reactive uptake of NO<sub>3</sub>  
479 radicals on organic surfaces can vary by three orders of magnitude according to the surface

480 type (George and Abbatt, 2010). Moreover, experiments were conducted only at 40% RH, but  
481 the relative humidity level could also change the degradation rates indirectly by influencing  
482 the uptake of NO<sub>3</sub> radicals by competition mechanisms, as heterogeneous reactivity  
483 degradation by ozone was already described as dependent on the relative humidity (Pöschl et  
484 al., 2001; Kaiser et al., 2011; Mattei et al., 2018).

485 Finally, it is expected that degradation of the pesticides under study leads to the formation of  
486 nitrogenated compounds such as hydroxyl nitrate or carbonylnitrate compounds through  
487 nitrooxyradicals intermediates or to the formation of a carbonyl or hydroxyl-substituted  
488 compounds (Kwok et al., 1995; Perring et al., 2009). These degradation products were not  
489 detected in samples possibly because of their thermolability, their volatilization or their too  
490 low concentrations. As observed for the heterogeneous degradation of the same pesticides by  
491 ozone (Socorro et al., 2016), the degradation products can be of different health and  
492 environmental effects than the parent pesticides. They should be included in the evaluation  
493 studies of air quality.

494

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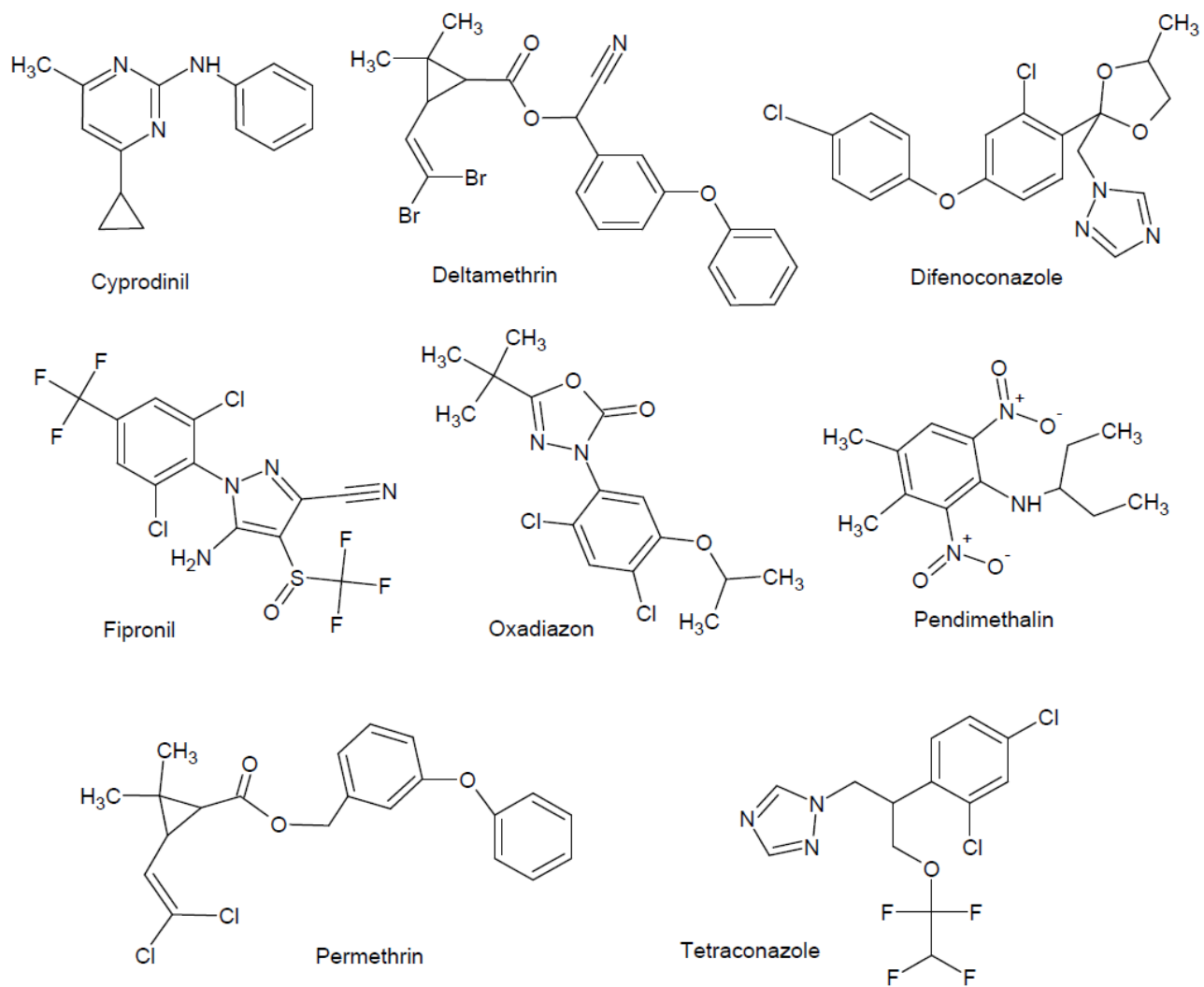
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761 SUPPORTING INFORMATION

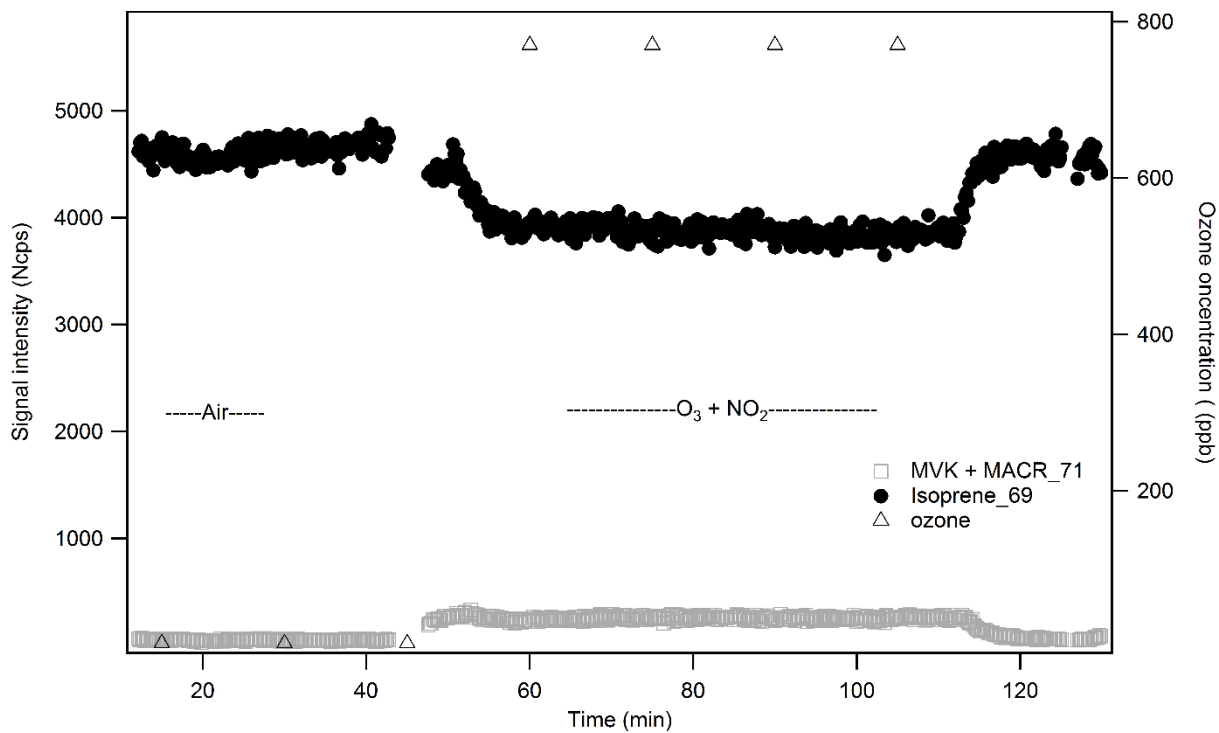
762 Pesticides under study



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766 Figure S1: Chemical structures of the 8 pesticides under study



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768 Figure S2: PTR-MS signal intensity for isoprene ( $m/z=69$ ) and its main degradation product

769 ( $m/z=71$ ) under different oxidation conditions, at 43% RH

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Table S1: The physicochemical properties of the pesticides

Compounds	Cyprodinil	Deltamethrin	Difenoconazole	Fipronil	Oxadiazon	Pendimethalin	Permethrin	Tetraconazole
<b>CAS number</b>	121552-61-2	52918-63-5	119446-68-3	120068-37-3	19666-30-9	40487-42-1	52645-53-1	112281-77-3
<b>Chemical family</b>	Pyrimidine	Pyrethroid	Triazole	Pyrazole	Oxadiazole	Dinitroaniline	Pyrethroid	Triazole
<b>Nature</b>	Fungicide	Insecticide	Fungicide	Insecticide	Herbicide	Herbicide	Insecticide	Fungicide
<b>Molecular weight (g mol<sup>-1</sup>)</b>	225.29	505.20	406.26	437.15	345.22	281.31	391.29	372.15
<b>Vapour pressure at 25°C (Pa)<sup>a</sup></b>	5.1·10 <sup>-4</sup>	1.2·10 <sup>-8</sup>	3.3·10 <sup>-8</sup>	2.0·10 <sup>-6</sup>	6.7·10 <sup>-4</sup>	1.9·10 <sup>-3</sup>	7.0·10 <sup>-6</sup>	1.8·10 <sup>-4</sup>
<b>Henry's constant at 25°C (atm m<sup>3</sup> mol<sup>-1</sup>)<sup>b</sup></b>	1.91·10 <sup>-6</sup>	6.06·10 <sup>-8</sup>	1.69·10 <sup>-11</sup>	3.17·10 <sup>-18</sup>	3.22·10 <sup>-8</sup>	1.45·10 <sup>-6</sup>	2.88·10 <sup>-7</sup>	6.20·10 <sup>-7</sup>
<b>Molar volume (cm<sup>3</sup> mol<sup>-1</sup>) at 20°C and 760 Torr<sup>c</sup></b>	186.1 ± 3.0	316.7 ± 3.0	287.1 ± 7.0	233.6 ± 7.0	262.4 ± 7.0	231.5 ± 3.0	302.5 ± 3.0	247.1 ± 7.0
<b>Partitioning in particle phase<sup>d</sup></b>	0.07	0.91	0.99	0.84	0.62	0.01	0.97	0.38
<b>Solubility in water at 20°C (mg L<sup>-1</sup>)<sup>a</sup></b>	13	0.0002	15	3.78	0.57	0.33	0.2	156.6
<b>Characteristic ions</b>	224.05 / 225.10 / 210.03	180.92 / 250.88 / 171.82	322.91 / 324.86	366.87 / 368.84 / 212.87	174.85 / 176.84 / 257.97	252.03 / 161.94	182.98 / 164.84	335.96 / 337.91

<sup>a</sup> PPDB: Pesticide Properties DataBase ([sitem.herts.ac.uk/aeru/ppdb](http://sitem.herts.ac.uk/aeru/ppdb))

<sup>b</sup> HENRYWIN<sup>TM</sup> Software V3.2

<sup>c</sup> SciFinder, calculated using Advanced Chemistry Development (ACD/Labs) Software V11.02 (© 1994-2014 ACD/Labs)

<sup>d</sup> AEROWIN<sup>TM</sup> Software V1.0 using the Junge-Pankow adsorption mode

## 1 Silica particles coating

2 A uniform particle surface coverage and a coating below a monolayer are assumed to  
3 calculate the amount of pesticide adsorbed on the silica particle surface. The particle is  
4 considered as a sphere and its radius ( $r_i$ , cm) is calculated by eq S1:

$$5 \quad r_i = \sqrt[3]{\frac{3 \times V_m}{4 \times \pi \times N_A}} \quad (\text{S1})$$

6 where  $V_m$  is the molar volume ( $\text{cm}^3 \cdot \text{mol}^{-1}$ ) of pesticide and  $N_A$  is the Avogadro number. The  
7 molar volume is calculated using Advanced Chemistry Development (ACD/Labs) Software  
8 V11.02 (© 1994-2014 ACD/Labs).

9  $S$  is the surface ( $\text{cm}^2$ ) defined by eq S2 where  $n$  is adsorbed pesticide in mole:

$$10 \quad S = 4 \times \pi \times r_i^2 \times N_A \times n \quad (\text{S2})$$

11 The percentage of the coated aerosol surface  $T$  is described by equation S3:

$$12 \quad T = \frac{S}{S_1} \times 100 \quad (\text{S3})$$

13 where  $S_1$  is the silica particle surface ( $\text{m}^2 \text{g}^{-1}$ ).

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15 Table S2: Kinetic constants for the possible reactions in the reactor

Reaction	Kinetic constant (cm <sup>3</sup> molecules <sup>-1</sup> s <sup>-1</sup> )	Reference
O <sub>3</sub> + NO <sub>2</sub> → NO <sub>3</sub> + O <sub>2</sub>	(3.50 ± 0.87) × 10 <sup>-17</sup>	Graham et al., 1974, Huie et al., 1974, Davis et al., 1974
NO <sub>3</sub> + isoprene → Products	(6.5 ± 0.2) × 10 <sup>-13</sup>	Atkinson et al., 1984, Berndt et al., 1997, Stabel et al., 2005, Zhao et al., 2011, Suh et al., 2001, Wille et al., 1991, Dlugokencky et al., 1989
O <sub>3</sub> + isoprene → Products	(9.6 ± 0.7) × 10 <sup>-18</sup>	Karl et al., 2004
NO <sub>2</sub> + isoprene → Products	(10.3 ± 0.3) × 10 <sup>-20</sup>	Atkinson, 1984
NO <sub>3</sub> + O <sub>3</sub> → Products	1 · 10 <sup>-17</sup>	Hjorth et al., 1992
NO <sub>3</sub> + NO <sub>2</sub> → O <sub>2</sub> + NO + NO <sub>2</sub>	6.56 · 10 <sup>-16</sup>	DeMore, 1997

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