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Heterogeneous atmospheric degradation of current-use pesticides by nitrate radicals

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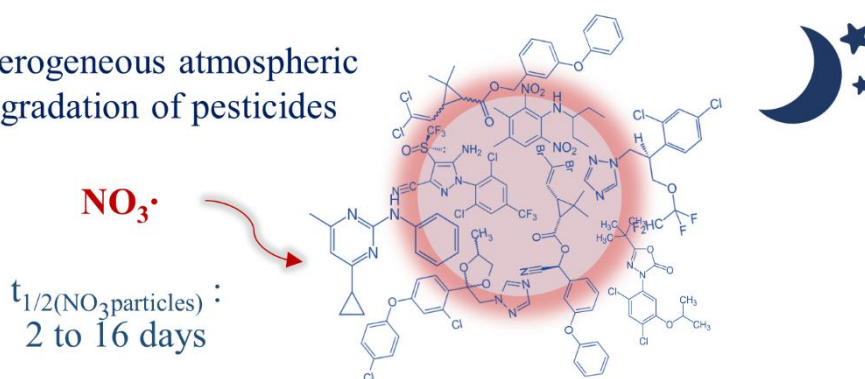
22 ABSTRACT

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 NO₃ radicals
- 46 • Current-use pesticide studied were degraded by NO₃ radicals in the particle phase
- 47 • Heterogeneous half-lives of pesticides toward NO₃ radicals range from 2 to 16 days
- 48 • NO₃ 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, AOPWINTM 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 (O₃), hydroxyl radicals (OH), and nitrate radicals
69 (NO₃). 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 NO₃ radicals compared to
80 OH radicals leads to a similar or greater oxidation power of NO₃ (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 10⁻¹⁴ cm³
85 molecule⁻¹ s⁻¹ and 10⁻¹² cm³ molecule⁻¹ s⁻¹, which correspond to heterogeneous half-life
86 regarding NO₃ radicals of a few hours. This suggests a significant degradation of pesticides by
87 NO₃ 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 NO₃ 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 NO₃ radicals concentrations (48 ppt to 635 ppt), temperature (25°C) and relative humidity
100 (40% RH) conditions.

101

102 **EXPERIMENTAL SECTION**

103 **Chemicals**

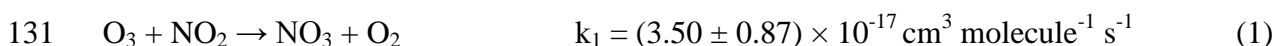
104 Isoprene (purity > 99.5%) and the eight pesticides (PESTANAL®, analytical standard) :
105 cyprodinil (99.8%), deltamethrin (99.7%), difenoconazole (97.0%), fipronil (97.5%),
106 oxadiazon (99.9%), pendimethalin (98.8%), permethrin (98.3%), and tetraconazole (99.0%)
107 were purchased from Sigma-Aldrich 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 SiO₂ content > 99.8 wt%, mean primary particle size ranges from 5 nm to 50
114 nm, specific surface area (BET method) of (260 ± 30) m² g⁻¹ (Evonik, 2015)) were coated
115 with pesticides according to a liquid/solid adsorption. In an amber Pyrex bulb of 500 cm³, 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⁻¹ 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 NO₃ 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 NO₃ radicals (Doussin, 2003; Boyd et al., 2015; Nah et al., 2016),
129 measurement of NO₃ 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 NO₂ 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⁻¹. The reaction
135 between NO₂ and O₃ occurred inside the bulb where pesticides were exposed to oxidants

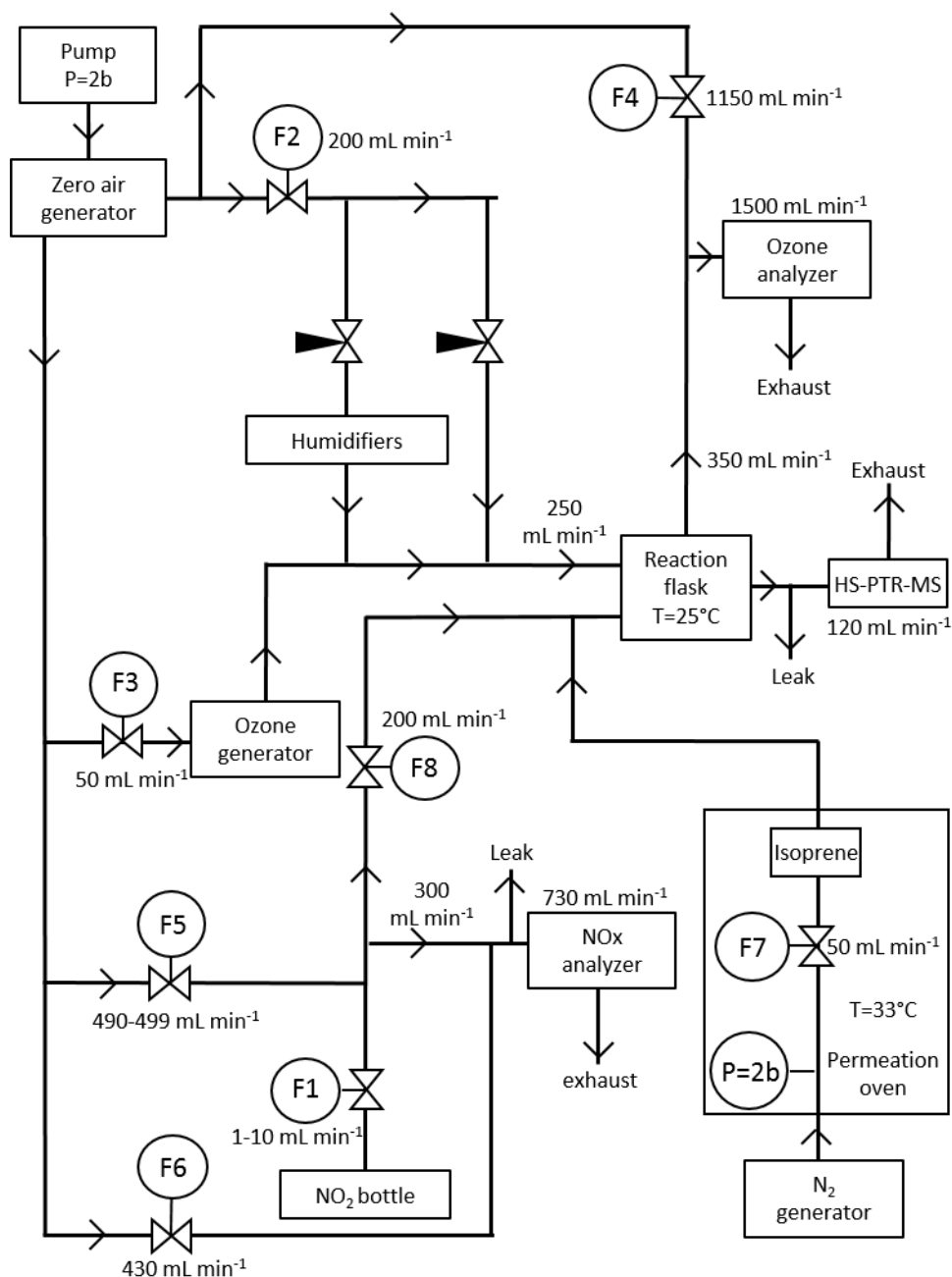
136 (Figure 1). A constant NO₂ gaseous flow (F1), (F1 to F8, all Brooks SLA Series mass flow
137 controller; accuracy, ±1%) was generated from a gas cylinder (a certified mixture of NO₂ (100
138 ppm) in Helium, Linde gas 5.0). Successive dilutions of NO₂ flux (from 1 mL min⁻¹ to 10 mL
139 min⁻¹) with purified air (zero air generator ZA-1500, F-DGS; F5, 490-499 mL min⁻¹) were
140 made to provide the specified NO₃ radicals concentration. The NO₂ 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_x, NO₂, and NO concentrations.

144 Ozone was generated with a constant flow (F3) of 50 mL min⁻¹ 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⁻³ (i.e., (760
148 ± 60) ppb). The ozone concentrations were monitored continuously online by a photometric
149 ozone analyzer (O₃ 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⁻¹) 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 NO_2 and O_3 and between NO_3 radicals and isoprene as well as to minimize
162 all other possible reactions such as O_3 with isoprene, NO_2 with isoprene, NO_3 radicals with
163 O_3 , or NO_3 radicals with 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_3 radicals.

172

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

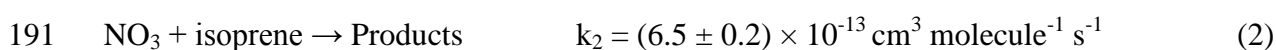
174 $(1.19 \pm 0.06) \times 10^9$ molecule cm^{-3} to $(1.59 \pm 0.11) \times 10^{10}$ molecule cm^{-3} (i.e., from 48 to 635

175 ppt). In the atmosphere, NO_3 radicals are predominantly formed by the reaction of nitrogen

176 dioxide (NO₂) with ozone (O₃). 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., 2.5×10^7 molecule
180 cm⁻³ and 3.75×10^9 molecule cm⁻³) and can reach up to 420 ppt (Atkinson et al., 1985), or
181 even 800 ppt (Asaf et al., 2010) (i.e., 2×10^{10} molecule cm⁻³) 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 O₂ can indirectly influence the degradation mechanism of organic compounds
185 by NO₃ radicals (Docherty and Ziemann, 2006) and might, therefore, influence the kinetics as
186 well.

187 **Indirect measurement of NO₃ radicals**

188 Isoprene was used as a gaseous tracer to determine the NO₃ radicals concentrations (Zhang et
189 al., 2016) (eq 2). It was chosen for its effective and well-described reactivity with NO₃
190 radicals.



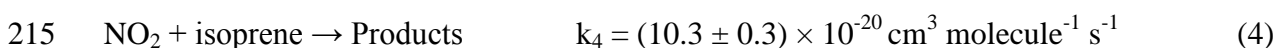
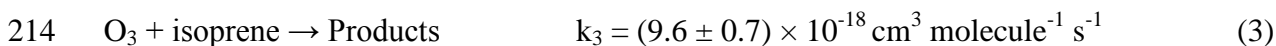
192 where k_2 is the average rate constant for the reaction (Atkinson et al., 1984; Dlugokencky and
193 Howard, 1989; Wille et al., 1991; Berndt and Böge, 1997; Suh et al., 2001; Stabel et al., 2005;
194 Zhao et al., 2011).

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 N₂) to pass through. N₂
200 was generated by a Domnick Hunter Nitrox UHPLCMS12 nitrogen generator, at 99.5% purity

201 (0.5% O₂). A pure N₂ constant flow (F7) continuously passed at a rate of 50 mL min⁻¹ 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_{drift} = 600 V, T_{drift} = 50 °C,
 208 P_{drift} = 2.02 mbar. U_{drift} is the electric potential applied to the drift tube; T_{drift} and P_{drift} are the
 209 temperature and the pressure in the drift tube, respectively. E is the strength of the electrical
 210 field in V cm⁻¹ and N is the gas number density in cm³. The ratio E/N in Townsend (1
 211 Townsend = 10⁻¹⁷ cm² V⁻¹) is a defining characteristic of the drift tube.

212 Isoprene reacts in the bulb with NO₃ radicals (eq 2), but can also react with O₃ (eq 3), and
 213 NO₂ (eq 4) as follows:



216 where k₃ and k₄ are the rate constants for the reaction of isoprene with O₃ (Karl et al., 2004)
 217 and NO₂ (Atkinson et al., 1984), respectively.

218 The NO₃ 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 NO₃ 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 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 NO_3 radicals (eq 2), k_3 is the rate constant of
229 the reaction between isoprene and O_3 (eq 3), and k_4 is the rate constant of the reaction
230 between isoprene and NO_2 (eq 4).

231 **Extraction and pesticides quantification**

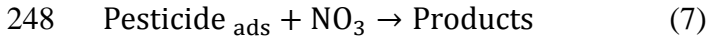
232 During exposure, 30 mg aliquots of particles were regularly sampled in order to quantify the
233 remaining adsorbed pesticides on their surface. Each 30 mg aliquot of particles was
234 individually extracted by accelerated solvent extraction (ASE 350, Dionex) with
235 dichloromethane. For this purpose, 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).

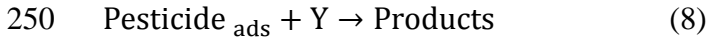
243 More details about ASE extraction, concentration, and GC/MS-MS analysis are available
244 elsewhere (Socorro et al., 2015).

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 NO_3
247 radicals with a pesticide, the following procedure was applied:



249 All degradation reactions of a pesticide not initiated by NO₃ 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 NO₃ radicals with unsaturated volatile organic compounds could lead to the formation of HO₂
 254 or OH radicals (Canosa-Mas et al., 1999; Salisbury, 2001). Also the combination of NO₃
 255 radical and NO₂ could lead to the formation of N₂O₅ which is known to be heterogeneously
 256 reactive with organic compounds (Knopf et al., 2011). However, according to the
 257 concentrations of NO₂ and NO₃ in the reactor and the kinetic constants (Table SI2) leading to
 258 the formation of N₂O₅, the formation of N₂O₅ 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} (cm³ molecule⁻¹ s⁻¹) are the second-order rate constants of the
 263 heterogeneous reactions with NO₃ radicals and all other species different than NO₃ radicals,
 264 respectively. $k_{des(part)}^I$ (s⁻¹) is the first order kinetic desorption rate constant and $k_{hydr(part)}^I$ (s⁻¹)
 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 5×10^8 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 5×10^8 molecule cm^{-3} and an exposure time of 12 h,
310 as presented previously.

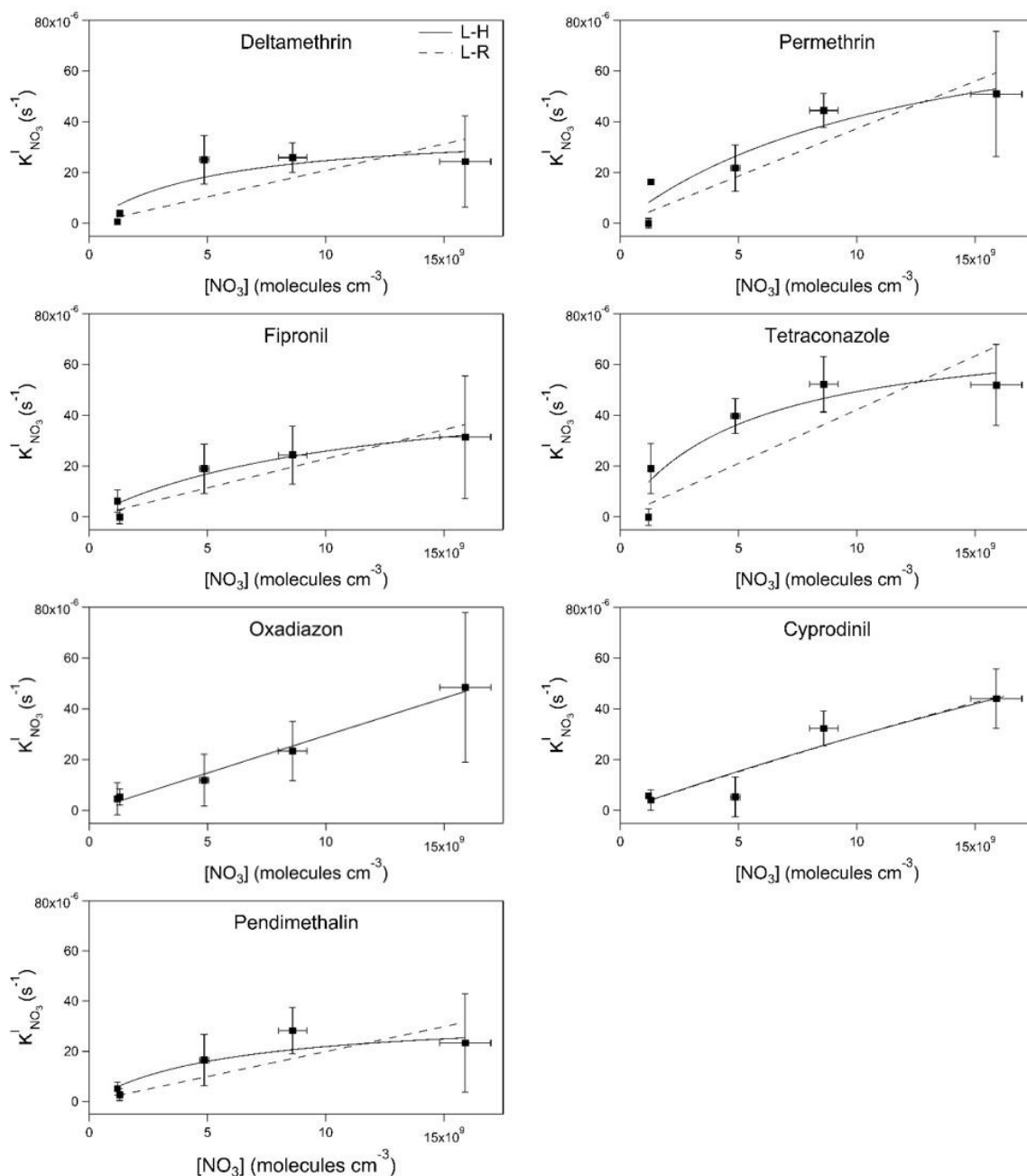
311 RESULTS AND DISCUSSION

312 Heterogeneous reactivity kinetics

313 Oxidation experiments were conducted for five nitrate radicals concentrations (i.e., (1.2 ± 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 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 cm^{-3} to $(1.6 \pm 0.1) \times 10^{10}$ molecule 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 NO₃ 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 NO₃ radicals

Chemical Family	Pesticide	Relative humidity (%)	Temperature (°C)	NO ₃ radical concentration (molecule cm ⁻³)	Surface	Langmuir - Rideal model		Langmuir - Hinshelwood model			Reference
						$k_{NO_3(part)}^H$ (cm ³ molecule ⁻¹ s ⁻¹)	t _{1/2} NO _{3(part)} (d)	k _(max) (s ⁻¹)	K _{NO3} (cm ³ molecule ⁻¹)	t _{1/2} NO _{3(part)} (d)	
Carbamate	Carbaryl	~ 10	25	Unknown	Azelaic acid	4.4×10^{-13}	0.7	/			Yang et al. (2011)
Dinitroaniline	Pendimethalin	40 ± 2	25 ± 1	(1.2 – 16.0) × 10⁹	Hydrophobic silica	(1.99 ± 0.42) × 10⁻¹⁵	16.1	(3.47 ± 1.33) × 10⁻⁵	(1.71 ± 1.57) × 10⁻¹⁰	5.6	This work
Organophosphorus	Chlorpyrifos	~ 40	~ 15	(5.0 ± 0.3) × 10 ¹⁰	Azelaic acid	(3.4 ± 0.2) × 10 ⁻¹²	0.09	/			Li et al. (2014)
	Fenthion	~ 5	~ 20	10 ¹¹ – 10 ¹²	Azelaic acid	$3.3 \times 10^{-14} - 3.3 \times 10^{-13}$	0.9 – 9.3	/			Liu et al. (2012)
	Malathion	~ 5	~ 20	10 ¹¹ – 10 ¹²	Azelaic acid	$5.6 \times 10^{-14} - 5.6 \times 10^{-13}$	0.6 – 5.5	/			Liu et al. (2012)
	Parathion	~ 5	~ 20	10 ¹¹ – 10 ¹²	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 ⁹	Azelaic acid	$(2.97 \pm 0.13) \times 10^{-12}$	0.1	/			Liu et al. (2015)
	Phosmet	~ 5	~ 20	10 ¹¹ – 10 ¹²	Azelaic acid	$(1.92 \pm 0.09) \times 10^{-12}$	0.2	/			Liu et al. (2011)
	Phosmet	~ 5	~ 20	(2.7 – 8.5) × 10 ⁹	Azelaic acid	$(2.80 \pm 0.16) \times 10^{-12}$	0.1	/			Liu et al. (2015)
Oxadiazole	Oxadiazon	40 ± 2	25 ± 1	(1.2 – 16.0) × 10⁹	Hydrophobic silica	(2.95 ± 0.12) × 10⁻¹⁵	10.9	(1.71 ± 1.69) × 10⁻²	(1.72 ± 1.70) × 10⁻¹³	10.9	This work
Pyrazole	Fipronil	40 ± 2	25 ± 1	(1.2 – 16.0) × 10⁹	Hydrophobic silica	(2.29 ± 0.31) × 10⁻¹⁵	14	(5.45 ± 1.89) × 10⁻⁵	(9.05 ± 5.97) × 10⁻¹¹	6.7	This work

Pyrethroid	Deltamethrin	40 ± 2	25 ± 1	(1.2 – 16.0) × 10⁹	Hydrophobic silica	(2.08 ± 0.51) × 10⁻¹⁵	15.4	(3.75 ± 1.52) × 10⁻⁵	(1.93 ± 1.98) × 10⁻¹⁰	4.6	This work
	Fenvalerate	~ 5	~ 25	(1.5 – 10.2) × 10 ⁹	Azelaic acid	(1.86 ± 0.04) × 10 ⁻¹²	0.2	/			Wang et al. (2013)
	Permethrin	40 ± 2	25 ± 1	(1.2 – 16.0) × 10⁹	Hydrophobic silica	(3.73 ± 0.52) × 10⁻¹⁵	8.6	(9.48 ± 4.75) × 10⁻⁵	(7.93 ± 7.21) × 10⁻¹¹	4.4	This work
	Phenothrin	~ 5	~ 25	(1.5 – 10.2) × 10 ⁹	Azelaic acid	(1.61 ± 0.03) × 10 ⁻¹²	0.2	/			Wang et al. (2013)
	Resmethrin	~ 5	~ 25	(1.5 – 10.2) × 10 ⁹	Azelaic acid	(5.54 ± 0.14) × 10 ⁻¹²	0.1	/			Wang et al. (2013)
Pyrimidine	Cyprodinil	(0-80) ± 2	25 ± 1	(1.2 – 16.0) × 10⁹	Hydrophobic silica	(2.87 ± 0.32) × 10⁻¹⁵	11.2	(0.39 ± 1.62) × 10⁻³	(0.81 ± 3.70) × 10⁻¹¹	10.1	This work
	Pyrimicarb	~ 10	~ 25	(0.6 – 7.0) × 10 ⁹	Azelaic acid	(7.5 ± 0.3) × 10 ⁻¹³	0.4	/			Wang et al. (2012)
	Pirimophos-methyl	~ 10	~ 25	(0.6 – 7.0) × 10 ⁹	Azelaic acid	(9.9 ± 0.3) × 10 ⁻¹²	0.03	/			Wang et al. (2012)
Triazine	Ametryn	~ 5	~ 25	(0.7 – 7.9) × 10 ¹⁰	Azelaic acid	8.4 × 10 ⁻¹³	0.4	/			Liu et al. (2014)
Triazole	Difenoconazole	40 ± 2	25 ± 1	(1.2 – 16.0) × 10⁹	Hydrophobic silica	/	/	/			This work
	Tetraconazole	40 ± 2	25 ± 1	(1.2 – 16.0) × 10⁹	Hydrophobic silica	(4.22 ± 0.69) × 10⁻¹⁵	7.6	(7.59 ± 2.36) × 10⁻⁵	(1.85 ± 1.43) × 10⁻¹⁰	2.4	This work

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 NO₃ 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 NO₃ radicals give second-order rate constants ranged between 10⁻¹⁴ cm³
369 molecule⁻¹ s⁻¹ and 10⁻¹² cm³ molecule⁻¹ s⁻¹ (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 10⁻¹⁵ cm³ molecule⁻¹ s⁻¹). 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 10⁻¹⁴ cm³ molecule⁻¹ s⁻¹ and 10⁻¹² cm³ molecule⁻¹ s⁻¹. 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 NO₃ 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 NO₃ radicals. From a mechanistic point of view,
397 the nitration of a double bond (electrophilic addition of NO₃ radical, followed by an addition
398 of NO₂ molecule and an elimination of HNO₃ molecule, leading to the formation of a NO₂
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 NO₃
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 NO₃
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 NO₃ 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 NO₃ 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 ³ molecule ⁻¹ s ⁻¹)	$t_{1/2} NO_3(part)$ (d)	Reference
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Carbamate	Carbaryl ^a	25	3.37×10^{-13}	0.1	Cheng et al. (2017)
Organochlorine	DDT ^a	25	4.01×10^{-15}	8.0	Liu et al. (2014)
Organophosphorus	DEEP ^b	25 ± 2	$(3.4 \pm 1.4) \times 10^{-16}$	94.4	Aschmann et al. (2005a)
	DEMP ^b	25 ± 2	$(3.7 \pm 1.1) \times 10^{-16}$	86.7	Aschmann et al. (2005a)
	DEMPT ^b	23 ± 2	$(2.01 \pm 0.20) \times 10^{-15}$	16.0	Aschmann et al. (2006)
	DMEP ^b	25 ± 2	$(3.4 \pm 1.4) \times 10^{-16}$	94.4	Aschmann et al. (2005b)
	DMHP ^b	25 ± 2	$< 1.4 \times 10^{-16}$	> 229.2	Aschmann et al. (2005b)
	DMMP ^b	25 ± 2	$(2.0 \pm 1.0) \times 10^{-16}$	160.5	Aschmann et al. (2005b)
	IMMP ^b	23 ± 2	$(4.8 \pm 2.1) \times 10^{-16}$	66.9	Aschmann et al. (2010)
	TEP ^b	25 ± 2	$(2.4 \pm 1.4) \times 10^{-16}$	133.7	Aschmann et al. (2005a)
	TEPT ^b	23 ± 2	$(1.03 \pm 0.10) \times 10^{-15}$	31.2	Aschmann et al. (2006)
	TMP ^b	25 ± 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 ^a NO₃ radicals concentration calculated theoretically, ^b NO₃ radicals concentration unknown

420 Atmospheric half-lives calculated for an average concentration $[NO_3]_{(gas)} = 5 \times 10^8$ molecule cm⁻³ 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 NO₃ radicals range from 10^{-13} cm³ molecule⁻¹ s⁻¹ to 10^{-16} cm³ molecule⁻¹ s⁻¹ (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} cm³ molecule⁻¹ s⁻¹ (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 NO₃ 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 NO₃ radicals, showing that the probability of reactions are
450 different between OH and NO₃ radicals.

451 **Atmospheric implications**

452 Second-order rate constants calculated for the heterogeneous reactivity of pesticides under
453 study with NO₃ radicals were of the order of magnitude of 10⁻¹⁵ cm³ molecule⁻¹ s⁻¹, which is
454 faster than those obtained for the heterogeneous reactivity of the same pesticides with ozone
455 (i.e., $k_{NO_3(part)}^{II} \sim 10^{-18}$ cm³ molecule⁻¹ s⁻¹) (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, NO₃ radicals can have a significant influence on the atmospheric
458 fate of pesticides in particle-phase.

459 Considering an average NO₃ radicals concentration of 20 ppt over 12 hours (Atkinson, 1991),
460 the half-lives in particle-phase regarding NO₃ 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 NO₃ 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, NO₃ 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 NO₃
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 NO₃ 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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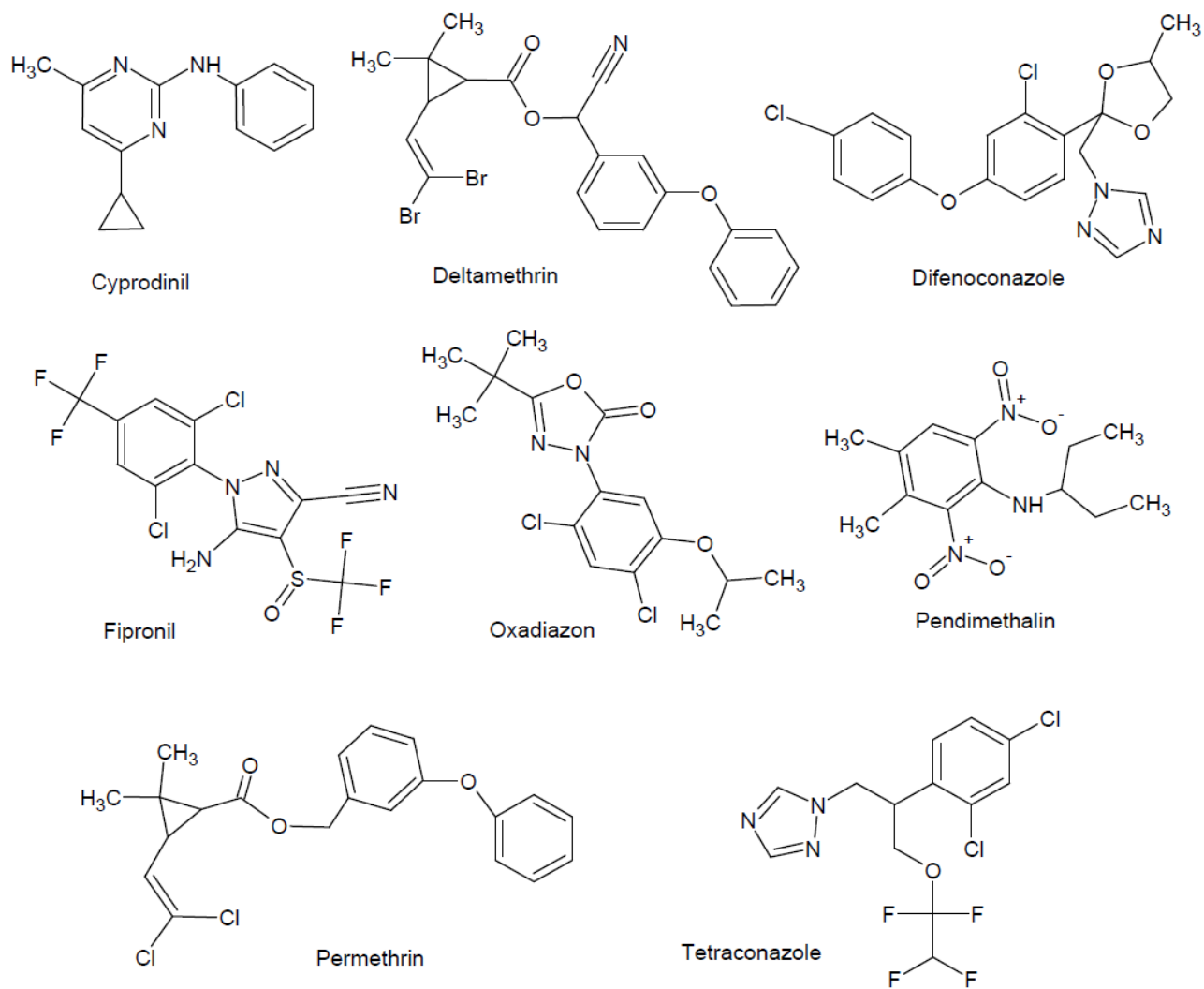
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761 **SUPPORTING INFORMATION**

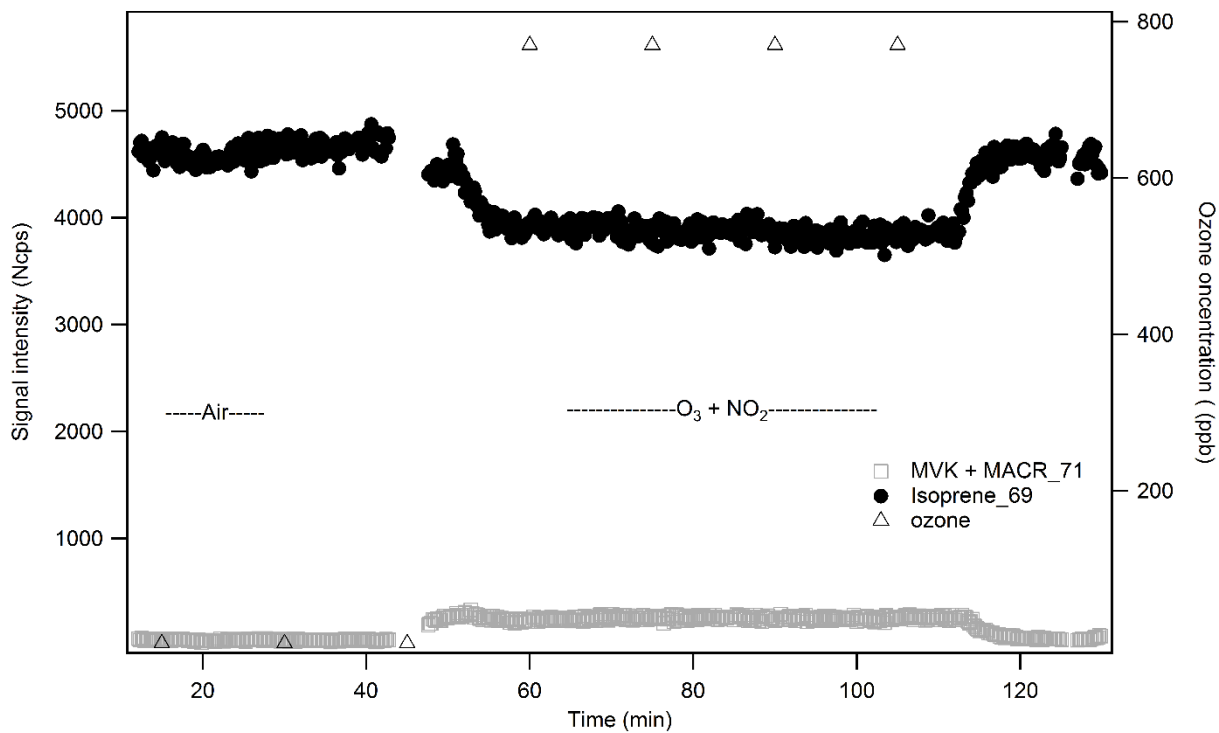
762 **Pesticides under study**



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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

770

Table S1: The physicochemical properties of the pesticides

Compounds	Cyprodinil	Deltamethrin	Difenoconazole	Fipronil	Oxadiazon	Pendimethalin	Permethrin	Tetraconazole
CAS number	121552-61-2	52918-63-5	119446-68-3	120068-37-3	19666-30-9	40487-42-1	52645-53-1	112281-77-3
Chemical family	Pyrimidine	Pyrethroid	Triazole	Pyrazole	Oxadiazole	Dinitroaniline	Pyrethroid	Triazole
Nature	Fungicide	Insecticide	Fungicide	Insecticide	Herbicide	Herbicide	Insecticide	Fungicide
Molecular weight (g mol⁻¹)	225.29	505.20	406.26	437.15	345.22	281.31	391.29	372.15
Vapour pressure at 25°C (Pa)^a	5.1·10 ⁻⁴	1.2·10 ⁻⁸	3.3·10 ⁻⁸	2.0·10 ⁻⁶	6.7·10 ⁻⁴	1.9·10 ⁻³	7.0·10 ⁻⁶	1.8·10 ⁻⁴
Henry's constant at 25°C (atm m³ mol⁻¹)^b	1.91·10 ⁻⁶	6.06·10 ⁻⁸	1.69·10 ⁻¹¹	3.17·10 ⁻¹⁸	3.22·10 ⁻⁸	1.45·10 ⁻⁶	2.88·10 ⁻⁷	6.20·10 ⁻⁷
Molar volume (cm³ mol⁻¹) at 20°C and 760 Torr^c	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
Partitioning in particle phase^d	0.07	0.91	0.99	0.84	0.62	0.01	0.97	0.38
Solubility in water at 20°C (mg L⁻¹)^a	13	0.0002	15	3.78	0.57	0.33	0.2	156.6
Characteristic ions	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

^a PPDB: Pesticide Properties DataBase (sitem.herts.ac.uk/aeru/ppdb)

^b HENRYWINTM Software V3.2

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

^d AEROWINTM 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 (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 ($\text{m}^2 \text{g}^{-1}$).

14

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

Reaction	Kinetic constant (cm ³ molecules ⁻¹ s ⁻¹)	Reference
O ₃ + NO ₂ → NO ₃ + O ₂	(3.50 ± 0.87) × 10 ⁻¹⁷	Graham et al., 1974, Huie et al., 1974, Davis et al., 1974
NO ₃ + isoprene → Products	(6.5 ± 0.2) × 10 ⁻¹³	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 ₃ + isoprene → Products	(9.6 ± 0.7) × 10 ⁻¹⁸	Karl et al., 2004
NO ₂ + isoprene → Products	(10.3 ± 0.3) × 10 ⁻²⁰	Atkinson, 1984
NO ₃ + O ₃ → Products	1 · 10 ⁻¹⁷	Hjorth et al., 1992
NO ₃ + NO ₂ → O ₂ + NO + NO ₂	6.56 · 10 ⁻¹⁶	DeMore, 1997

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