

Influence of pesticide concentration on their heterogeneous atmospheric degradation by ozone

Coraline Mattei, Julien Dupont, Henri Wortham, Etienne Quivet

► **To cite this version:**

Coraline Mattei, Julien Dupont, Henri Wortham, Etienne Quivet. Influence of pesticide concentration on their heterogeneous atmospheric degradation by ozone. *Chemosphere*, Elsevier, 2019, 228, pp.75-82. 10.1016/j.chemosphere.2019.04.082 . hal-02107106

HAL Id: hal-02107106

<https://hal.archives-ouvertes.fr/hal-02107106>

Submitted on 23 Apr 2019

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Accepted Manuscript

Influence of pesticide concentration on their heterogeneous atmospheric degradation by ozone

Coraline Mattei, Julien Dupont, Henri Wortham, Etienne Quivet



PII: S0045-6535(19)30729-5

DOI: <https://doi.org/10.1016/j.chemosphere.2019.04.082>

Reference: CHEM 23590

To appear in: *ECSN*

Received Date: 28 February 2019

Revised Date: 8 April 2019

Accepted Date: 11 April 2019

Please cite this article as: Mattei, C., Dupont, J., Wortham, H., Quivet, E., Influence of pesticide concentration on their heterogeneous atmospheric degradation by ozone, *Chemosphere* (2019), doi: <https://doi.org/10.1016/j.chemosphere.2019.04.082>.

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

1 **Influence of pesticide concentration on their heterogeneous atmospheric**
2 **degradation by ozone**

3
4
5
6 Coraline MATTEI ^{a,b}, Julien DUPONT^a, Henri WORTHAM ^a, Etienne QUIVET ^{a,*}

7
8 ^a Aix Marseille Univ, CNRS, LCE, Marseille, France

9 ^b French Environment and Energy Management Agency 20, avenue du Grésillé, BP
10 90406, 49004 Angers Cedex 01, France

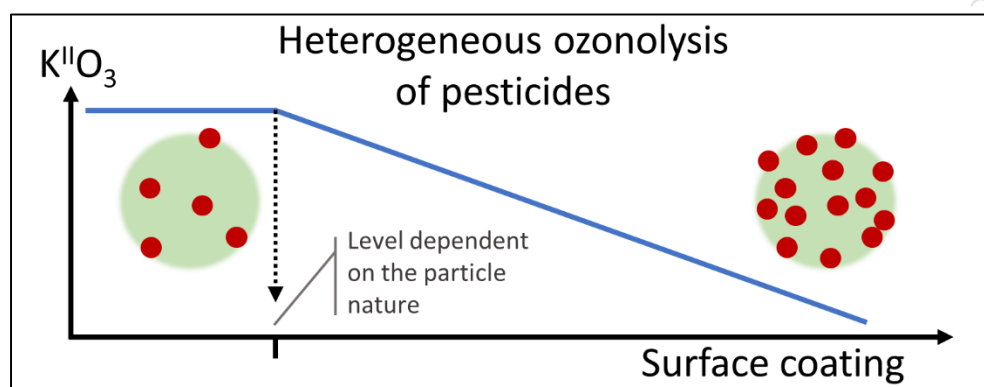
11
12
13
14 **Submitted to Chemosphere**

15
16
17
18
19
20 ***Corresponding author:** Phone: +33 413551054; fax: +33 413551060; e-mail address:
21 etienne.quivet@univ-amu.fr

22 **Highlights**

- 23 • Experimental study of pesticides heterogeneous degradation by ozone
- 24 • The increase of the surface coating slows the degradation kinetics down
- 25 • The surface coating is influenced by the nature of particles

26

27 **Graphical abstract**

28

29 **Keywords**

30 Atmosphere, Surface coating, Degradation, Heterogeneous, Ozone, Pesticides

31 **Abstract**

32 A fraction of the atmospheric pesticides can be adsorbed on particles surface according to
33 their physicochemical properties. After adsorption, pesticides can undergo heterogeneous
34 reactivity with atmospheric oxidants such as ozone, but the influence of the pesticide surface
35 coating (i.e., the percentage of the particle surface covered by pesticide molecules) on the
36 degradation kinetics is not well-understood. To estimate the importance of this phenomenon,
37 the influence of the surface coating level in pesticides on the heterogeneous ozonolysis of
38 cyprodinil, deltamethrin, permethrin, and pendimethalin adsorbed on hydrophobic and
39 hydrophilic silicas was investigated. Surface coating level varied from 0.3% to 15% of a
40 monolayer. Generally, the increase of the surface coating level induced a slower degradation
41 of the pesticides above 1% to 3% of a monolayer. This decrease was attributed to a shielding
42 effect. More aggregates of pesticides form with increasing surface coating leading to lower
43 accessibility for ozone to the adsorbed pesticide molecules. Moreover, it was observed that
44 the particle type could play a role in the influence of the surface coating level on the
45 degradation rates. Results obtained will contribute to a better understanding of the
46 atmospheric fate of pesticides and semi-volatile organic compounds in the particulate phase
47 and show the importance of working with consistent surface coating level in order to compare
48 the obtained degradation constants.

49

50 1. Introduction

51 Numerous studies have reported the presence of pesticides in the atmosphere in
52 concentrations ranging from a few picograms per cubic meter to hundreds of nanograms per
53 cubic meter (Coscollà et al. 2010; Estellano et al. 2015; Lopez et al. 2017; Désert et al. 2018;
54 Villiot et al. 2018). At the same time, many adverse effects of pesticides on human health
55 (Clementi et al. 2008; Hatcher et al. 2008; Marks et al. 2010; Inserm 2013; Parrón et al. 2014;
56 Kim et al. 2017) and on the environment (Santadino et al. 2014; Carvalho 2017) have been
57 evidenced. In particular, harmful health effects associated with pesticide exposure by
58 inhalation of ambient air have been highlighted (Lee et al. 2002; Li et al. 2014; Lopez et al.
59 2017). Therefore, it is important to improve our understanding of the atmospheric fate of
60 pesticide.

61 In the atmosphere, pesticides are distributed between aqueous, gaseous, and particulate phases
62 according to their physicochemical properties. Nevertheless, they are generally poorly present
63 in the aqueous phase due to the low water solubility of most of them. Numerous pesticides are
64 semi-volatile compounds, and a fraction of them is adsorbed on the atmospheric particles
65 surface (Sauret et al., 2008). Pesticides can react with atmospheric oxidants such as ozone,
66 hydroxyl (OH) and nitrate (NO₃) radicals. Their atmospheric reactivity in the gas phase has
67 been widely studied and the modeling software AOPWINTM (Atmospheric Oxidation
68 Program for Microsoft Windows, Software, Meylan and Howard 1993) allows to estimate
69 their rate constants with OH radicals and, to a lesser extent with ozone. For the particle phase,
70 a few studies have investigated the heterogeneous degradation of pesticides with ozone
71 (Mattei et al, 2018 and references therein), OH radicals (Socorro et al. 2016 and references
72 therein), and NO₃ radicals (Mattei 2019b, submitted). The influences of relative humidity and
73 particle type on the pesticide reactivity have already been demonstrated (Mattei et al. 2018,

74 2019a). However, the influence of the amount of pesticide on the surface on the degradation
75 kinetics was poorly investigated.

76 Before studying heterogeneous reactivity, authors calculate or estimate the particle surface
77 coating level in the organic compounds under study. Assuming the formation of a uniform
78 monolayer on the particle surface, these calculations are usually expressed in percentage of a
79 monolayer. For pesticides, the total surface coating (i.e., the percentage of the particle surface
80 covered by pesticide molecules, considering all the compounds adsorbed on the surface)
81 varies greatly from a study to another, from 0.04% (Pflieger et al. 2009) to 69% (Al Rashidi et
82 al. 2013).

83 To the best of our knowledge, only one study focusing on the heterogeneous ozonolysis of
84 chlorpyrifos (insecticide) adsorbed on sand particles investigated and demonstrated the
85 influence of the particle coating level on pesticide degradation (El Masri et al., 2016). The
86 cited work shows that the increase of surface coating level from 6% to 60% of a monolayer
87 slows the heterogeneous degradation kinetics down. If very few data are available for
88 pesticides, further information on the influence of the surface coating level was published on
89 other semi-volatile organic compounds such as Polycyclic Aromatic Hydrocarbons (PAH)
90 adsorbed on fused silica plates (Wu et al. 1984), on nonactivated silica gel (Alebic-Juretic et
91 al. 1990), on soot particles (Pöschl et al. 2001), and on graphite and silica particles (Perraudin
92 et al. 2007; Miet et al. 2009). For PAH, the reaction rates seem to be also influenced by the
93 surface coating level.

94 The aim of this study is to investigate the influence of the surface coating level (0.3 to 15% of
95 a monolayer) on the heterogeneous ozonolysis of four pesticides (cyprodinil, deltamethrin,
96 permethrin, and pendimethalin) adsorbed on two types of model mineral particles
97 (hydrophobic and hydrophilic silicas). These four pesticides were selected based on their
98 presence in the atmosphere up to a dozen of ng m^{-3} (Désert et al., 2018), on their toxicity

99 (APVMA, 2017), and on their distribution between the gas and particle phases (AOPWINTM,
100 Meylan and Howard 1993). Moreover, they have been the subject of numerous studies of
101 reactivity towards ozone (Socorro et al. 2015; Mattei et al. 2018) and OH radicals (Socorro et
102 al. 2016; Mattei et al. 2019). The two particle types were chosen as models for mineral
103 atmospheric particles. They have different surface properties but a very close composition and
104 morphology. For this work, particles coated with a various amount of pesticides were exposed
105 in realistic conditions of temperature, relative humidity, and gaseous ozone concentration.

106 2. Materials and methods

107 2.1. Chemicals

108 Cyprodinil (purity 99.8%), deltamethrin (99.7%), pendimethalin (98.8%), and permethrin
109 (98.3%) were purchased from Sigma-Aldrich (PESTANAL[®], analytical standard) and were
110 used as received. The chemical structures of the pesticides under study are depicted in
111 Supplementary Information (SI) Fig. S11 and their physicochemical properties are given in SI
112 Table S11.

113 2.2. Particles

114 Atmospheric mineral aerosols were mimicked using two commercial silica particles:
115 AEROSIL R812 (Degussa) hereafter referred to as “hydrophobic silica”, and AEROSIL 255
116 (Evonik Industries) referred to as “hydrophilic silica”. *Composition:* hydrophobic and
117 hydrophilic silicas (>99.8 wt%) contain primarily SiO₂. *Particle size:* the average primary
118 particle size of hydrophobic and hydrophilic silica particles ranges from 5 nm to 50 nm
119 (Evonik, 2015). However, most of them can be arranged as agglomerates with an aggregate
120 size coarsely measured mainly around 5 µm, sometimes up to 25 µm. Field observations show
121 that pesticides are distributed in the fine (0.1–1 µm), ultrafine (0.03–0.1 µm), and coarse (1–
122 10 µm) particle size fraction, and no pesticides were detected in the size fraction >10 µm

123 (Coscollà et al., 2014, 2013; Xu et al., 2011). *Specific surface area (SSA; BET method)*:
124 hydrophobic and hydrophilic silica particles have a specific surface area of $(260 \pm 30) \text{ m}^2 \text{ g}^{-1}$
125 and $(255 \pm 25) \text{ m}^2 \text{ g}^{-1}$, respectively (Evonik, 2015). *Surface chemistry and hygroscopicity*:
126 surfaces of hydrophobic particles are mainly covered by siloxanes whereas hydrophilic silica
127 particles are mainly covered by silanols groups. Silanol groups have a hydrophilic nature but
128 the siloxane groups are chemically inert and hydrophobic.

129 **2.3. Particles coating**

130 Hydrophobic and hydrophilic silica particles were independently coated with pesticides
131 according to a liquid/solid adsorption. In an amber Pyrex bulb of 500 cm^3 , 600 mg of particles
132 were mixed with a pesticide solution in dichloromethane (each of the 4 pesticides at a
133 concentration of 20 mg L^{-1} in dichloromethane for HPLC, $\geq 99.8\%$, Sigma-Aldrich) of a
134 variable volume according to the coating level required and 40 mL of dichloromethane. After
135 a 5-min ultrasound treatment, dichloromethane was evaporated by a rotary evaporator
136 (Rotavapor R-114, Büchi) at 40°C and 850 mbar. For a given volume of solution, this process
137 allows a reproducible coating of the pesticides on the particle's surface (Socorro et al. 2015).

138 The percentage of particle surface coated with pesticides was calculated considering the
139 following assumptions: the particles surface coating is uniform and below a monolayer. The
140 pesticide molecule is considered as a sphere and its radius (r_i , cm) is calculated by Equation
141 (1):

$$142 \quad r_i = \sqrt[3]{\frac{3 \times V_m}{4 \times \pi \times N_A}} \quad (1)$$

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

146 S_i is the surface (cm^2) covered by the pesticide under study. It is defined by Equation (2)

147 where n is the amount of adsorbed pesticide (mole):

$$148 \quad S_i = 4 \times \pi \times r_i^2 \times N_A \times n \quad (2)$$

149 The percentage of the coated aerosol surface T_i (%) by the adsorbed pesticide i is calculated as
150 follow:

$$151 \quad T_i = \frac{S_i}{S_1} \times 100 \quad (3)$$

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

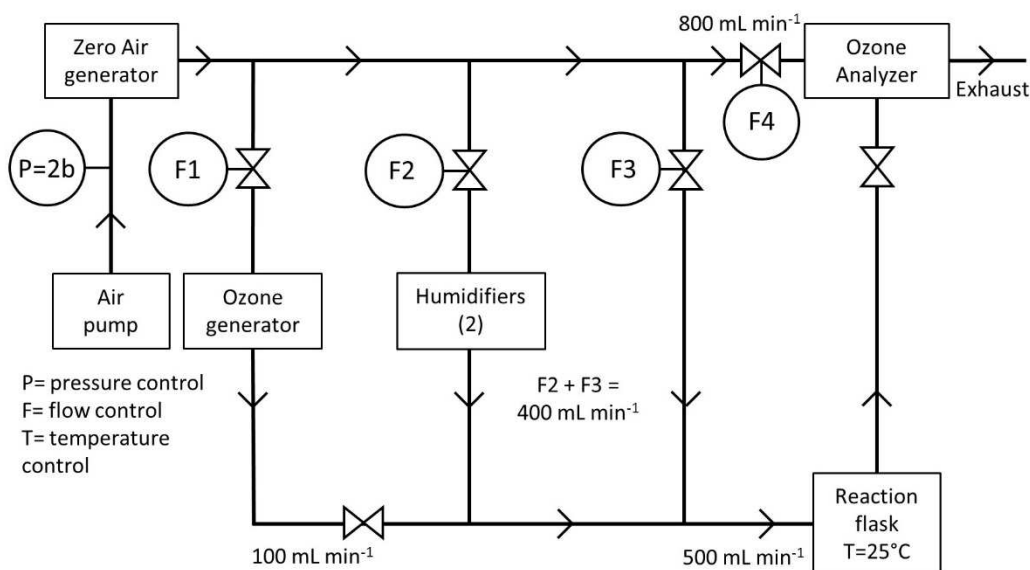
153 The total surface coated (including all compounds under study) was calculated by adding
154 individual percentages of the aerosol coated surface:

$$155 \quad T = \sum T_i \quad (4)$$

156 As a result, the percentage of the particle surface coated with total pesticide was between
157 0.3% and 15% of the monolayer according to the different experiments for hydrophobic and
158 hydrophilic silicas, which correspond to pesticide loadings between 0.166 mg g^{-1} and 8.45 mg
159 g^{-1} .

160 **2.4. Ozonolysis experiments**

161 The experimental setup was previously detailed in Socorro et al. (2015) (Fig. 1).



162

163 Fig. 1: Experimental setup to study the heterogeneous ozonolysis of pesticides

164 Briefly, a 500 cm³ amber Pyrex bulb containing about 500 mg of dried particles coated with
 165 the mixture of pesticides was fixed to a modified rotary evaporator and placed in a
 166 thermostated water bath (25 ± 1 °C). Ozone was generated by flowing purified air through an
 167 ozone generator (UVP, LLC Upland, UK). Particles coated with pesticides were exposed to
 168 an air flux containing an ozone mixing ratio of 410 ppb (i.e., 1.03·10¹³ molecules cm⁻³)
 169 constantly measured with a photometric ozone analyzer (O₃ 41M, Environnement S.A). The
 170 relative humidity (RH) was set at 55% ± 2%. The humidity level was reached by mixing dry
 171 and wet gaseous fluxes of purified air. Relative humidity was measured with a humidity probe
 172 (Hydrolog NT, Rotronic, USA, uncertainty 2% RH) and the total of all air fluxes in the
 173 reaction flask was 500 mL min⁻¹. Experiments lasted for 26 h.

174 **2.5. Extraction and pesticides quantification**

175 During ozone exposure, 30 mg aliquots of particles were regularly sampled in order to
 176 quantify the remaining adsorbed pesticides on their surface. Each 30 mg aliquot of particles
 177 was individually introduced in a 33 mL stainless steel cell with an internal standard solution

178 (Triphenyl phosphate, 99.9%, Sigma-Aldrich) and pesticides were extracted by accelerated
 179 solvent extraction (ASE 350, Dionex) with dichloromethane. Then, the extracts were
 180 concentrated under a nitrogen flow with a concentration workstation (TurboVap II, Biotage).
 181 The obtained solutions were analyzed with gas chromatography coupled to tandem mass
 182 spectrometry (GC/MS-MS), with a Trace GC Ultra (Thermo Scientific) coupled to a TSQ
 183 Quantum™ Triple Quadrupole (Thermo Scientific) using electron impact ionization (70 eV).
 184 More details about ASE extraction, concentration, and GC/MS-MS analysis are available in
 185 Socorro et al. (2015).

186 2.6. Determination of second-order rate constants and half-lives toward ozone

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

$$189 \quad \ln \left(\frac{[Pesticide_{(ads)}]_t}{[Pesticide_{(ads)}]_0} \right) = -(k_{O_3(part)}^I + k_{des(part)}^I + k_{hyd(part)}^I) \times t \quad (5)$$

190 where $k_{O_3(part)}^I$ (s^{-1}) is the pseudo-first-order rate constant of the reaction between ozone and
 191 the pesticides, $k_{des(part)}^I$ (s^{-1}) is the first-order desorption rate constant, $k_{hyd(part)}^I$ (s^{-1}) is the
 192 pseudo-first-order hydrolysis rate constant, t (s) is the time of ozone exposure, and
 193 $\frac{[Pesticide_{(ads)}]_t}{[Pesticide_{(ads)}]_0}$ is the pesticide concentration normalized to the initial pesticide concentration.

194 The pseudo-first-order reaction rate constants for the heterogeneous ozonolysis of the particle-
 195 phase pesticides were determined by analyzing their corresponding temporal profiles in a time
 196 frame from 0 to 26 h, for 410 ppb ozone mixing ratio (i.e., $1.03 \cdot 10^{13}$ molecules cm^{-3}).
 197 $(k_{des(part)}^I + k_{hyd(part)}^I)$ was determined experimentally by exposing the pesticides adsorbed
 198 on the surface of particles to a flow of humidified air, using the same experimental conditions
 199 as for the ozonolysis experiments but in absence of ozone. In order to determine the second-

200 order rate constants $k_{O_3(part)}^{II}$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$), the experimental pseudo-first-order
201 reaction rate constants $k_{O_3(part)}^I$ were plotted as a function of the ozone concentrations. To
202 simulate the kinetic mechanisms of the heterogeneous reactivity, the second-order rate
203 constants $k_{O_3(part)}^{II}$ were calculated assuming only one ozone mixing ratio, i.e., 410 ppb, using
204 a Langmuir-Rideal model, as done in previous studies concerning pesticide degradation by
205 ozone and hydroxyl radicals (Mattei et al., 2018, 2019a). Indeed, the linearity of the first order
206 kinetic constants versus the ozone concentration (with ozone mixing ratios ranging from 215
207 ppb to 917 ppb) was already demonstrated in Socorro et al. (2015). The second-order rate
208 constant was calculated as follows:

$$209 \quad k_{O_3(part)}^{II} = k_{O_3(part)}^I / [O_{3(gas)}] \quad (6)$$

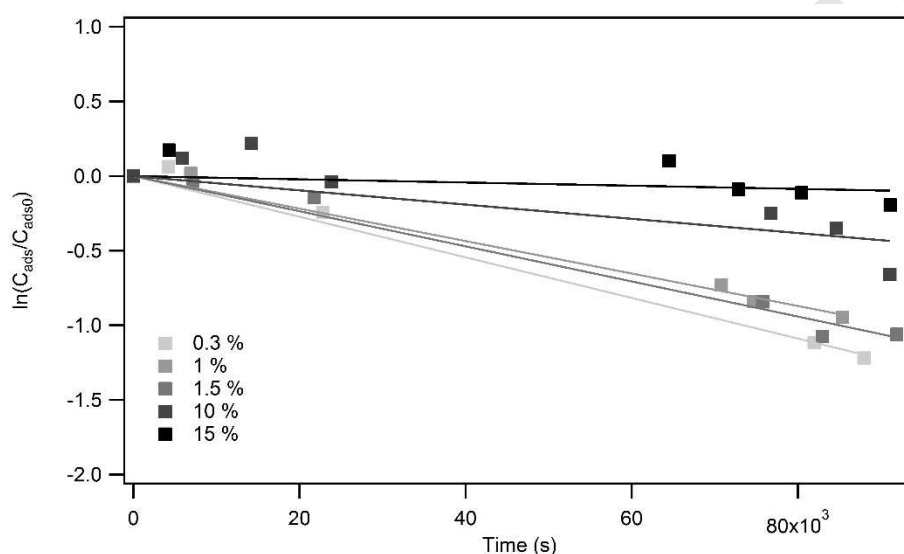
210 where $[O_{3(gas)}]$ is the constant ozone mixing ratio of 410 ppb used in the experiments, which
211 is representative of a highly polluted atmosphere (Finlayson-Pitts and Pitts 2009).

212 3. Results and discussion

213 3.1 Degradation kinetics

214 In order to study the influence of pesticide surface coating level on the heterogeneous
215 ozonolysis kinetics, four pesticides (cyprodinil, deltamethrin, permethrin, and pendimethalin)
216 were adsorbed together on mineral model particles (hydrophobic and hydrophilic silicas) at
217 five levels of surface coating ($T = 0.3\%$, 1% , 1.5% (only hydrophilic silica), 2.8% (only
218 hydrophobic silica), 10% , and 15% of a monolayer) and exposed to 410 ppb of ozone. As an
219 example, Fig. 2 represents the degradation kinetics for permethrin adsorbed on hydrophilic
220 silica at different surface coating levels. Those data are not corrected by the loss of permethrin
221 induced by hydrolysis and desorption. After correcting the raw data, pseudo-first-order and
222 then second-order degradation rate constants were calculated according to section 2.6

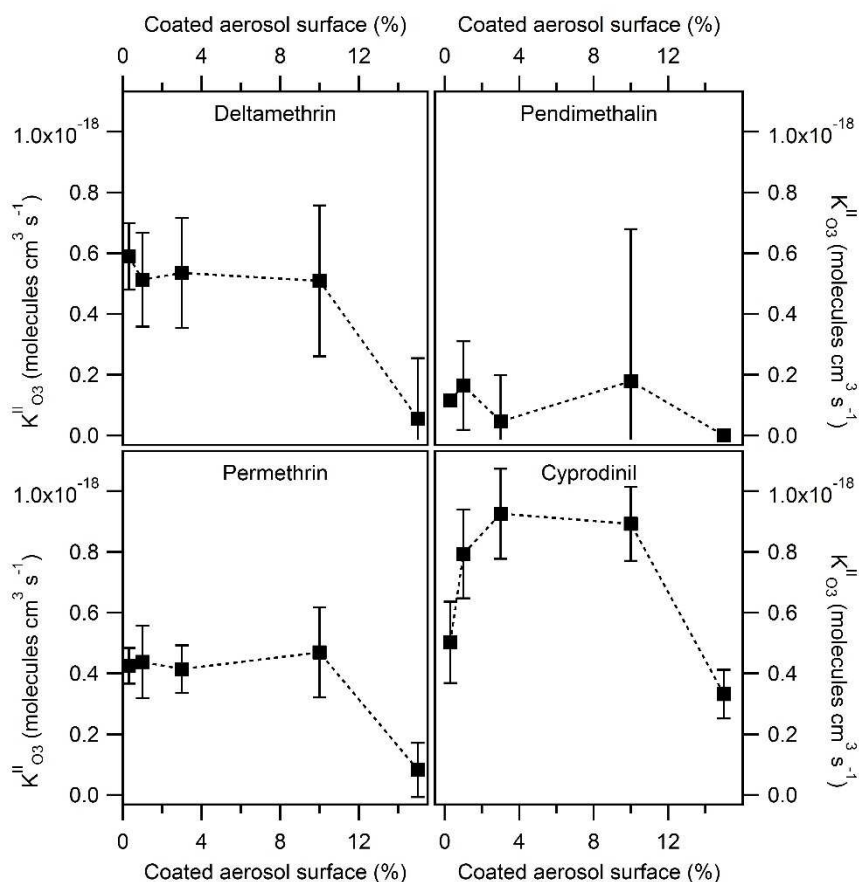
223 (Determination of second-order rate constants and half-lives toward ozone). Pesticides were
 224 exposed together to ozone and the corrections with the hydrolysis and desorption kinetic rate
 225 constants were applied for all of them. The results show that the four pesticides were
 226 degraded by ozone and their second-order kinetic rate constants ranged from $(1.1 \pm 0.9) \cdot 10^{-19}$
 227 $\text{cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ (permethrin, $T = 15\%$, hydrophilic silica) to $(1.2 \pm 0.1) \cdot 10^{-18} \text{ cm}^3$
 228 $\text{molecules}^{-1} \text{ s}^{-1}$ (deltamethrin, $T = 1\%$, hydrophilic silica).



229
 230 Fig. 2: Raw data of the degradation kinetics for permethrin on hydrophilic silica exposed to
 231 410 ppb of ozone adsorbed at five surface coating levels

232 3.2 Influence of the surface coating for pesticides adsorbed on hydrophobic silica

233 Fig. 3 presents the second-order kinetic rate constants for the ozonolysis of the four pesticides
 234 under study adsorbed on hydrophobic silica as a function of the surface coating level that
 235 ranged from 0.3% to 15% of a monolayer.



236

237 Fig. 3: Second-order kinetic rate constants for the ozonolysis of four pesticides adsorbed on
 238 hydrophobic silica at 5 surface coating levels from 0.3% to 15% of a monolayer.

239 When they were adsorbed on hydrophobic silica, all four pesticides were degraded by ozone.
 240 However, two different types of behavior toward the surface coating level were observed
 241 according to the pesticide nature.

242 Firstly, deltamethrin, permethrin, and pendimethalin had a parallel behavior; second-order
 243 kinetic rate constants were approximately stable given the uncertainties until a given surface
 244 coating level, and above this level, their degradation kinetics decreased with increasing
 245 surface coating level. Second-order kinetic rate constants obtained for deltamethrin and
 246 permethrin, two pyrethroid insecticides, adsorbed on hydrophobic silica were similar, i.e., $(5.4$
 247 $\pm 1.8) \cdot 10^{-19} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ and $(4.7 \pm 1.2) \cdot 10^{-19} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ from 0.3% to 10%
 248 of surface coating, respectively. No statistically significant degradation was observed at 15%

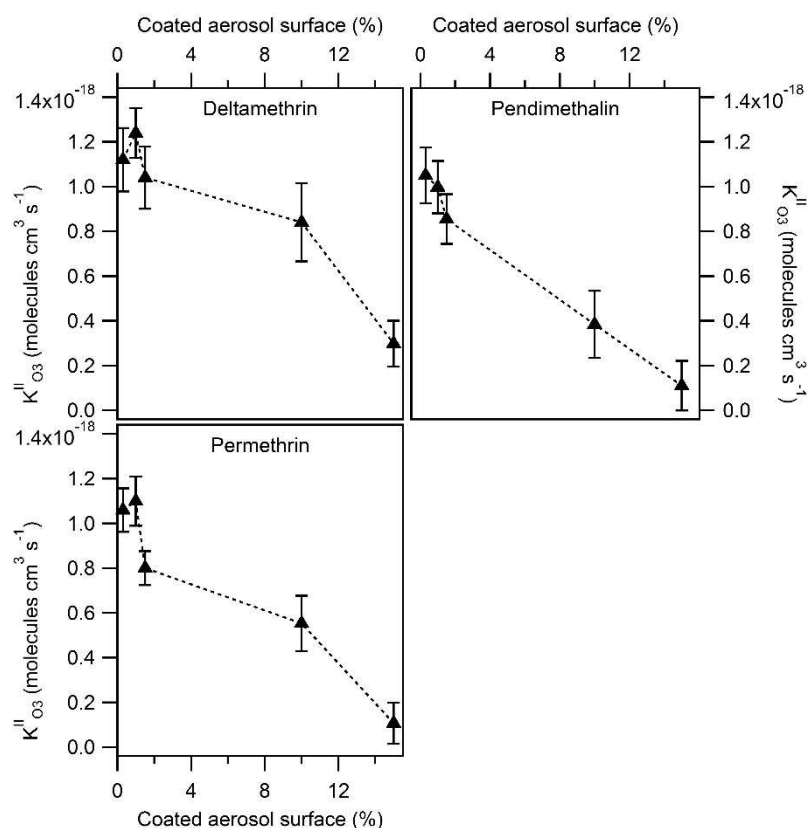
249 surface coating. The kinetic behavior of pendimethalin was close to those of permethrin and
250 deltamethrin with constant kinetic rates from 0.3% to 1% of surface coating (about (1.4 ± 0.8)
251 $\cdot 10^{-19} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$) and not statistically significant (i.e., negligible degradation rate
252 constants) from 2.8% to 15% surface coating.

253 Secondly, the behavior of cyprodinil was different from those of deltamethrin, permethrin,
254 and pendimethalin. With increasing coating level, second-order kinetic rate constants
255 increased and then decreased. The second-order kinetic rate constant for cyprodinil at 0.3% of
256 surface coating ($(5.0 \pm 1.3) \cdot 10^{-19} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$) was slower than those obtained from
257 1% to 10% (about $(8.7 \pm 1.4) \cdot 10^{-19} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$). Cyprodinil degradation rate was
258 then the slowest at 15% of surface coating ($(3.2 \pm 0.8) \cdot 10^{-19} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$).

259 **3.3 Influence of the surface coating for pesticides adsorbed on hydrophilic silica**

260 When they were adsorbed on hydrophilic silica, all four pesticides were degraded by ozone.
261 However, results concerning cyprodinil were associated with high uncertainties (about 10
262 times higher than for the other pesticides). Therefore, results for cyprodinil are not included in
263 the discussion.

264 Fig. 4 presents the second-order kinetic rate constants for the ozonolysis of deltamethrin,
265 pendimethalin, and permethrin adsorbed on hydrophilic silica as a function of the surface
266 coating level from 0.3% to 15% of a monolayer.



267

268 Fig. 4: Second-order kinetic rate constants for the ozonolysis of deltamethrin, pendimethalin,
 269 and permethrin adsorbed on hydrophilic silica at 5 surface coating levels from 0.3% to 15% of
 270 a monolayer.

271 The three pesticides (deltamethrin, permethrin, and pendimethalin) followed the same trend
 272 given the uncertainties, i.e., steady degradation rates at low surface coating level (from 0.3%
 273 to 1.5%) and a gradual decrease of the degradation at higher surface coating level ($\geq 1.5\%$).

274 The second-order degradation rate constant of pendimethalin was stable at 0.3%, 1%, and
 275 1.5% of surface coating (about $(9.7 \pm 1.2) \cdot 10^{-18} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$), 2 times slower at 10%
 276 of surface coating ($(3.8 \pm 1.5) \cdot 10^{-19} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$), and 9 times slower at 15% of
 277 surface coating ($(1.1 \pm 1.1) \cdot 10^{-19} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$). The same trend was observed for
 278 permethrin and deltamethrin. The second-order degradation rate constants for permethrin and
 279 deltamethrin were about $(1.0 \pm 0.1) \cdot 10^{-18} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ and about $(1.1 \pm 0.1) \cdot 10^{-18} \text{ cm}^3$
 280 $\text{molecules}^{-1} \text{ s}^{-1}$ from 0.3% to 1.5% of surface coating, $(5.5 \pm 1.2) \cdot 10^{-19} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$

281 and $(8.4 \pm 1.8) \cdot 10^{-19} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ at 10% of surface coating, and $(1.1 \pm 0.9) \cdot 10^{-19} \text{ cm}^3$
282 $\text{molecules}^{-1} \text{ s}^{-1}$ and $(3.0 \pm 1.0) \cdot 10^{-19} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ at 15% of surface coating,
283 respectively, which represent a degradation 9 and 3 times slower between the highest and
284 lowest rate constant values.

285 **3.4 Discussion on the influence of the surface coating on the degradation kinetics**

286 *Aggregate shielding effect*

287 On both hydrophilic and hydrophobic silicas, the degradation kinetics were generally slowed
288 down by an increase of the surface coating level (El Masri et al., 2016). Indeed, when the
289 surface coating increases, the probability of pesticides forming aggregates also increases. This
290 can induce an ‘aggregate shielding’ effect, making a fraction of the pesticide molecules less
291 accessible to oxidation by ozone. The shielding effect was observed in this study as a decrease
292 of the kinetic constants with increasing surface coating level, and even with the total
293 inhibition of the reactivity of some of the pesticides at the highest surface coating level tested.

294 To our knowledge, only a few studies investigated the influence of the surface coating level of
295 organic compounds on their heterogeneous degradation by ozone. One study only focused on
296 the degradation of a pesticide (chlorpyrifos) (El Masri et al., 2016). Other studies took an
297 interest on the heterogeneous degradation of PAH and especially of benzo[a]pyrene (BaP) by
298 ozone (Wu et al. 1984; Alebic-Juretic et al. 1990; Pöschl et al. 2001; Perraudin et al. 2007;
299 Miet et al. 2009).

300 The heterogeneous ozonolysis of chlorpyrifos adsorbed on sand particles has been shown to
301 be strongly influenced by the surface coating level of the pesticide (El Masri et al., 2016).
302 This was possibly due to the use of high pesticide concentrations adsorbed on particles
303 ranging from $10 \mu\text{g g}^{-1}$ to $100 \mu\text{g g}^{-1}$ which correspond to a surface coating level of 6% to
304 60% of a monolayer. Degradation rate constants were found to be 70 times slower at 60% of

305 surface coating level than at 6%. This decrease in kinetic constants followed an exponential
306 trend, explained by the authors as a shielding effect induced by the increasing coating level.
307 Our results also show a decrease of the kinetic constants, however, coating levels employed in
308 our study were lower (from 0.3% to 15%) than theirs (from 6% to 60%). In the present work
309 the decrease in kinetic constants was observed only above a given surface coating level (1%
310 to 3%) whereas El Masri et al. (2016) observed the decrease of the kinetic constants over the
311 entire surface coating level range from 6% to 60%. This allows us to show that, with
312 increasing surface coating level, degradation rates are at first constant, as observed in our
313 study, and then, they start to decrease, as observed in our study and by El Masri et al. (2016).

314 It could be expected that the ‘aggregate shielding’ effect would decrease as the compound is
315 degraded. However, this would only be the case if the degradation products would desorb to
316 the gas phase. Yet, it was previously shown that the heterogeneous ozonolysis of deltamethrin
317 and permethrin leads to degradation products including some that remain in the particle phase
318 (Socorro et al. 2016). Also, the study of the degradation of chlorpyrifos (El Masri et al., 2016)
319 also focuses on one of its degradation products: chlorpyrifos oxon. This degradation product
320 is not reacting with ozone, and it remains in the particle phase, acting as a barrier to ozone
321 diffusion. In this way, even as pesticides are degraded by ozone, the ‘aggregate shielding’
322 effect can remain.

323 The heterogeneous ozonolysis of PAH on diverse surfaces (silica gel, silica particles, fused
324 silica plates, graphite, and soot particles) was also shown to be influenced by the surface
325 coating level, with kinetic constants slowed down by the increase of the surface coating (Wu
326 et al. 1984; Alebic-Juretic et al. 1990; Pöschl et al. 2001; Perraudin et al. 2007; Miet et al.
327 2009). Unfortunately, most of those studies only considered the variation in the degradation
328 on the degradation kinetics between the sub-monolayer and super-monolayer coating and
329 therefore underline the difference in reactivity for PAH in the bulk phase and the dispersed

330 phase due to shielding effect. Nevertheless, Wu et al. (1984) pointed out that the kinetic
331 constants for the ozonolysis of PAH adsorbed on fused silica plates is proportional to the
332 ozone concentration for low surface coating level (one-third of a monolayer) but that this
333 cannot be extended for higher surface coatings (aggregates or bulk phase). Again, this
334 indicates that under a given surface coating level, no aggregates are formed, and so kinetic
335 constants are independent of the surface coating level and that above this surface coating
336 level, the formation of aggregates induces a shielding effect affecting the degradation kinetics.

337 *Influence of particle nature*

338 Generally, literature is consistent with the fact that the increase of the surface coating level
339 induces a decrease in the degradation kinetics constants, as observed in this study. However,
340 some studies mentioned a shielding effect appearing above the level of the monolayer coating
341 (Wu et al. 1984; Alebic-Juretic et al. 1990; Pöschl et al. 2001; Perraudin et al. 2007; Miet et
342 al. 2009). In this study, as well as in the study by Wu et al. (1984), the shielding effect was
343 observed far below a monolayer. Aggregate formation is therefore possible for a low
344 concentration of adsorbed compounds (i.e., 1-1.5% of a monolayer). Figures 3 and 4 show
345 that the surface coating level for which second-order kinetic rate constants start to decrease
346 seems to be dependent on the particle type (it is lower on hydrophilic silica than on
347 hydrophobic silica). This probably shows that the nature of the interaction between organic
348 compound and particle is crucial in the formation of aggregates. Indeed, if there is a good
349 affinity, the organic compound is likely to adsorb homogeneously on the surface, but in case
350 of poor affinity, organic compounds are likely to adsorb on a few sites and then to form
351 aggregates around the prior-adsorbed compounds. Therefore, the nature of the particle and of
352 the adsorbed compound also plays a role in the effect of the surface coating level.

353 In the present work, carried out with silica particles, the kinetic profiles do not show any
354 plateau, thereby suggesting that the shielding effect is only partial (it only significantly slows

355 down the degradation kinetics but does not entirely hinder degradation). But some studies
356 concerning the heterogeneous degradation of PAH by oxidants such as ozone, NO₂ and
357 hydroxyl radicals reported the presence of a plateau in the degradation time trends (Esteve et
358 al. 2004, 2006; Perraudin et al. 2007; Miet et al. 2009). This means that, some molecules are
359 not accessible to the oxidant, because they are hidden by other PAH or by particle phase
360 degradation products. In those studies, this plateau phenomenon was observed on the surface
361 of organic particles (soot, diesel particles) but not on the surface of silica particles, possibly
362 because of a different disposition of PAH molecules according to the nature of the surface.
363 Thus, because of different surface repartition of molecules, the particle type can influence the
364 degradation kinetics.

365 Lastly, our previous study (Mattei et al. 2018) showed a faster ozonolysis of deltamethrin,
366 permethrin, and pendimethalin when adsorbed on hydrophilic silica than hydrophobic silica at
367 a surface coating of about 3% of a monolayer in the same experimental conditions as in this
368 study, explained by a greater affinity of ozone for hydrophilic silica than hydrophobic silica.
369 This observation is also valid for low surface coating ($\leq 10\%$), as can be seen in Figure 3 and
370 4. However, at 15% surface coating, kinetic constants were comparable whatever the particle
371 surface was. This shows that for a high surface coating level, the particle nature does not have
372 an influence on the degradation kinetics because the ‘aggregate shielding’ effect dominates
373 over the particle nature effect.

374 **4. Atmospheric implications and conclusion**

375 The influence of surface coating between 0.3% and 15% of a monolayer on the heterogeneous
376 ozonolysis kinetics of four commonly used pesticides (cyprodinil, deltamethrin, permethrin,
377 and pendimethalin) was investigated. Degradation rate constants were slowed down when the
378 surface coating level increased above 1% to 3% of a monolayer, by a factor of maximum 10,
379 due to shielding effect. This effect is due to the formation of aggregates of the organic

380 compound on the particle surface, which makes the reaction between the oxidant and the
381 molecules included in the aggregates more difficult or impossible. The surface coating level
382 for which this shielding effect appears depends on the surface type, probably because of the
383 variability of affinity between the organic compound and the surface.

384 As already mentioned for relative humidity and particle type (Mattei et al. 2018), these results
385 highlight the need to be consistent in surface coating when doing experimental determination
386 of kinetic rate constants in order to be able to compare results from different laboratories and
387 different studies.

388 Moreover, this work was conducted regarding the degradation of pesticides by ozone, but it
389 could be likely that the shielding effect observed could also affect the degradation kinetic
390 rates of pesticides with other atmospheric oxidants such as hydroxyl and nitrate radicals.

391 This study shows that pesticide degradation was slowed down for weak surface coating level
392 (i.e., weak pesticide loading) without taking into account the presence of other SVOC.
393 However, they can also participate to the shielding effect as mentioned for PAH (Wu et al.
394 1984; Alebic-Juretic et al. 1990; Pöschl et al. 2001; Perraudin et al. 2007; Miet et al. 2009). In
395 fact, the highest the surface coating in SVOC is, the slowest their degradation will be,
396 influencing, as a result, the ability of those compounds to spread in the environment and
397 impact air quality.

398 Finally, few field studies measured atmospheric concentrations with respect to particle surface
399 sizes, making it impossible to calculate the real surface coating in SVOC. This shows the need
400 for more field measurements to better describe the real surface coating of pesticides on
401 atmospheric particles.

402 **Acknowledgments**

403 This work has been carried out thanks to the support of the COPP'R project "Modelling of
404 atmospheric contamination by plant protection products at the regional scale" funded by the
405 PRIMEQUAL – AGRIQA « Agriculture et qualité de l'air » program. C. Mattei received a
406 doctoral grant from the French Environment and Energy Management Agency (ADEME) and
407 the Region Provence-Alpes-Côte d'Azur.

408 **References**

- 409 Al Rashidi, M.J., Chakir, A., Roth, E., 2013. Heterogeneous Ozonolysis of Folpet and
410 Dimethomorph: A Kinetic and Mechanistic Study. *J. Phys. Chem. A* 117, 2908–2915.
411 <https://doi.org/10.1021/jp3114896>
- 412 Alebic-Juretic, A., Cvitas, T., Klasinc, L., 1990. Heterogeneous Polycyclic Aromatic
413 Hydrocarbon Degradation with Ozone on Silica Gel Carrier. *Environ. Sci. Technol.*
414 24:1. <https://doi.org/10.1021/es00071a005>
- 415 APVMA [Australian Pesticide and Veterinary Medicines Authority], 2017. Acceptable Daily
416 Intakes for Agricultural and Veterinary Chemicals. Office of Chemical Safety, Office
417 of Health Protection, Department of Health and Ageing. Australian Government 113p.
418 <https://apvma.gov.au/sites/default/files/publication/26796-adi.pdf>.
- 419 Carvalho, F.P., 2017. Pesticides, environment, and food safety. *Food Energy Secur.* 6, 48–60.
420 <https://doi.org/10.1002/fes3.108>
- 421 Clementi, M., Tiboni, G.M., Causin, R., La Rocca, C., Maranghi, F., Raffagnato, F., Tenconi,
422 R., 2008. Pesticides and fertility: An epidemiological study in Northeast Italy and
423 review of the literature. *Reprod. Toxicol.*, 36th Annual Conference of the European
424 Teratology Society 26, 13–18. <https://doi.org/10.1016/j.reprotox.2008.05.062>
- 425 Coscollà, C., Colin, P., Yahyaoui, A., Petrique, O., Yusà, V., Mellouki, A., Pastor, A., 2010.
426 Occurrence of currently used pesticides in ambient air of Centre Region (France).
427 *Atmos. Environ.* 44, 3915–3925. <https://doi.org/10.1016/j.atmosenv.2010.07.014>
- 428 Coscollà, C., Muñoz, A., Borrás, E., Vera, T., Ródenas, M., Yusà, V., 2014. Particle size
429 distributions of currently used pesticides in ambient air of an agricultural
430 Mediterranean area. *Atmos. Environ.* 95, 29–35.
431 <https://doi.org/10.1016/j.atmosenv.2014.06.022>
- 432 Coscollà, C., Yahyaoui, A., Colin, P., Robin, C., Martinon, L., Val, S., Baeza-Squiban, A.,
433 Mellouki, A., Yusà, V., 2013. Particle size distributions of currently used pesticides in
434 a rural atmosphere of France. *Atmos. Environ.* 81, 32–38.
435 <https://doi.org/10.1016/j.atmosenv.2013.08.057>
- 436 Désert, M., Ravier, S., Gille, G., Quinapallo, A., Armengaud, A., Pochet, G., Savelli, J.-L.,
437 Wortham, H., Quivet, E., 2018. Spatial and temporal distribution of current-use
438 pesticides in ambient air of Provence-Alpes-Côte-d’Azur Region and Corsica, France.
439 *Atmos. Environ.* 192, 241–256. <https://doi.org/10.1016/j.atmosenv.2018.08.054>
- 440 El Masri, A., Laversin, H., Chakir, A., Roth, E., 2016. Influence of the coating level on the
441 heterogeneous ozonolysis kinetics and product yields of chlorpyrifos ethyl adsorbed
442 on sand particles. *Chemosphere* 165, 304–310.
443 <https://doi.org/10.1016/j.chemosphere.2016.09.036>
- 444 Estellano, V., Pozo, K., Efstathiou, C., Pozo, K., Corsolini, S., Focardi, S., 2015. Assessing
445 levels and seasonal variations of current-use pesticides (CUPs) in the Tuscan
446 atmosphere, Italy, using polyurethane foam disks (PUF) passive air samplers. *Environ.*
447 *Pollut.* 205, 52–59. <https://doi.org/10.1016/j.envpol.2015.05.002>
- 448 Finlayson-Pitts, B.J., Pitts, J.N., 2009. Chemistry of the upper and lower atmosphere: theory,
449 experiments, and applications, Nachdr. ed. Academic Press, San Diego, Calif.
- 450 Hatcher, J.M., Pennell, K.D., Miller, G.W., 2008. Parkinson’s disease and pesticides: a
451 toxicological perspective. *Trends Pharmacol. Sci.* 29, 322–329.
452 <https://doi.org/10.1016/j.tips.2008.03.007>
- 453 Inserm, 2013. Pesticides : Effets sur la santé - Une expertise collective de l’Inserm.
- 454 Kim, K.-H., Kabir, E., Jahan, S.A., 2017. Exposure to pesticides and the associated human
455 health effects. *Sci. Total Environ.* 575, 525–535.
456 <https://doi.org/10.1016/j.scitotenv.2016.09.009>

- 457 Lee, S., McLaughlin, R., Harnly, M., Gunier, R., Kreutzer, R., 2002. Community exposures to
458 airborne agricultural pesticides in California: ranking of inhalation risks. *Environ.*
459 *Health Perspect.* 110, 1175–1184.
- 460 Li, H., Ma, H., Lydy, M.J., You, J., 2014. Occurrence, seasonal variation and inhalation
461 exposure of atmospheric organophosphate and pyrethroid pesticides in an urban
462 community in South China. *Chemosphere* 95, 363–369.
463 <https://doi.org/10.1016/j.chemosphere.2013.09.046>
- 464 Lopez, A., Yusà, V., Muñoz, A., Vera, T., Borràs, E., Ródenas, M., Coscollà, C., 2017. Risk
465 assessment of airborne pesticides in a Mediterranean region of Spain. *Sci. Total*
466 *Environ.* 574, 724–734. <https://doi.org/10.1016/j.scitotenv.2016.08.149>
- 467 Marks Amy R., Harley Kim, Bradman Asa, Kogut Katherine, Barr Dana Boyd, Johnson
468 Caroline, Calderon Norma, Eskenazi Brenda, 2010. Organophosphate Pesticide
469 Exposure and Attention in Young Mexican-American Children: The CHAMACOS
470 Study. *Environ. Health Perspect.* 118, 1768–1774.
471 <https://doi.org/10.1289/ehp.1002056>
- 472 Mattei, C., Wortham, H., Quivet, E., 2019. Heterogeneous degradation of pesticides by OH
473 radicals in the atmosphere: Influence of humidity and particle type on the kinetics. *Sci.*
474 *Total Environ.* 664, 1084–1094. <https://doi.org/10.1016/j.scitotenv.2019.02.038>
- 475 Mattei, C., Wortham, H., Quivet, E., 2018. Heterogeneous atmospheric degradation of
476 pesticides by ozone: Influence of relative humidity and particle type. *Sci. Total*
477 *Environ.* 625, 1544–1553. <https://doi.org/10.1016/j.scitotenv.2018.01.049>
- 478 Meylan, W.M., Howard, P.H., 1993. Computer estimation of the Atmospheric gas-phase
479 reaction rate of organic compounds with hydroxyl radicals and ozone. *Chemosphere*
480 26, 2293–2299. [https://doi.org/10.1016/0045-6535\(93\)90355-9](https://doi.org/10.1016/0045-6535(93)90355-9)
- 481 Miet, K., Le Menach, K., Flaud, P.M., Budzinski, H., Villenave, E., 2009. Heterogeneous
482 reactions of ozone with pyrene, 1-hydroxypyrene and 1-nitropyrene adsorbed on
483 particles. *Atmos. Environ.* 43, 3699–3707.
484 <https://doi.org/10.1016/j.atmosenv.2009.04.032>
- 485 Parrón, T., Requena, M., Hernández, A.F., Alarcón, R., 2014. Environmental exposure to
486 pesticides and cancer risk in multiple human organ systems. *Toxicol. Lett.*,
487 *Environmental contaminants and target organ toxicities* 230, 157–165.
488 <https://doi.org/10.1016/j.toxlet.2013.11.009>
- 489 Perraudin, E., Budzinski, H., Villenave, E., 2007. Kinetic Study of the Reactions of Ozone
490 with Polycyclic Aromatic Hydrocarbons Adsorbed on Atmospheric Model Particles. *J.*
491 *Atmospheric Chem.* 56, 57–82. <https://doi.org/10.1007/s10874-006-9042-x>
- 492 Pflieger, M., Grgić, I., Kitanovski, Z., Nieto, L., Wortham, H., 2011. The heterogeneous
493 ozonation of pesticides adsorbed on mineral particles: Validation of the experimental
494 setup with trifluralin. *Atmos. Environ.* 45, 7127–7134.
495 <https://doi.org/10.1016/j.atmosenv.2011.09.031>
- 496 Pöschl, U., Letzel, T., Schauer, C., Niessner, R., 2001. Interaction of Ozone and Water Vapor
497 with Spark Discharge Soot Aerosol Particles Coated with Benzo[a]pyrene: O₃ and
498 H₂O Adsorption, Benzo[a]pyrene Degradation, and Atmospheric Implications. *J.*
499 *Phys. Chem. A* 105, 4029–4041. <https://doi.org/10.1021/jp004137n>
- 500 Santadino, M., Coviella, C., Momo, F., 2014. Glyphosate Sublethal Effects on the Population
501 Dynamics of the Earthworm *Eisenia fetida* (Savigny, 1826). *Water. Air. Soil Pollut.*
502 225, 2207. <https://doi.org/10.1007/s11270-014-2207-3>
- 503 Sauret, N., Wortham, H., Putaud, J.-P., Mirabel, P., 2008. Study of the effects of
504 environmental parameters on the gas/particle partitioning of current-use pesticides in
505 urban air. *Atmos. Environ.* 42, 544–553.
506 <https://doi.org/10.1016/j.atmosenv.2007.09.012>

- 507 Socorro, J., Gligorovski, S., Wortham, H., Quivet, E., 2015. Heterogeneous reactions of ozone
508 with commonly used pesticides adsorbed on silica particles. *Atmos. Environ.* 100, 66–
509 73. <https://doi.org/10.1016/j.atmosenv.2014.10.044>
- 510 Socorro, J., Durand, A., Temime-Roussel, B., Gligorovski, S., Wortham, H., Quivet, E., 2016.
511 The persistence of pesticides in atmospheric particulate phase: An emerging air quality
512 issue. *Sci. Rep.* 6. <https://doi.org/10.1038/srep33456>
- 513 Villiot, A., Chrétien, E., Drab-Sommesous, E., Rivière, E., Chakir, A., Roth, E., 2018.
514 Temporal and seasonal variation of atmospheric concentrations of currently used
515 pesticides in Champagne in the centre of Reims from 2012 to 2015. *Atmos. Environ.*
516 174, 82–91. <https://doi.org/10.1016/j.atmosenv.2017.11.046>
- 517 Wu, C.H., Salmeen, I., Niki, H., 1984. Fluorescence spectroscopic study of reactions between
518 gaseous ozone and surface-adsorbed polycyclic aromatic hydrocarbons. *Environ. Sci.*
519 *Technol.* 18, 603–607. <https://doi.org/10.1021/es00126a007>
- 520 Xu, H., Du, S., Cui, Z., Zhang, H., Fan, G., Yin, Y., 2011. Size distribution and seasonal
521 variations of particle-associated organochlorine pesticides in Jinan, China. *J. Environ.*
522 *Monit.* 13, 2605. <https://doi.org/10.1039/c1em10394f>
523