Pathogenicity study of *Mycoplasma hyorhinis* and *M. flocculare* in specific-pathogen-free pigs pre-infected with *M. hyopneumoniae*

Sarah Fourour, Véronique Tocqueville, Frédéric Paboeuf, Gérald Lediguerher, Nadège Morin, Isabelle Kempf, Corinne Marois-Créhan

► To cite this version:

Sarah Fourour, Véronique Tocqueville, Frédéric Paboeuf, Gérald Lediguerher, Nadège Morin, et al.. Pathogenicity study of *Mycoplasma hyorhinis* and *M. flocculare* in specific-pathogen-free pigs pre-infected with *M. hyopneumoniae*. *Veterinary Microbiology*, 2019, 232, pp.50 - 57. 10.1016/j.vetmic.2019.04.010 . hal-03485001

HAL Id: hal-03485001

<https://hal.science/hal-03485001>

Submitted on 21 Dec 2021

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.

Distributed under a Creative Commons Attribution - NonCommercial| 4.0 International License

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

Coraline MATTEI ^{a,b}, Julien DUPONT^a, Henri WORTHAM ^a, Etienne QUIVET ^{a,*}

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

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

Submitted to Chemosphere

*Corresponding author: Phone: +33 413551054; fax: +33 413551060; e-mail address:
etienne.quivet@univ-amu.fr

Highlights

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

Graphical abstract

Keywords

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

Abstract

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

1. Introduction

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

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

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

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

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

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

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

2. Materials and methods

2.1. Chemicals

Cyprodinil (purity 99.8%), deltamethrin (99.7%), pendimethalin (98.8%), and permethrin (98.3%) were purchased from Sigma-Aldrich (PESTANAL®, analytical standard) and were used as received. The chemical structures of the pesticides under study are depicted in Supplementary Information (SI) Fig. SI1 and their physicochemical properties are given in SI Table SI1.

2.2. Particles

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

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

2.3. Particles coating

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

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

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

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

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

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

2.5. Extraction and pesticides quantification

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

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

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

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

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

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

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

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

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

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

3. Results and discussion

3.1 Degradation kinetics

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

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

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

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

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

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

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

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

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

Secondly, the behavior of cyprodinil was different from those of deltamethrin, permethrin, and pendimethalin. With increasing coating level, second-order kinetic rate constants increased and then decreased. The second-order kinetic rate constant for cyprodinil at 0.3% of 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 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 then the slowest at 15% of surface coating ($(3.2 \pm 0.8) \cdot 10^{-19} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$).

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

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

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

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

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

The second-order degradation rate constant of pendimethalin was stable at 0.3%, 1%, and 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% 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 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 permethrin and deltamethrin. The second-order degradation rate constants for permethrin and deltamethrin were about $(1.0 \pm 0.1) \cdot 10^{-18} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ and about $(1.1 \pm 0.1) \cdot 10^{-18} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ from 0.3% to 1.5% of surface coating, $(5.5 \pm 1.2) \cdot 10^{-19} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$

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

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

Aggregate shielding effect

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

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

The heterogeneous ozonolysis of chlorpyrifos adsorbed on sand particles has been shown to be strongly influenced by the surface coating level of the pesticide (El Masri et al., 2016). This was possibly due to the use of high pesticide concentrations adsorbed on particles 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 60% of a monolayer. Degradation rate constants were found to be 70 times slower at 60% of

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

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

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

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

Influence of particle nature

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

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

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

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

4. Atmospheric implications and conclusion

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

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

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

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

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

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

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.

References

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

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

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