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# Heterogeneous oxidation of two triazole pesticides (diniconazole and tebuconazole) by OH-radicals and ozone.

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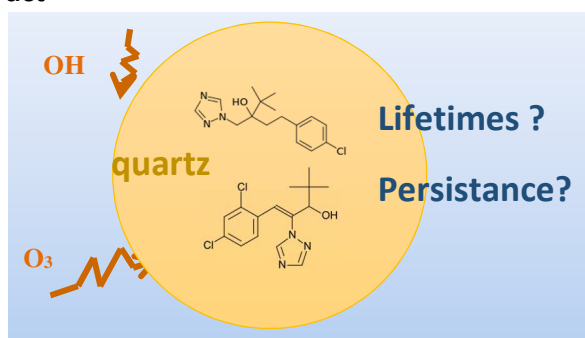
## Abstract

Tebuconazole (Tbz) and diniconazole (Dnz) were deposited as thin film on quartz plaques. They were submitted to OH-radicals and ozone and their kinetic was measured. OH-radical oxidation was performed relative to a reference whose rate constant is well known. Terbutylazine (Tbt) and Chlorpyrifos Ethyl (Clp) were chosen as reference for Tbz and Dnz kinetics determination, respectively. OH-radical rate constants of Tbz and Dnz were found to be:  $k_{OH+Tbz} = (1.7 \pm 0.2) 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and  $k_{OH+Dnz} = (1.74 \pm 1.21) 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

<sup>1</sup>, respectively. Ozone heterogeneous oxidation rate constants were determined in an absolute way:  $k_{\text{O}_3+\text{Tbz}} = (0.5 \pm 0.2) \cdot 10^{-20} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ;  $k_{\text{O}_3+\text{Dnz}} = (1.4 \pm 0.2) \cdot 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

Dnz is ten times more reactive towards OH-radicals than Tbz and 27 times more reactive than Tbz towards ozone maybe because of the presence of a double bond in Dnz. Lifetimes of Tbz and Dnz on quartz like surfaces against OH-radicals are of 68 days and 8 days, respectively and 4 months and several years against ozone, respectively.

#### Graphical abstract



#### Highlights:

The heterogeneous reaction of OH-radicals with tebuconazole is negligible

Tebuconazole on quartz like surfaces is non-reactive toward ozone

Particulate tebuconazole may be submitted to long-range atmospheric transport

Diniconazole is more reactive than Tebuconazole against ozone and OH-radicals

**Keywords:** pesticide, diniconazole, tebuconazole, OH-radicals, ozone, heterogeneous reaction

## 1. Introduction

When spread on culture, pesticides can reach soil where they can further undergo soil erosion (Cousins et al., 1999) or be released in the atmosphere. Once in the atmosphere, they are distributed in the gaseous, aqueous and particulate phases of the atmosphere according to their physicochemical properties. Because of their low volatility, pesticides can be found in the particulate phase of the atmosphere up to several hundred pg per cube meter (Coscolla et al., 2014). The atmospheric fate of pesticides in particulate phase is influenced by transport processes as well as heterogeneous transformations at the gas/particle interface induced by photo-oxidants. The pesticide lifetime on a particle is thus greatly dependant on its reactivity toward photo-oxidants. Some heterogeneous kinetic measurements toward ozone, OH-radicals and nitrate radicals exist in the literature (Palm et al., 1998; Pflieger et al., 2009, Segal-Rosenheimer et al., 2011; Yang et al., 2011). The heterogeneous reactivity of pesticides toward these oxidant is impacted by the chemical structure, the nature of the surface of the solid support (Mattei et al., 2019; Lester et al., 2017; Segal-Rosenheimer et al., 2011) and the humidity (Mattei et al., 2019; Palm et al., 1997). However existing studies do not provide a full overview of the atmospheric persistence and reactivity regarding to the pesticides' structure and particle nature diversities. To assess the persistence of pesticides on solid/gas interfaces towards atmospheric oxidants, more heterogeneous kinetic measurements are thus necessary. We propose to study the kinetic of heterogeneous degradation of two triazole pesticides tebuconazole (Tbz) and diniconazole (Dnz) with OH-radicals and ozone and investigate the

structure-reactivity relations. Since the seventies, triazoles compounds are widely used as broad spectrum fungicides for many crops or biocides in various industrial products like wood preservative. On the market since 1986, Tbz occupies the first position in terms of triazole global sales but is also present in the French National Pesticide List for Pesticides to be assessed in ambient air (Anses, 2010). Meanwhile Dnz was introduced in 1983 but is no longer approved under the EC Regulation 1107/2009.

The structures of Dnz and Tbz are close but differ by the presence of a carbon-carbon double bond and an additional chlorine atom on the aromatic cycle in diniconazole. A vapor pressure of  $1.3 \cdot 10^{-3}$  mPa at 25 °C for tebuconazole (Tbz) suggest that it might exist in the particulate phase in the atmosphere. (Tomlin, 2000). Indeed TBZ was measured up to 8.18 ng/m<sup>3</sup> in the vicinity of maize and cereal crops in gathered particle and gas phase samples (Scheyer et al., 2007). Tbz concentrations of about  $32 \pm 8$  ng/m<sup>3</sup> were detected in total suspended particles (Coscolla et al., 2014): a size distribution profile of tebuconazole concentration showed that Tbz was especially in the fine fraction of the atmospheric aerosol below 1 µm. More recently, Tbz was detected in air samples gathering gaseous and particle phases in the south of France around 0.01 ng/m<sup>3</sup> (Désert et al., 2018). Moreover Tbz has a great affinity with soils and sediments: it was detected at around 0.1 µg per kg lake sediment in northern Greece (Kalogridi et al., 2014). Less studies deals with the spread and persistence of Dnz in the environment. The sunlight photodegradation of diniconazole as a thin film on glass surface showed the formation of aldehydes and ketones (Sharma and Chibber, 1997) within 21h. Dnz was detected in plants and showed a half-life time around 3 days in tea leaves (Xinzhong et al., 2018).

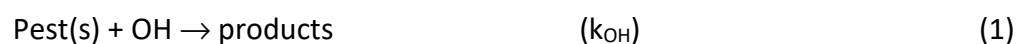
In terms of atmospheric reactivity, no study was found in the literature for these species. Regarding the presence of Tbz especially in the particulate phase of the atmosphere and knowing that the main components of atmospheric mineral dust include quartz, feldspar, carbonate and clay, we propose to study the heterogeneous oxidation of Tbz and Dnz deposited on quartz plaques with OH-radicals and ozone which are two of the most important atmospheric oxidants. Lifetimes will be deduced from rate constants and compared with gaseous rate constants and heterogeneous rate constant of other pesticides family.

## 2. Materials and Methods

### 2.1 Method

#### 2.1.1 OH-radical oxidation

The relative method was used to study the kinetics of degradation of target pesticides. This method consists in simultaneously monitoring the temporal evolution concentration of the pesticide (Pest) and a reference compound (Ref). These species are consumed mainly by following reactions:



where  $k_{\text{OH}}$  and  $k_{\text{ref}}$  ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) are the second order rate constants of the heterogeneous reactions between the studied pesticide and the reference, respectively.

109 Other secondary reactions of first order such as photolysis or volatilization may as well take  
110 place leading to pesticide or reference loss:



113  $k_p$  and  $k'_p$  are the sum of the first order rate constants ( $s^{-1}$ ) of secondary reactions consuming  
114 the pesticide and the reference, respectively.

115 Kinetic analysis of reactions (1), (2), (3) and (4) leads to the following relation:

116 
$$\frac{1}{t} \cdot \ln \left( \frac{[\text{Pest}]_{t_0}}{[\text{Pest}]_t} \right) = \frac{R}{t} \cdot \ln \left( \frac{[\text{Ref}]_{t_0}}{[\text{Ref}]_t} \right) + (k_p - R \cdot k'_p) \quad (5)$$

117 With  $R = \frac{k_{\text{Pest}}}{k_{\text{Ref}}}$ , the ratio between the rate constant of the studied pesticide and the  
118 reference toward OH-radicals.  $[\text{Pest}]_{t_0}$  and  $[\text{Ref}]_{t_0}$  are the initial concentrations of the studied  
119 pesticide and the reference pesticide at time  $t_0$ , respectively;  $[\text{Pest}]_t$  and  $[\text{ref}]_t$  are the  
120 concentrations of the studied pesticide and the reference pesticide at time  $t$ .

121 According to equation (5), a plot of  $\frac{1}{t} \cdot \ln \left( \frac{[\text{Pest}]_{t_0}}{[\text{Pest}]_t} \right)$  as a function of  $\frac{1}{t} \cdot \ln \left( \frac{[\text{Ref}]_{t_0}}{[\text{Ref}]_t} \right)$  results in a  
122 linear fit whose slope is equal to  $R = \frac{k_{\text{Pest}}}{k_{\text{Ref}}}$ . Knowing the rate constant between OH and the  
123 reference we can deduce the rate constant between OH-radicals and the studied pesticide.

124 The reference compounds were chosen because their kinetic rate constants, in  
125 heterogeneous phase, are well known and were determined in conditions close to ours.  
126 Terbutylazine (Tbt) was selected as the reference to study Tbz. For this reference  
127 compound two determinations exist in the literature. Pflieger et al. (2013) have determined  
128 a rate constant of  $k_{\text{Tbt}} = (1.5 \pm 0.8) \cdot 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for the heterogeneous OH-reaction

of Tbt on hydrophobic silica and relative humidity below 1%. Meanwhile Palm et al. (1998) have determined a rate constant of  $1.1 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for the heterogeneous OH-reaction of Tbt on hydrophilic silica at a humidity of 50%. It is known that, humidity has a great influence on the heterogeneous degradation of pesticides by OH-radicals (Mattei et al., 2019). Therefore, in this work it is better to use the value of OH reactivity of terbuthylazine reported by Pflieger et al. (2013).

The reactivity of Dnz toward OH-radicals was study relative to Chlorpyrifos ( $k_{\text{Clp}} = (5.8 \pm 4.0) \cdot 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) whose reactivity was studied in the same device by El Masri et al. (2014).

### 2.1.2 Ozonolysis of pesticides

The absolute method was used to study the ozonolysis of Tbz and Dnz. Experiment conditions were set so that ozone concentration didn't vary more than 10% during an experiment (Table 1). In such conditions, the pesticide's concentration decay can be modelled by a pseudo first order kinetic:

$$\frac{[\text{Pest}]_t}{[\text{Pest}]_{t_0}} = \exp(-k_{\text{app}} \cdot t) \quad (6)$$

where  $[\text{Pest}]_{t_0}$  and  $[\text{Pest}]_t$  are the initial pesticide concentration at  $t_0$  and the pesticide concentration at time  $t$ , respectively.  $k_{\text{app}} \text{ (s}^{-1}\text{)}$  is the sum of first order or pseudo first order rate constants of pesticide degradation pathways including volatilization.  $k_{\text{app}}$  was obtained from the linearization of equation (6) as the slope of the plot of  $\ln([\text{P}]_{t_0}/[\text{P}])$  as a function of time.



150 Once  $k_{app}$  were determined using (6) for different ozone concentration (Table 1), the gas  
 151 immediate surface reaction (GSR) model or Eley Rideal model was used to analyze  $k_{app}$ .

152 This model states that gaseous ozone reacts with the solid pesticide with a rate constant  $k_{O_3}$ :



154 This equation results in the following kinetic law :

155 
$$\frac{d[Pest]}{dt} = k_{O_3} \cdot [Pest] \cdot [O_{3(g)}] + k_0 \cdot [Pest] = k_{app} \cdot [Pest] \quad (8)$$

156 Where  $k_{app}$  is the apparent first order rate of pesticide removal during the experiment.  $k_{app}$  is  
 157 the sum of the product of the gaseous ozone concentration and the second order rate  
 158 constant of  $O_3$  with the pesticide and the first order rate constant resulting from other first  
 159 order phenomena removing the pesticide mainly the volatilization:

160 
$$k_{app} = k_{O_3} \cdot [O_{3(g)}] + k_0 \quad (9)$$

161 The plot of  $k_{app}$  as a function of  $[O_{3(g)}]$  results in a straight line where  $k_{O_3}$  is the slope and  $k_0$   
 162 the intercept.

163

### 164 2.1.3 Lifetime

165 The lifetime of pesticides against an oxidant can be deduced from the rate constant by  
 166 calculating their lifetime against the oxidant,  $\tau_X$ :

167 
$$\tau_X = \frac{1}{k_X \cdot [X]} \quad (10)$$

Where [X] is the average oxidant concentration or ozone in the atmosphere and  $k_x$  the rate coefficient of the pesticide reaction with the oxidant X.

## 2.2 Experimental procedure

The experimental procedure has been depicted in a previous study in detail (Rashidi et al., 2011). Thus, it will only be described briefly herein. Experiments were performed in a one meter long Pyrex cell with a diameter of 5 cm. Quartz windows closed both extremities of the cell to allow a UV beam issued from a deuterium lamp to pass through it. Beam was focalized on an Avaspec CCD camera (Avantes) to be analyzed. The pressure of the reaction mixture inside the reactor was measured by a pressure sensor (0 – 1000 mbar MKS Baratron capacitance). Two platinum resistance sensors, positioned at each cell extremities, were used to measure the reaction temperature. Experiments were performed at  $25 \pm 2$  °C in the case of OH-oxidation and at  $20 \pm 2$  °C in the case of the oxidation by ozone.

Pesticide coated plaques were prepared by transferring 1 mL of 1 mg L<sup>-1</sup> of standard pesticide solution (Pestanal®, Sigma-Aldrich) in dichloromethane in 6x3x1 (Lxhxh) cm<sup>3</sup> quartz plaques. Pesticide coated plaques with 1 µg of pesticide were obtained after evaporation of the solvent. The surface coverage of quartz plaques were 82 %, 72 %, 63% and 84 % for Tbz, Dnz, Clp and Tbt, respectively. Pesticides were all quality from Sigma Aldrich.

- **Ozonolysis experiments:** Eight pesticide coated plaques were initially placed in the reaction. Ozone was produced in an ozonizer using an oxygen flow. The mixture ozone/oxygen was completed with air to reach  $400 \pm 50$  Torr and swept in the reactor. According to Beer Lambert's law, ozone concentration in the reactor was measured at 254 nm and 270 nm where  $\sigma_{254}^{O_3} = 1.13 \cdot 10^{-17}$  cm<sup>2</sup> molecule<sup>-1</sup> and  $\sigma_{270}^{O_3} = 7.9 \cdot 10^{-18}$  cm<sup>2</sup> molecule<sup>-1</sup> respectively (Brion et al., 1997; Malicet et al., 1995). At

determined exposure time, the reactor was emptied from ozone, and open to remove a plaque. Remaining plaques were then again exposed to same ozone concentration. The average ozone concentration did not vary more than 10% (Table 2). For one ozone concentration, 8 to 16 measures at different time were performed resulting in the determination of one apparent constant plotted in figure 1.

- **Oxidation by OH-radicals:** The reactor was initially filled with 4 plaques coated with the studied pesticide and 4 plaques coated with the reference. OH-radicals were obtained by the photolysis of HONO. HONO was produced by adding drops of a sulphuric acid solution (10%) to a nitrite sodium solution (0.2 M) and carried into the reactor by a slight flow of synthetic air. Pressure was adjusted between 300 and 400 Torr with synthetic air. The concentration of the OH-radicals precursor, HONO was measured optically at 354 nm using the Beer-Lambert with  $\sigma_{\text{HONO}} = 4.87 \cdot 10^{-19} \text{ cm}^2 \text{ molecule}^{-1}$  (Sanders et al., 2006). The concentration of HONO was varied between (1 to 7)  $10^{16} \text{ molecule cm}^{-3}$ . Lamps were switched on to begin the reaction. At increasing time, the reactor was emptied, open and one plaque of the pesticide and one of the reference were systematically removed together. More than 45 measures for the studied pesticide and for the reference were performed. Each point on Figure 2 and 3 represent the average of 2 to 3 independent measures.

Once removed from the reactor, plaques were extracted 3 times with 0.5 mL of dichloromethane by manual shaking for a final volume of 2 mL. Extraction recovery were over 95% for the 4 pesticides. Extracts were analysed by gas chromatography (GC) coupled to a mass spectrometer (Thermo Fisher TraceUltra DSQII) in the positive electron ionization mode using the selective ion monitoring (SIM) mode. Helium (ALPHAGAZ 2 provided by Air

Liquid) was used as a carrier gas at a constant flow rate of 1.2 mL min<sup>-1</sup>. GC/MS analytical parameters and analysis conditions are summarized in Table 1S (supplementary file).

### 3. Results and discussion

#### 3.1 Pesticides ozonolysis

Ozonolysis experiments of both pesticides were performed at different ozone concentrations. The first order apparent rate constants  $k_{app}$  were determined from the fit of equation (9). The error on  $k_{app}$  was set at 2 times the statistical error given by the software Origin Pro. Values of  $k_{app}$  for Tbz and Dnz at different ozone concentrations are gathered in Table 1.

**Table 1:**  $k_{app}$  measurements for different ozone concentrations and related  $k_{O_3}$

	$[O_{3(g)}]$ (molecule cm <sup>-3</sup> )	$k_{app}$ (s <sup>-1</sup> )	$k_{O_3}$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )
TBZ	$(1.8 \pm 0.2) 10^{15}$	$(0.9 \pm 0.1) 10^{-5}$	$(0.5 \pm 0.2) 10^{-20}$
	$(2.5 \pm 0.2) 10^{15}$	$(1.2 \pm 0.1) 10^{-5}$	
	$(3.1 \pm 0.2) 10^{15}$	$(1.6 \pm 0.2) 10^{-5}$	
	$(4.1 \pm 0.3) 10^{15}$	$(2.2 \pm 0.2) 10^{-5}$	
DNZ	$(1.5 \pm 0.1) 10^{15}$	$(1.9 \pm 0.1) 10^{-4}$	$(1.4 \pm 0.2) 10^{-19}$
	$(2.0 \pm 0.2) 10^{15}$	$(3.1 \pm 0.3) 10^{-4}$	
	$(2.9 \pm 0.2) 10^{15}$	$(4.5 \pm 0.4) 10^{-4}$	
	$(4.4 \pm 0.4) 10^{15}$	$(5.9 \pm 0.5) 10^{-4}$	

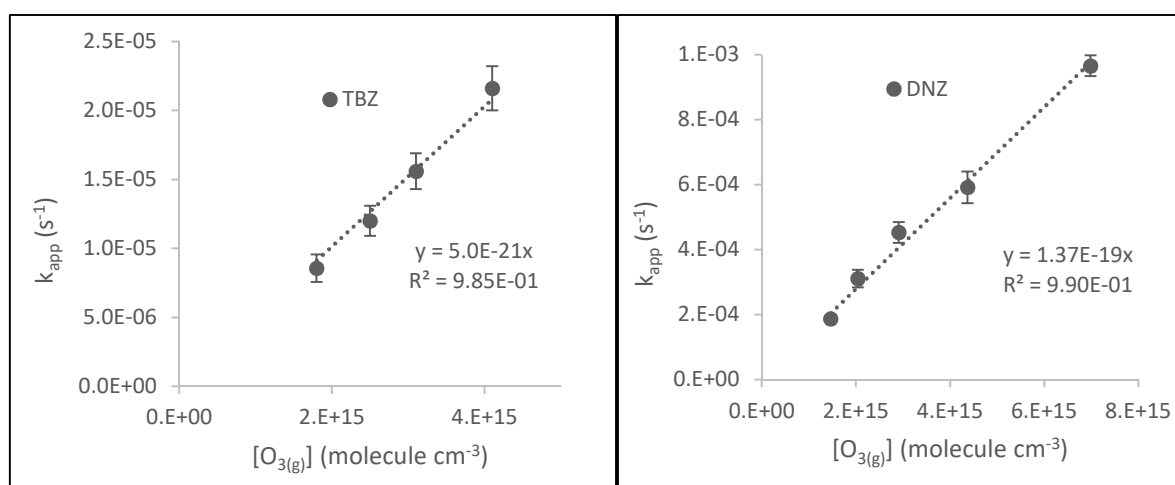
	$(7.0 \pm 0.6) 10^{15}$	$(9.7 \pm 0.4) 10^{-4}$	
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226

227 The gas surface reaction model was used to analyze ozonolysis results. Plots of  $k_{app}$  as a  
 228 function of the ozone concentration in the reactor, measured by UV spectroscopy, result in a  
 229 straight line passing through the origin for both pesticides confirming that no volatilization of  
 230 pesticide occurs due to the opening of the reactor during an experiment (Figure 1). As a  
 231 matter of fact, experiments without any introduction of oxidant and with all the  
 232 manipulations of plaques and the gas flow mixtures/pression adjustments showed that TBZ  
 233 and DNZ do not volatilize during experiments as awaited from their low vapor pressure  
 234 values. Thus the pesticide decrease along time was only due to its reaction with ozone. The  
 235 rate constant of the heterogeneous ozonolysis corresponds to the slope of the plots on  
 236 Figure 1:  $k_{O_3+Tbz} = (0.5 \pm 0.2) 10^{-20} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  ;  $k_{O_3+Dnz} = (1.4 \pm 0.2) 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$   
 237 <sup>1</sup>.

238

239



240

241 **Figure 1:** Plot of  $k_{app}$  as a function of ozone concentration for Tbz and Dnz

242

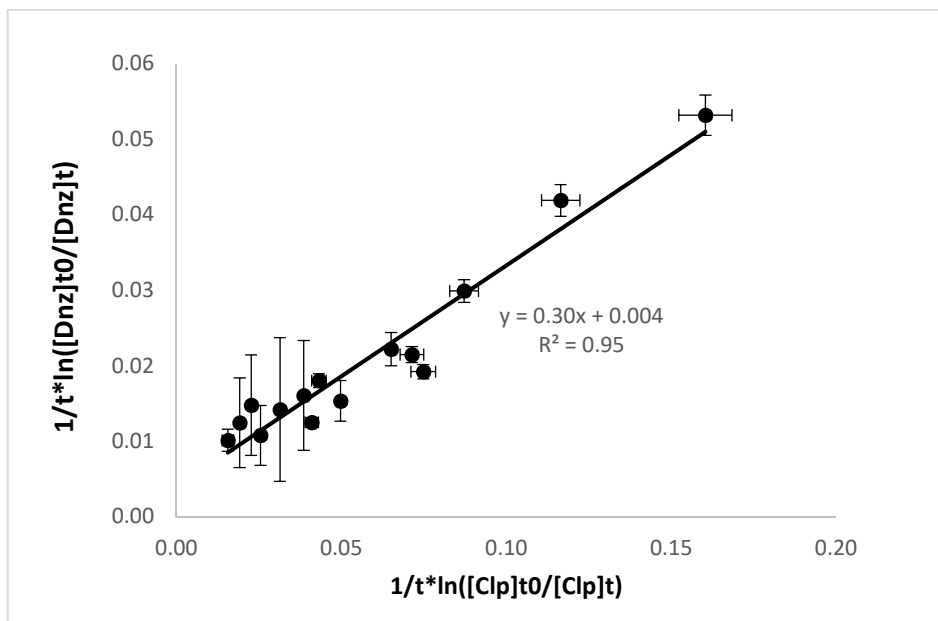
243     Uncertainties on the rate constant between the pesticide and ozone are two times the  
244     standard deviation calculated with the weighted error method with Origin Pro. With a rate  
245     coefficient lower than  $10^{-20} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  Tbz can be considered as non-reactive toward  
246     ozone. As expected, Dnz is more reactive than Tbz towards ozone probably due to the  
247     double bond.

248

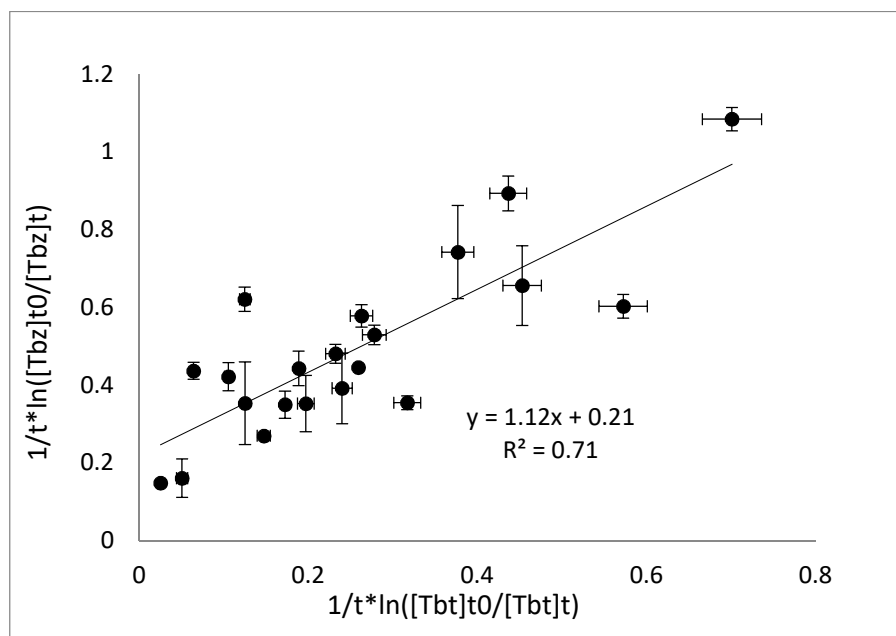
### 249     **3.2 Pesticides reaction with OH-radicals**

250             Rate constant of Tbz and Dnz deposited on quartz plaques against OH-radicals were  
251     determined relative to Tbt and Clp, respectively. Figures 2 and 3 show the plot of  $\frac{1}{t} \cdot$   
252      $\ln\left(\frac{[Pest]_{t0}}{[Pest]_t}\right)$  as a function of  $\frac{1}{t} \cdot \ln\left(\frac{[Ref]_{t0}}{[Ref]_t}\right)$  for Tbz and Dnz associated to their corresponding  
253     reference. As expected from equation (9), a good linear plot is observed with a correlation  
254     coefficient greater than 95% in Figure 2. Meanwhile, in figure 3, points are relatively  
255     dispersed, and the linear plot is obtained with a correlation coefficient of 0.7.

256



**Figure 2:** Plot of  $\ln([Dnz]_{t0}/[Dnz]_t)/t$  as a function of  $\ln([Clp]_{t0}/[Clp]_t)/t$



**Figure 3:** Plot of  $\ln([Tbz]_{t0}/[Tbz]_t)/t$  as a function of  $\ln([Tbt]_{t0}/[Tbt]_t)/t$

263 A linear fit of data on Figure 2 and 3 gives slopes  $R = 0.30 \pm 0.03$  and  $R = 1.12 \pm 0.16$  for Dnz and  
264 Tbz, respectively. Uncertainties were calculated by the weighted method using OriginPro.

265 The rate constant between Dnz and Tbz and OH-radicals were deduced from the relation

266 
$$R = \frac{k_{pest}}{k_{Ref}};$$

267  $k_{OH+Tbz} = (1.70 \pm 0.93) 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  ;  $k_{OH+Dnz} = (1.8 \pm 1.3) 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

268 Errors were determined using the propagation of errors:

269 
$$\Delta k_{pest} = k_{pest} \cdot \sqrt{\left(\frac{\Delta R}{R}\right)^2 + \left(\frac{\Delta k_{Ref}}{k_{Ref}}\right)^2} \quad (10)$$

270 Where  $k_{Ref}$ ,  $\Delta k_{Ref}$  are the reference rate coefficient and its uncertainty respectively;  $\Delta R$  is the  
271 uncertainty of  $R = k_{pes}/k_{Ref}$ .

272 Errors on rate constants are 56% for Tbz and 76% for Dnz. According to the relation (10) the  
273 error on the rate coefficient is mainly impacted by the uncertainty of  $k_{ref}$ . This error is  
274 relatively large, about 53% for the reference, Tbt, and about 69% for the reference Clp. The  
275 uncertainty on the ratio  $R$  is influenced by the measure of the concentrations of the  
276 pesticide and the reference compound. Chromatographic analysis of each sample was  
277 repeated 2 to 3 times to control the reproducibility of the results. Errors in GC-MS  
278 concentration measurements for Dnz and Tbz didn't vary more than 5 %.

279

### 280 3.3 Reactivity trend

281 Table 2 summarizes and compares the rate constants obtained in this work and those of  
282 other pesticides.



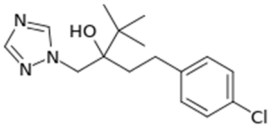
**OH-Reaction:** Heterogeneous rate constants of pesticides toward OH-radicals range between  $7.1 \cdot 10^{-14}$  to  $1.8 \cdot 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Dnz is the more reactive triazole compound. Tbz is ten times less reactive than Dnz. According to the chemical structure of Tbz, the reaction between Tbz and OH-radicals is expected to proceed via several pathways including the addition to the aromatic C<sub>6</sub>-cycle or to the C<sub>5</sub> aromatic N-heterocycle and H-abstraction processes from different sites. However, without mechanistic studies, it is difficult to identify the most favorable site. Dnz can undergo the same mechanism than Tbz and an addition to its olefinic bond. The fact that Dnz is ten times more reactive toward OH-radicals than Tbz when deposited on a quartz plaque is thus an indication that the dominant pathway proceeds mainly via addition to the olefinic bond in the case of Dnz.

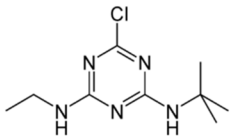
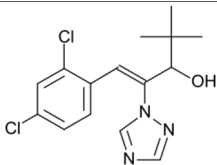
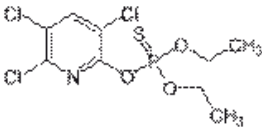
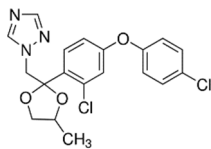
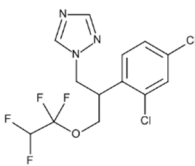
Overall rate constants against OH-radicals of Dnz and Tbz in gas phase were calculated with the SAR method using AOPWIN v1.92 (Meylan and Howard, 1993; Kwok and Atkinson, 1995). The estimated gas phase rate constant values are  $11.5 \cdot 10^{-12} \text{ molecule cm}^{-3} \text{ s}^{-1}$  and  $96 \cdot 10^{-12} \text{ molecule cm}^{-3} \text{ s}^{-1}$  for the rate constant of the reaction of gaseous Tbz and Dnz with OH-radicals, respectively. These values are 100 times higher than heterogeneous rate constants determined in this work. This shows that the use of quartz as a solid support has an inhibitory effect on the reaction between OH-radicals and pesticides probably by steric hindrance. Such a difference between gaseous and heterogeneous rate constants has already been highlighted in other studies (Pflieger et al., 2013; El Masri et al., 2014; Al Rashidi et al., 2014; Socorro et al., 2016; Lester et al., 2017).

To the best of our knowledge, only two pesticides of the azole pesticide family, difenoconazole and tetraconazole, have been studied in terms of reactivity toward OH-radicals under experimental conditions similar to those of this study (Table 2) (Al Rashidi et al., 2011; Mattei et al., 2019). They both present a lower reactivity against OH-radicals than

Tbz showing that the chemical structure largely impacts the kinetics of the reaction between the pesticide and OH-radicals. Their structure contains less alkyl groups than Tbz, maybe explaining the lower reactivity of difenoconazole and tetraconazole in comparison to Tbz. Tebuconazole and Terbutylazine differ mainly by the presence of a C<sub>5</sub>-N heterocycle in tebuconazole and a C<sub>6</sub>-aromatic group and a C<sub>6</sub>-N heterocycle and amine groups in terbutylazine. Recent experimental studies on the reactivity of C<sub>5</sub> and C<sub>6</sub> N-heterocyclic compounds toward OH-radicals in gas phase showed that C<sub>5</sub> heterocyclic compounds were largely more reactive than C<sub>6</sub> heterocyclic compounds and C<sub>6</sub> aromatic group (Samir, 2018). Nevertheless, Tbz and Tbt present the same reactivity indicating thus that their reactivity might be governed by the alkyl or amine H abstraction in the heterogeneous phase. Clp belongs to the family of organophosphorus compounds and contains a P=S double bond which is very sensitive to OH oxidation (El Masri et al., 2014, Munoz et al., 2014) : Clp is 3 times more reactive to OH-radicals than Dnz probably due to the presence of this functional group.

**Table 2:** Summary of heterogeneous OH-oxidation rate constants for investigated compounds in this study as well as for other pesticides from the literature.

Compound	Formula	substrate	k <sub>oz</sub> cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	k <sub>oh</sub> cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>
Tebuconazole		Quartz plaques	(5.1 ± 0.5) 10 <sup>-21</sup> <b>This work</b>	(1.70 ± 0.93) 10 <sup>-13</sup> <b>This work</b>
		Gas phase		11.5 10 <sup>-12</sup> AOPWIN

<i>Terbutylazine</i> (reference for <i>Tbz</i> )		Silica	$< 0.5 \cdot 10^{-19} *$ Pflieger et al., 2009	$(1.5 \pm 0.8) \cdot 10^{-13} *$ Pflieger et al., 2013
		Gas phase		$9.5 \cdot 10^{-12}$ AOPWIN
<i>Diniconazole</i>		Quartz plaques	$(1.37 \pm 0.09) \cdot 10^{-19}$ <b>This work</b>	$(1.8 \pm 1.3) \cdot 10^{-12}$ <b>This work</b>
		Gas phase	$1.67 \cdot 10^{-19}$ AOPWIN	$96.9 \cdot 10^{-12}$ AOPWIN
<i>Chlorpyrifos</i> (reference for <i>Dnz</i> )		Quartz plaques	$(1.2 \pm 0.1) \cdot 10^{-19}$ El Masri et al., 2014	$(5.8 \pm 4.0) \cdot 10^{-12}$ El Masri et al., 2014
		Gas phase		$91.7 \cdot 10^{-12}$ AOPWIN
<i>Difenoconazole</i>		Quartz plaques	$(2.6 \pm 0.4) \cdot 10^{-20}$ Al Rashidi et al., 2011	$(7.1 \pm 0.8) \cdot 10^{-14}$ Al Rashidi et al., 2011
		Silica	$< 3.4 \cdot 10^{-19} *$ Socorro et al., 2015	$\leq 10^{-13} *$ and ** Mattei et al., 2019
		Gas phase		$21.6 \cdot 10^{-12}$ AOPWIN
<i>Tetraconazole</i>		Silica	$< 3.4 \cdot 10^{-19} *$ Socorro et al., 2015	$\leq 10^{-13} *$ Mattei et al., 2019
		Gas phase		$10.9 \cdot 10^{-12}$ AOPWIN

324 \* hydrophobic silica AEROSOL R812

\*\* hydrophilic silica AEROSIL 255

### ***Ozonolysis reaction:***

Heterogeneous rate constants of pesticides summarized in Table 2 range between  $5.1 \cdot 10^{-21}$  and  $1.37 \cdot 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  ie over more than one range order (Table 3). The comparison of the kinetic coefficients of the ozone reaction with the triazole family pesticides shows that Dnz is the most reactive towards ozone. This can be explained by the presence of the olefinic bond. Unsaturated chemical bonds are known to be subjected to form an ozonide by addition of ozone which quickly dissociates into an aldehyde and a ketone (Grosjean et al., 1996). Unfortunately, we didn't observed the formation of products maybe due to the lack of sensitivity of our analytical technic. Dimethomorph, which contains also a double bond, has a heterogeneous rate constant towards ozone in conditions similar to ours in the same range order (Al Rashidi et al., 2013). Moreover, Tbz is 5 times less reactive toward ozone than Difenconazole. Difenconazole includes one more aromatic cycle than Tbz presenting more double bonds on which ozone can add to form an ozonide.

### **3.3 Atmospheric implication**

The tropospheric lifetimes of pesticides relative to reactions with both oxidants were estimated according to equation (10). Lifetimes were calculated using the rate constants obtained in this work. A 24 h daytime average global tropospheric OH concentration of  $1 \times 10^6 \text{ molecule cm}^{-3}$  and an ozone concentration of 40 ppb corresponding to  $7 \cdot 10^{11} \text{ molecules cm}^{-3}$  were used (Atkinson et al., 1997; Vingarzan et al., 2004) (Table 3). Tbz on quartz like surfaces

is more persistent toward OH-radicals and ozone than Dnz (Table 3). Lifetime of Dnz against ozone is several months in comparison to one week against OH-radicals. Tbz is more persistent in the atmospheric aerosol explaining that it can be detected in atmospheric particles (Scheyer et al., 2007; Hart et al. 2012; Coscolla et al., 2013; Coscolla et al., 2014).

**Table 3:** Lifetimes of Tebuconazole and Diniconazole regarding OH-radicals and ozone

Compound		$\tau_{OH}^*$	$\tau_{O_3}^{**}$
<i>Tebuconazole</i>	Quartz plaques	68 days	Non reactive
			(9 years)
<i>Diniconazole</i>	Quartz plaques	8 days	4 months

\* calculated for  $[OH] = 10^6 \text{ molecules cm}^{-3}$

\*\* calculated for  $[O_3] = 7 \cdot 10^{11} \text{ molecules cm}^{-3}$

## Conclusion

. The rate constant between two atmospheric oxidants (OH-radicals and ozone) and these two pesticides (Tebuconazole and Diniconazole) deposited on quartz plaques were determined. Diniconazole is found to be 10 times more reactive toward OH-radicals than Tebuconazole. Their lifetimes toward OH-radicals are around 2 months and 1 week for Tebuconazole and Diniconazole, respectively. Tebuconazole is non-reactive toward ozone. Diniconazole is resistant to oxidation by ozone with a lifetime of about 4 months. Even if Tbz is more persistent than Dnz toward the two major atmospheric oxidants, the use of Tbz is

366 still allowed and raise the concern of transborder redeposition and long range  
367 contamination of the Atmosphere. For a more accurate lifetime assessment and better  
368 understanding of the environment fate, heterogeneous phase reaction with other  
369 atmospheric oxidants ( $\text{NO}_3$ , Cl) should be carried out.

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