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Influence of pesticide mixture on their heterogeneous atmospheric degradation by ozone and OH radicals[☆]

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ABSTRACT

Pesticides in the atmosphere can exist in both gaseous and particulate phases due to their semi-volatile properties. They can undergo degradation when exposed to atmospheric oxidants like ozone and hydroxyl radicals. The majority of studies on the atmospheric reactivity of pesticides study them in combination, without considering potential mixture effects that could induce uncertainties in the results. Therefore, this study aims to address this gap, through laboratory studies using a flow reactor, and by evaluating the degradation kinetics of pendimethalin mixed with folpet, tebuconazole, and S-metolachlor, which were simultaneously adsorbed on hydrophobic silica particles that mimic atmospheric aerosols. The comparison with other mixtures, including pendimethalin, from the literature has shown similar reactivity with ozone and hydroxyl radicals, indicating that the degradation kinetics of pesticides is independent of the mixture. Moreover, the degradation rates of the four pesticides under study indicate that they are not or slightly degraded by ozone, with half-lives ranging from 29 days to over 800 days. In contrast, when exposed to hydroxyl radicals, tebuconazole exhibited the fastest reactivity, with a half-life of 4 days, while pendimethalin had a half-life of 17 days.

1. Introduction

The worldwide use of pesticides has doubled since 1990, reaching 3.54 million tons in 2021, as reported by the UN Food and Agriculture Organization (FAOSTAT, 2023). However, this increase raises concerns about the potential negative impacts on human health, such as cancer, diabetes, respiratory and neurological disorders (Alavanja et al., 2003; Evangelou et al., 2016; Faria et al., 2005; Hernández et al., 2013; Li et al., 2014) and on the environment such as the deterioration of the air, water, and soil quality, widely affecting the ecosystems (Aktar et al., 2009; Carriger et al., 2006; Norman et al., 2020; van der Werf, 1996). In addition, the overuse of pesticides can lead to the development of pesticide-resistant pests, which can then require to use even more pesticide (Curutiu et al., 2017).

Several studies have measured the concentration of pesticides in the air, and have found that pesticide concentrations can range from some picograms per cubic meter to several micrograms per cubic meter (Désert et al., 2018; PhytAtmo, 2022; Ravier et al., 2019; Zivan et al.,

2017). This contamination comes from volatilization from soil or plant surfaces (Bedos et al., 2002; Das and Hageman, 2020; Zivan et al., 2017), spray drift during pesticide application (Hong et al., 2021), and evaporation from water bodies (Luo et al., 2012). Once in the atmosphere, pesticides can undergo several physical and chemical transformations that can affect their partitioning between different phases (e.g., gas, particle, liquid) and their persistence (Hancock et al., 2008; Sanusi et al., 1999). Because most pesticides in use are semi-volatile and have a low solubility in water, they are poorly presented in the aqueous phase. Instead, they tend to be divided between the gaseous and particulate phases (Désert et al., 2018; Sauret et al., 2008). Furthermore, it's common for pesticides to coexist with a combination of other pesticides and diverse forms of atmospheric pollutants (Désert et al., 2018; Miglioranza et al., 2021; Ravier et al., 2019). In fact, the degradation of pesticides in the atmosphere is controlled by direct and indirect photolysis (involving OH, O₃ and NO₃) (Atkinson et al., 1999; Burrows et al., 2002; Mattei et al., 2018, 2019b; 2019c; Socorro et al., 2015, 2017).

Over the past few years, the academic community has shown an

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increasing interest in studying the degradation kinetics, mechanisms, and identifying the degradation products of pesticides in the atmosphere (Al Rashidi et al., 2014, 2011; 2013; Borrás et al., 2017, 2015b; 2015a; Mattei et al., 2019b, 2019c; 2018; Rokbani et al., 2019; Socorro et al., 2017, 2015; Vera et al., 2015; Yang et al., 2015, 2012). However, a lack of documentation in the literature regarding the impact of pesticide mixtures on the kinetics of pesticide degradation remains. It becomes crucial to assess the validity of extrapolating results from a laboratory setting where pesticides are mixed with others of our choice to real atmosphere where numerous pesticides could coexist on the same aerosols.

This study aims to understand how pesticide mixtures, adsorbed on particle surfaces, impact the degradation kinetics of pesticides. To accomplish this, we compared the degradation kinetics of pendimethalin in various pesticide mixtures from the literature with this work's values (pendimethalin mixed with folpet, S-metolachlor, and tebuconazole). The selection of these pesticides was influenced by two key parameters: their presence in the particle phase and their occurrence in the atmosphere. This choice was guided by a prioritization work conducted by AtmoSud and Qualitair Corse in France. According to their findings, these 4 pesticides are frequently detected at sampling sites, with notably high concentrations (26 ng m^{-3}) for Folpet (Désert et al., 2018). Additionally, the heterogeneous degradation rates of the latter compounds were also determined towards ozone and OH radicals.

2. Materials and methods

2.1. Chemicals

Folpet (purity 99.9%), S-metolachlor (98.2%), pendimethalin (98.8%), and tebuconazole (99.4%) (PESTANAL®, analytical standard) as well as 2,3-dimethyl-2-butene (DMB, 98%), m-xylene (99.5%), and triphenyl phosphate (99.9%) were purchased from Sigma-Aldrich and were used as received. The chemical structures and physico-chemical properties of the pesticides under study are given in Supplementary Information (SI) Table S11.

2.2. Particles coating

Pesticides were adsorbed on hydrophobic silica particles AEROSIL R812 (purchased from Degussa) serving as a proxy for terrestrial aerosols. This simulates the complex physical and chemical nature of atmospheric aerosol content, as it has been demonstrated that approximately 10%–30% of atmospheric particles are composed of quartz or silica (Seinfeld and Pandis, 2016). Additionally, they were used for comparative purposes with other studies that used the same type of silica for a more comprehensive understanding of degradation (Barbas et al., 1996; Figueiredo et al., 2021, 2020; Mani et al., 2022; Mattei et al., 2019b, 2019c; 2019a, 2018; Net et al., 2009; Pflieger et al., 2013, 2011; 2009; Socorro et al., 2017, 2015). The main component of these particles is SiO_2 , accounting for more than 99.8% of their weight, while their surface is mainly covered with siloxane groups. The mean particle size ranges from 5 to 50 nm and presents a specific surface area of $(260 \pm 30) \text{ m}^2 \text{ g}^{-1}$ (Evonik, 2015). However, they can agglomerate and form aggregates that can vary in size from 5 μm up to 25 μm .

The coating was realized using a solid/liquid adsorption process. Six milliliters of dichloromethane (for HPLC, $\geq 99.8\%$, Sigma-Aldrich) containing the four pesticides under study (folpet, S-metolachlor, pendimethalin, and tebuconazole) at 20 mg L^{-1} each was mixed with 600 mg of silica particles in a Pyrex bulb of 500 cm^3 . This bulb underwent ultrasonication for 5 min. Then dichloromethane was evaporated at 40°C and $850 \pm 85 \text{ mbar}$, using a rotary evaporator (Rotavapor R-114, Büchi). Assuming a uniform particle surface coating for pesticides and a spherical geometry for particles, the percentage of the total coated particle surface was 1.6% in all experiments, which is much less than 3% of monolayer to prevent any shielding effect (Mattei et al., 2019a). The

validation of the particle coating process's effectiveness involves extracting 30 mg of coated particles and analyzing them. This analysis aims to determine the initial concentration of each pesticide adsorbed on the silica, ensuring the repeatability of our particles coating.

2.3. Experimental set-up for ozone and hydroxyl radicals exposure

The experimental set-ups used to expose pesticide-coated particles to ozone and hydroxyl radicals were previously outlined in detail in Socorro et al. (2015) (Fig. S1 and S2). Briefly, regardless of the specific oxidant being studied, the pesticide exposure is conducted using a rotary evaporator with a 500 cm^3 flask that has been modified for this type of experiment (Laborota 4000 efficient, Heidolph), with the refrigerant replaced by a system designed specifically for this purpose. By using the rotary evaporator, the flask containing the particles rotates continuously, ensuring uniform exposure of pesticides to the oxidants. The amber flask containing the pesticides, some of which may be photosensitive, is shielded from light using aluminum foil. The reactor's relative humidity is maintained at $55 \pm 2\%$, a realistic level often reached in the atmosphere (Soponronnarit et al., 1999). This is achieved by introducing a combination of two distinct air flows, one that is clean and dry, and the other that is clean and moist, into the reactor. To ensure the effectiveness of this process, the humidity level is measured both prior to and following each experiment at the reactor outlet with a humidity probe (Hydrolog NT, Rotronic, USA). A thermostated water bath regulates the reactor's temperature, which remains constant at $25 \pm 1^\circ\text{C}$. Additionally, the total gas flow rate at the reactor inlet is maintained at 500 ml min^{-1} , enabling a complete renewal of the gaseous contents in the balloon every minute, ensuring consistent concentrations of oxidants throughout the manipulation and aids in the removal of radicals formed during the degradation of pesticides.

2.4. Ozone and hydroxyl generation and measurement

A zero-air generator (ZA-1500, F-DGS) was employed to produce clean and dry air. This purified air was then passed through an ozone generator (UVP, LLC Upland, UK) to generate ozone by exposing the air to ultraviolet radiation emitted by a mercury vapor lamp with a wavelength of 185 nm. Particles coated with pesticides were exposed to an air flux containing 403 ppb of ozone (i.e., $1.01 \times 10^{13} \text{ molecules cm}^{-3}$) for 26 h, which was continuously monitored using a photometric ozone analyzer with a time resolution of 1 min (O_3 41M, Environnement S.A.). This ozone concentration can be detected in highly polluted areas; even a higher concentration of 500 ppb has been reported by Finlayson-Pitts and Pitts (2000).

OH radicals have a lifetime of less than 1 s in the atmosphere (Schlosser et al., 2009), so they must be generated in situ. One method of generating OH radicals is through the ozonolysis of an alkene, the 2, 3-dimethyl-2-butene (DMB), which is referred to as the "dark OH radical generation" technique (Lambe et al., 2007; Le Person et al., 2007; Mattei et al., 2019c; Pflieger et al., 2013; Segal-Rosenheimer et al., 2011). Ozone concentration in the reactor was set at $(3.3 \pm 0.1) \text{ ppm}$ (i.e., $(8.3 \pm 0.3) \times 10^{13} \text{ molecules cm}^{-3}$) during the experiments, due to the continuous and constant generation of DMB at a concentration of $(9 \pm 2) \text{ ppb}$ in the reactor. The concentration of OH radicals was measured by continuously injecting a gaseous tracer at a concentration of $(74 \pm 4) \text{ ppb}$ into the reactor and observing its consumption. m-xylene was used as a tracer because it reacts with OH radicals with a very known kinetic constant ($k_1 = (2.2 \pm 0.2) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) (Atkinson and Aschmann, 1989). The DMB degradation products ($m/z = 85, 71, 57, 43, 41$) and m-xylene ($m/z = 107$) concentrations were monitored using a High-Sensitivity Proton Transfer Reaction Mass Spectrometer (HS-PTR-MS, Ionicon Analytik) with a time resolution of 10 s. The HS-PTR-MS parameters are given in Table S12.

The hydroxyl radical concentration is given by the following equation:

$$[\text{OH}_{(\text{gas})}] = \ln \left(\frac{[\text{m-xylene}]_0}{[\text{m-xylene}]_t} \right) \times \frac{1}{k_1 \times t} \quad (1)$$

where $[\text{OH}_{(\text{gas})}]$ is the OH radical concentrations in the reactor during the experiment (molecules cm^{-3}), $[\text{m-xylene}]_0$ and $[\text{m-xylene}]_t$ are the initial and final concentrations of m-xylene in the reactor (molecules cm^{-3}), k_1 is the rate constant ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) and t the residence time of compounds in the gaseous phase in the reactor (s).

The hydroxyl radical concentration was set and kept constant prior to experiments at $(5.0 \pm 0.5) \times 10^7 \text{ molecules cm}^{-3}$. This value is in accordance with the summer concentrations of OH radicals in the atmosphere during periods of high photochemical pollution, which range from $10^5 \text{ molecules cm}^{-3}$ to $10^7 \text{ molecules cm}^{-3}$ depending on the pollution level (Hübler et al., 1984; Tuazon et al., 1981). Regarding this oxidant, pesticide-coated particles were exposed for 6 h.

2.5. Pesticides extraction and analysis

During O_3 and OH radical exposure, 30 mg aliquots of particles were sampled from the reactor at defined intervals to determine the amount of pesticides remaining adsorbed on the surface of the particles. Each sample was extracted individually in an accelerated solvent extraction (ASE 350, Dionex) with dichloromethane using a 33 mL stainless steel cell with triphenyl phosphate as an internal standard (TPP). Subsequently, the extracts were concentrated using a concentration workstation under a flow of nitrogen gas (TurboVap II, Biotage).

Analysis of the obtained solutions was realized using 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 ionisation (70 eV). More details on ASE extraction, concentration and GC/MS-MS analysis are given in Socorro et al. (2015).

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

The second-order degradation rate constants $k_{\text{O}_3}^{\text{H}}(\text{part})$ and $k_{\text{OH}}^{\text{H}}(\text{part})$ were calculated from the pseudo-first-order constants (k^{I}) according to the Langmuir-Rideal kinetic model. All kinetic constants obtained were corrected by subtracting the pesticides decay induced by hydrolysis and desorption (Mattei et al., 2018). The sum of these two constants ($k_{\text{hydrolysis}}^{\text{I}} + k_{\text{desorption}}^{\text{I}}$) is obtained through a prior blank manipulation where pesticides coated on silica particles are exposed to a humid air stream for 26 h. A sample of 30 mg of particles is extracted and analyzed at time 0 to determine the initial concentration of each pesticide adsorbed on the particles. Subsequent samples are taken every 2 h to monitor their concentration over time. This indicates that the decrease in pesticide concentration following exposure to the studied oxidants is solely attributable to their degradation and not their repartition in the gaseous phase, taking into account both hydrolysis and desorption constants. The details of calculation are given in the SI.

The atmospheric half-lives of the heterogeneous degradation of pesticides toward O_3 and OH radicals were calculated according to equations (2) and (3). For these calculations, O_3 concentration was $1.0 \times 10^{12} \text{ molecule cm}^{-3}$ with an exposure time of 24 h (Vingarzan, 2004) whereas for OH radicals, the concentration used was $1.5 \times 10^6 \text{ molecule cm}^{-3}$ with an exposure time of 12 h (Lawrence et al., 2001; Prinn et al., 2001).

$$t_{1/2 \text{ O}_3 (\text{part})} = \frac{\ln 2}{k_{\text{O}_3 (\text{part})}^{\text{H}} \times [\text{O}_3 (\text{gas})]} \quad (2)$$

$$t_{1/2 \text{ OH} (\text{part})} = \frac{\ln 2}{k_{\text{OH} (\text{part})}^{\text{H}} \times [\text{OH} (\text{gas})]} \quad (3)$$

where $t_{1/2 \text{ O}_3 (\text{part})}$ and $t_{1/2 \text{ OH} (\text{part})}$ (in s) are the atmospheric half-lives

resulting from pesticide degradation toward O_3 and OH radicals respectively, $k_{\text{O}_3 (\text{part})}^{\text{H}}$ and $k_{\text{OH} (\text{part})}^{\text{H}}$ (in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) are the second-order kinetic constants and $[\text{O}_3 (\text{gas})]$ and $[\text{OH} (\text{gas})]$ are the gaseous concentration of O_3 and OH radicals (in molecules cm^{-3}) respectively.

3. Results and discussion

3.1. Heterogeneous ozonolysis

All kinetic constants obtained were corrected by subtracting the pesticides decay induced by hydrolysis and desorption (Mattei et al., 2018). Under these conditions, the four pesticides, were not or slightly degraded with second-order rate constants $k_{\text{O}_3 (\text{part})}^{\text{H}}$ ranging from ($<10^{-20} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$; Tebuconazole) to $(5.5 \pm 3.0) \times 10^{-20} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$; S-metolachlor).

Table 1 presents all kinetic data available in the literature concerning the heterogeneous degradation by ozone of pesticides of the same chemical family as the 4 compounds under study, as well as the results of this study.

3.1.1. Pendimethalin (dinitroaniline family)

In this study, the order of magnitude for the ozonolysis rate of pendimethalin, when studied in a mixture, is $(2.8 \pm 0.4) \times 10^{-19} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ whereas it is $(6.8 \pm 0.6) \times 10^{-19} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ when studied individually. However, it is premature to conclude that the presence of a pesticide mixture slowdown the kinetics. Previous studies on the same hydrophobic silica particles and under similar experimental conditions report ozonolysis rates of $(3.4 \pm 0.1) \times 10^{-19} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ (Socorro et al., 2015) and even $(4.7 \pm 0.4) \times 10^{-20} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ (Mattei et al., 2018). The slight discrepancy observed among these studies is likely attributed to the slow kinetics, which approach the limit of observable phenomena with the underutilized experimental setup, leading to an inevitable dispersion of results.

It can also be noted that trifluralin, and isopropalin, two dinitroaniline herbicides, were studied using the same silica particles, and shown similar ozone degradation rates constants $(2.9 \pm 0.1) \times 10^{-19} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ to $(1.05 \pm 0.06) \times 10^{-19} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ (Pflieger et al., 2011, 2009; Yang et al., 2012). Generally, results and literature are in accordance with the fact that pesticides of the dinitroaniline family undergo an effective but slow heterogeneous degradation with ozone (half-lives regarding ozone in the particulate phase are all greater than 12 days). This corroborate the hypothesis from Mattei et al. (2018), who proposed that the kinetic data obtained for a single pesticide within the dinitroaniline family could be extrapolated to the entire chemical family.

3.1.2. Folpet (dicarboximide family)

Under our experimental conditions, folpet, a pesticide belonging to the dicarboximide family, adsorbed on hydrophobic silica particles has a reaction rate with ozone of $(2.3 \pm 3) \times 10^{-20} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$. A separate study conducted by Al Rashidi et al. (2013) using a different adsorption surface (quartz) measured an analogous reactivity of folpet towards ozone, with a rate of $(2.6 \pm 0.2) \times 10^{-20} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$. In a different study that focused on the ozonolysis of vinclozolin (which belongs to the same chemical family) adsorbed on azelaic acid particles, the degradation rate was significantly accelerated, recording $(2.4 \pm 0.4) \times 10^{-17} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$. This is approximately a thousand times faster than the reaction of folpet on silica particles and quartz (Gan et al., 2010). The disparity in the degradation rates between vinclozolin and folpet can be attributed to the presence of the alkene functional group in vinclozolin, which is known to exhibit a higher reactivity towards ozone (Paulson and Orlando, 1996).

Table 1

Kinetic data for the ozonolysis of pesticides under study (in bold) and atmospheric half-lives compared to the literature data.

Chemical Family	Pesticide	Surface	Relative Humidity (%)	T (°C)	Ozone (ppm)	($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) $k_{O_3}^{II}(\text{part})$	(days) ^a $t_{1/2} O_{3(\text{part})}$	Reference
Dinitroaniline	Pendimethalin	HSi	55 ± 3	25 ± 1	0.4	(6.8 ± 0.6) × 10⁻¹⁹	12	This study (alone)
		HSi	55 ± 3	25 ± 1	0.4	(2.8 ± 0.4) × 10⁻¹⁹	29	This study (in mixture)
		HSi	55 ± 5	25 ± 1	0.055 to 0.97	(3.4 ± 0.1) × 10 ⁻¹⁹	24	Socorro et al. (2015)
	Trifluralin	HSi	55	25 ± 1	0.4	(4.7 ± 0.4) × 10 ⁻²⁰	173	Mattei et al. (2018)
		HSi	1	25	(5–42) ± 3%	(2.9 ± 0.1) × 10 ⁻¹⁹	28	Pflieger et al. (2009)
	HSi	<1	26 ± 1	(1–16) ± 3%	(1.05 ± 0.06) × 10 ⁻¹⁹	78	Pflieger et al. (2011)	
Dicarboximide	Isopropalin	HSi	Unknown	20	0.237 to 12	(2.70 ± 0.27) × 10 ⁻¹⁹	30	Yang et al. (2012)
	Folpet	HSi	55 ± 3	25 ± 1	0.4	(2.3 ± 3) × 10⁻²⁰	354	This study
		Quartz	Unknown	20 ± 2	34 to 93	(2.6 ± 0.2) × 10 ⁻²⁰	313	Al Rashidi et al. (2013)
	Vinclozolin	Azelaic acid	~5	24 ± 1	4 to 55	(2.4 ± 0.4) × 10 ⁻¹⁷	0.3	Gan et al. (2010)
Triazole	Tebuconazole	HSi	55 ± 3	25 ± 1	0.4	< 10⁻²⁰	> 800	This study
		QP	Unknown	20 ± 2	73 to 285	(5.1 ± 0.2) × 10 ⁻²¹	1597	Rokbani et al. (2019)
	Diniconazole	QP	Unknown	20 ± 2	73 to 285	(1.37 ± 0.09) × 10 ⁻¹⁹	59	Rokbani et al. (2019)
	Difenoconazole	HSi	55 ± 5	25 ± 1	0.055 to 0.97	<3.4 × 10 ⁻¹⁹	>24	Socorro et al. (2015)
		HSi	(0–80) ± 2	25 ± 1	0.4	<10 ⁻²⁰	>800	Mattei et al. (2018)
		HySi	(0–80) ± 2	25 ± 1	0.4	<10 ⁻²⁰	>800	Mattei et al. (2018)
		Arizona Dust	(0–80) ± 2	25 ± 1	0.4	<10 ⁻²⁰	>800	Mattei et al. (2018)
		QP	Unknown	29 ± 2	10 to 45	(2.6 ± 0.4) × 10 ⁻²⁰	313	Al Rashidi et al. (2011)
	Tetraconazole	HSi	55 ± 5	25 ± 1	0.055 to 0.97	<3.4 × 10 ⁻¹⁹	>24	Socorro et al. (2015)
		HSi	(0–80) ± 2	25 ± 1	0.4	<10 ⁻²⁰	>800	Mattei et al. (2018)
HySi		(0–80) ± 2	25 ± 1	0.4	<10 ⁻²⁰	>800	Mattei et al. (2018)	
Arizona Dust		(0–80) ± 2	25 ± 1	0.4	<10 ⁻²⁰	>800	Mattei et al. (2018)	
Chloroacetanilide	Bitertanol	Seeds	10% (w/w)	Unknown	50	1.4 × 10 ⁻¹⁹	58	Bourgin et al. (2013)
	S-metolachlor	HSi	55 ± 3	25 ± 1	0.4	(5.5 ± 3) × 10⁻²⁰	148	This study
	Alachlor	HSi	1	25	40 ± 2	<5 × 10 ⁻²⁰	>163	Pflieger et al. (2009)

HSi: Hydrophobic Silica.

HySi: Hydrophilic Silica.

QP: Quartz Plaques.

^a Atmospheric half-lives calculated for $[O_{3(\text{gas})}] = 9.85 \times 10^{11} \text{ molecule cm}^{-3}$ with an exposure time of 24h (Vingarzan, 2004).

3.1.3. Tebuconazole (triazole family)

Tebuconazole demonstrated the lowest reactivity towards ozone compared to pendimethalin, folpet, and S-metolachlor, with a degradation rate for ozone less than $10^{-20} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. This finding aligns with previous research, where the ozonolysis of tebuconazole adsorbed on quartz exhibited a similar magnitude of reactivity (Rokbani et al., 2019). Most studies available in the literature regarding triazole compounds, such as tetraconazole and difenoconazole, consistently indicate no degradation ($<10^{-20} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) when exposed to ozone, regardless of the nature of the adsorbed surface, even under high ozone concentrations (50 ppm), as observed in the case of bitertanol (Bourgin et al., 2013). In contrast, among the compounds examined, only diniconazole exhibits a noticeable reactivity towards ozone. Its degradation rate of $(1.37 \pm 0.09) \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ suggests that this reactivity can be attributed to the presence of an alkene bond in the molecule (Rokbani et al., 2019). This alkene bond enables the formation of ozonides, which then undergoes decomposition to generate a diverse range of products (Socorro et al., 2016b).

3.1.4. S-metolachlor (chloroacetanilide family)

S-metolachlor degradation follows a rate constant of $(5.5 \pm 3) \times 10^{-20} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ when exposed to ozone. The result is similar to what Pflieger et al. (2009) obtained for alachlor, which belongs to the same chloroacetanilide family ($<5 \times 10^{-20} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). This

slow reactivity with ozone can be linked to various factors associated with its chemical structure. One such factor is the presence of electron-withdrawing groups, such as nitro (-NO₂) or cyano (-CN) groups, within the molecule. These groups diminish the electron density around the carbon-carbon double bonds, making them less prone to nucleophilic attack by ozone. Consequently, the reaction rates are slowed down as the electron-withdrawing groups stabilize the double bonds, thereby reducing their reactivity towards electrophilic species like ozone (Cataldo, 2006).

3.2. Heterogeneous degradation by OH radicals

All kinetic constants obtained were corrected by subtracting the pesticides decay induced by hydrolysis, desorption, ozonolysis, and reactivity with possible intermediate species formed into the reactor (Mattei et al., 2019c). Under these conditions, the four pesticides, were degraded with second-order rate constants, $k_{OH}^{II}(\text{part})$ ranging from $((6.2 \pm 1.0) \times 10^{-13}) \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$, pendimethalin to $((2.6 \pm 0.2) \times 10^{-12}) \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$, tebuconazole).

The different reaction rate constants of heterogeneous degradation by OH radicals and their associated atmospheric half-lives are summarized by chemical family of pesticides under study and compared to literature data in Table 2.

Table 2

Kinetic data available in the literature concerning the heterogeneous degradation by OH radicals of pesticides of the same chemical family as those under study, as well as the results of this study (in bold).

Chemical family	Pesticide	Surface	Relative Humidity (%)	T (°C)	OH radical (molecules cm ⁻³)	(cm ³ molecule ⁻¹ s ⁻¹) $k_{OH(part)}^H$	(days) ^b $t_{1/2 OH(part)}$	Reference
Dinitroaniline	Pendimethalin	HSi	55 ± 3	25 ± 1	(5.0 ± 0.5) × 10⁷	(6.2 ± 1.0) × 10⁻¹³	17.2	This study
		HSi	55 ± 5	25 ± 1	3.1 × 10 ⁷ - 1.45 × 10 ⁸	(4.3 ± 2.2) × 10 ⁻¹³	24.9	Socorro et al. (2016a)
		HSi	0–70	25	6.61 × 10 ⁷	≤10 ⁻¹³ to (4.08 ± 0.27) × 10 ⁻¹²	3 to ≥ 100	Mattei et al. (2019c)
		HSi	55	25	6.61 × 10 ⁷	(4.3 ± 2.05) × 10 ⁻¹³	24.9	Mattei et al. (2019c)
		HySi	0–70	25	6.61 × 10 ⁷	≤10 ⁻¹³ to (4.08 ± 0.27) × 10 ⁻¹²	3 to ≥ 100	Mattei et al. (2019c)
		HySi	55	25	6.61 × 10 ⁷	(8.2 ± 1.9) × 10 ⁻¹³	13	Mattei et al. (2019c)
Dicarboximide	Folpet	HSi	55 ± 3	25 ± 1	(5.0 ± 0.5) × 10⁷	(8.2 ± 1.2) × 10⁻¹³	13	This study
		Quartz cells	0.7	29 ± 2	Unknown	(1.6 ± 0.9) × 10 ⁻¹³	67	Al Rashidi et al. (2014)
Triazole	Tebuconazole	HSi	55 ± 3	25 ± 1	(5.0 ± 0.5) × 10⁷	(2.6 ± 0.2) × 10⁻¹²	4.1	This study
		QP	Unknown	25 ± 2	Unknown	(1.7 ± 0.93) × 10 ⁻¹³	63	Rokbani et al. (2019)
	Diniconazole	QP	Unknown	25 ± 2	Unknown	(1.8 ± 1.3) × 10 ⁻¹²	6	Rokbani et al. (2019)
	Difenoconazole	HSi	0–70	25	6.61 × 10 ⁷	<10 ⁻¹³	>100	Mattei et al. (2019c)
		HySi	0–70	25	6.61 × 10 ⁷	<10 ⁻¹³	>100	Mattei et al. (2019c)
	Tetraconazole	HSi	55 ± 5	25 ± 1	3.1 × 10 ⁷ - 1.45 × 10 ⁸	< (4.3 ± 2.2) × 10 ⁻¹³	>25	Socorro et al. (2016a)
		QP	0.7	29 ± 2	Unknown	(7.1 ± 0.8) × 10 ⁻¹⁴	151	Al Rashidi et al. (2011)
		HSi	0–70	25	6.61 × 10 ⁷	<10 ⁻¹³	>100	Mattei et al. (2019c)
HySi		0–70	25	6.61 × 10 ⁷	<10 ⁻¹³	>100	Mattei et al. (2019c)	
Chloroacetanilide	S-metolachlor	HSi	55 ± 3	25 ± 1	(5.0 ± 0.5) × 10 ⁷	(8.0 ± 1.2) × 10 ⁻¹³	13.4	Socorro et al. (2016a)
		HSi	55 ± 3	25 ± 1	(5.0 ± 0.5) × 10⁷	(8.0 ± 1.2) × 10⁻¹³	13.4	This study

HSi: Hydrophobic Silica.

HySi: Hydrophilic Silica.

QP: Quartz Plaques.

^b Atmospheric half-life calculated for $[OH_{(gas)}^*] = 1.5 \times 10^6$ molecules.cm⁻³ with an exposure time of 12h (Lawrence et al., 2001; Prinn et al., 2001).

3.2.1. Pendimethalin (dinitroaniline family)

In this study, pendimethalin had a degradation rate of $(6.2 \pm 1.0) \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹. This is in accordance with the literature, in which similar rates were obtained by using the same experimental conditions (Mattei et al., 2019c; Socorro et al., 2016a).

3.2.2. Folpet (dicarboximide family)

For folpet, a kinetic constant of $(8.2 \pm 1.2) \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹ was obtained. This is similar to a study conducted by Al Rashidi et al. (2014), who obtained a value of $(1.6 \pm 0.9) \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹ falling within the same order of magnitude. The factor of 5 between these two values could be attributed to the different adsorption phase.

3.2.3. Tebuconazole (triazole family)

Tebuconazole, which falls under the category of triazoles, has a kinetic constant of $(2.6 \pm 0.2) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ which demonstrates a higher reactivity towards OH radicals than the other three pesticides under study. Only one study in the literature has determined a kinetic constant for this pesticide towards OH radicals; Rokbani et al. (2019) found a value 15 times smaller than our result, with a kinetic constant of $(1.7 \pm 0.93) \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹. This disparity may be attributed, among other possible factors, to the surface type. In the

latter study, tebuconazole was adsorbed on quartz supports that might have reduced the reactivity of tebuconazole towards OH radicals. The same study by Rokbani et al. demonstrated that diniconazole, which is also a triazole compound, exhibited a reactivity 10 times greater than tebuconazole on the same quartz support. However, the reactivity of diniconazole was similar to that obtained in our work on hydrophobic silica. Other triazoles such as difenoconazole and tetraconazole showed no degradation in the presence of OH radicals ($k_{OH(part)}^H < 10^{-13}$ cm³ molecules⁻¹ s⁻¹, which corresponds to $t_{1/2 OH(part)} > 100$ days) regardless of the type of particles used.

3.2.4. S-metolachlor (chloroacetanilide family)

For the chloroacetanilide family, the degradation of S-metolachlor shows a rate constant of $(8.0 \pm 1.2) \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹. However, there is a lack of available literature regarding the heterogeneous degradation of S-metolachlor or any chloroacetaniline compound by hydroxyl radicals. This reaction likely occurs due to the abstraction of a hydrogen atom from the S-metolachlor molecule by the hydroxyl radical, leading to the formation of a chlorine-centered radical that is highly reactive and can participate in further reactions.

3.3. Influence of pesticide mixtures on heterogeneous degradation rate constants

The impact of pesticide mixture on heterogeneous kinetics was assessed by comparing the kinetic constants of pendimethalin exposed to OH radical or ozone in three distinct mixtures.

- Mixture A: **Pendimethalin alone** (this work)
- Mixture B: **Pendimethalin, S-metolachlor, tebuconazole, and folpet** (this work)
- Mixture C: **Pendimethalin, cyprodinil, deltamethrin, difenoconazole, fipronil, permethrin, oxadiazon, and tetraconazole** (Mattei et al., 2019c, 2018)
- Mixture D: **Pendimethalin, cyprodinil, deltamethrin, difenoconazole, fipronil, permethrin, oxadiazon, and tetraconazole** (Socorro et al., 2016a, 2015)

The total surface coverage of these three mixtures is less than 3% of a monolayer: 0.4% (Mixture A, this study), 1.6% (Mixture B, this study), and 2.8% (Mixture C and D (Mattei et al., 2019c, 2018; Socorro et al., 2016a, 2015)). Thus, the shielding effect should not be involved (Mattei et al., 2019a). Therefore, what is observed here is only the presence or absence of competition for reactivity based on the diversity and nature of the present compounds. The experiments were carried out at a RH of 55%, pesticides were adsorbed on hydrophobic silica, and all the experimental conditions were strictly identical.

Fig. 1a presents the second-order rate constants for pendimethalin degradation by ozone as follows: $(6.8 \pm 0.6) \times 10^{-19} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ for mixture 1, $(2.8 \pm 0.4) \times 10^{-19} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ for mixture 2 and $(3.4 \pm 0.1) \times 10^{-19} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ for mixture 3. The last mixture has been replicated in another study in the literature, with a lower value of $(4.7 \pm 0.4) \times 10^{-20} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ (Mattei et al., 2018). Apart from this result, the constants are nearly identical within the uncertainties, and pendimethalin is slightly degraded by ozone. Pendimethalin alone or in a mixture with other pesticides appears to

have degradation rates of the same order of magnitude, so, under the tested conditions, there appears to be no mixture effect inducing variability in the heterogeneous kinetic degradation constants by ozone.

Fig. 1b presents the second-order kinetic constant for the heterogeneous degradation of pendimethalin by OH radicals when adsorbed in two different pesticides mixtures. A value of $(6.2 \pm 1.0) \times 10^{-13} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ was observed in mixture 2 and values of $(4.1 \pm 0.3) \times 10^{-13} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ and $(4.3 \pm 2.2) \times 10^{-13} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ were measured in mixture 3. The similarity between the 3 rate constants shows that, in the tested conditions, the pesticide mixture does not influence the degradation rates concerning OH radicals.

Regarding the impact of the mixture on the kinetics, a prior study conducted by Pflieger et al. (2012) found no notable differences in the ozonolysis rate of isoproturon and trifluralin when tested individually or in a mixture.

To our knowledge, only two studies in the literature, focused on pesticides that are also used in our present work. Al Rashidi et al. (2013, 2014), despite studying folpet degradation on quartz surfaces and using a different experimental set-up, obtained results that are consistent with ours. Fig. 2a–and b presents the degradation constant of folpet in our mixture (folpet mixed with pendimethalin, tebuconazole, and S-metolachlor) and that determined in Al Rashidi's mixture (folpet mixed with dimethomorph) for both ozone and hydroxyl radicals. For ozone, the kinetic constant measured in the two studies are identical, and for OH radicals, they are in the same order of magnitude. This corroborates the hypothesis that the pesticide mixture does not influence the reaction kinetics.

Additionally, a result of another study conducted by Rokbani et al. (2019), on tebuconazole shows that the degradation towards ozone is very slow $(5.1 \pm 0.2) \times 10^{-21} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$, which correlates with our findings. However, towards OH radicals a factor of 15 is observed between the two results which could be attributed to the difference in surface type.

In general, the mixture appears to have no significant impact on the degradation rate constants of pesticides by ozone and hydroxyl radicals. However, since there is a lack of supporting studies, further data is required, particularly involving different pesticides and types of

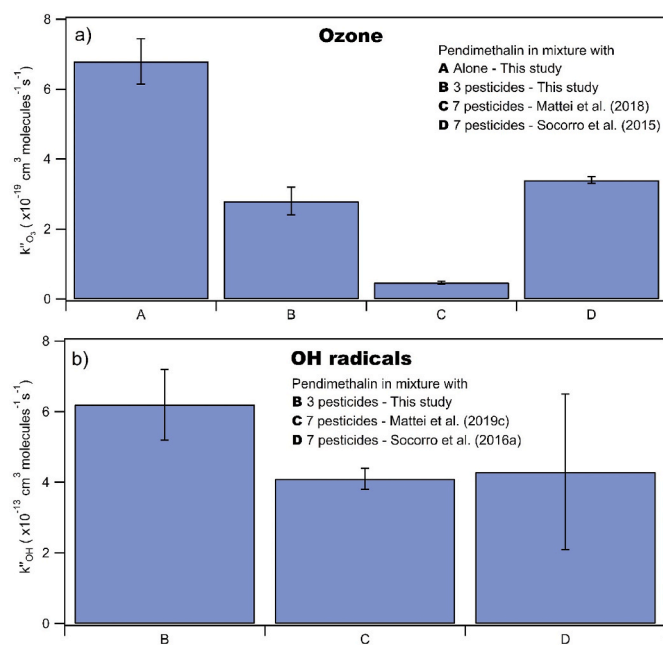


Fig. 1. a, and b: Second-order rate constants for ozone and OH degradation of pendimethalin adsorbed on hydrophobic silica at 55% RH (A: Pendimethalin alone, this study; B: pendimethalin in mixture with folpet, S-metolachlor and tebuconazole, this study; C & D: pendimethalin in mixture with cyprodinil, deltamethrin, difenoconazole, fipronil, permethrin and tetraconazole (Mattei et al., 2018, 2019c, Socorro et al., 2015, 2016a).

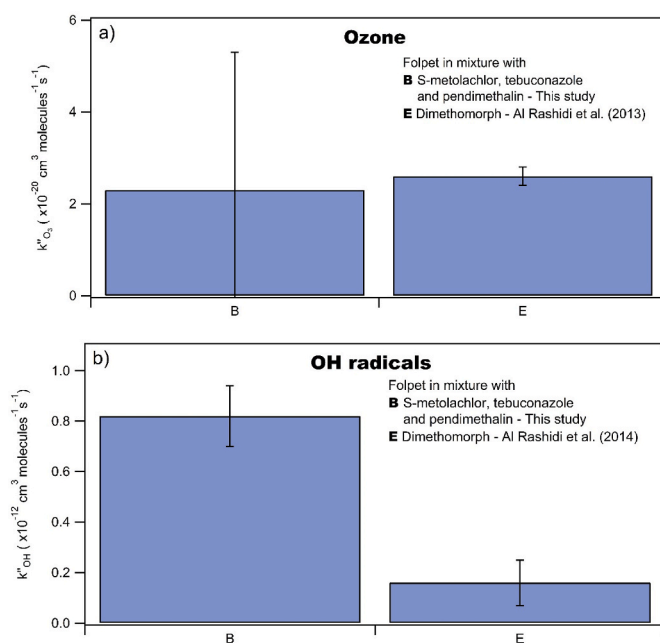


Fig. 2. a, and b: Second-order rate constants for ozone and OH degradation of folpet adsorbed on hydrophobic silica and quartz cells (B: Folpet in mixture with pendimethalin, S-metolachlor and tebuconazole, this study; E: Folpet in mixture with dimethomorph (Al Rashidi et al., 2013, 2014).

particles, to validate this hypothesis. Additionally, it is important to note that further investigation should be performed using a mixture containing various other SVOC pollutants, that are more abundant in the atmosphere, such as polychlorinated biphenyl (PCB) and polycyclic aromatic hydrocarbons (PAH), to determine if they could mask the pesticides reactivity or even compete with the present oxidants (Alebic-Juretic et al., 1990; Miet et al., 2009; Perraudin et al., 2007; Wu et al., 1984).

3.4. Atmospheric implications

According to the Stockholm Convention (UNEP, 2001), a pesticide is considered a persistent organic pollutant (POP), when the atmospheric half-life in the gas phase exceeds two days.

Heterogeneous half-lives calculated for pendimethalin, folpet, S-metolachlor and tebuconazole for a concentration of 40 ppb of ozone, reflecting the typical ozone levels found in the mid-latitudes of the Northern Hemisphere (Vingarzan, 2004), ranged from 29 days (Pendimethalin) to more than 800 days (Tebuconazole). Moreover, the particulate half-lives determined in this study when these pesticides are exposed to a concentration of OH radical of 1.5×10^6 molecules cm^{-3} with an average exposure time of 12h (Lawrence et al., 2001; Prinn et al., 2001), reflecting the measured concentration of hydroxyl radicals (OH) in moderately polluted regions (Hübner et al., 1984), ranged from 4 days (Tebuconazole) to 14 days (Pendimethalin).

These half-lives are long enough to allow aerial transportation at a global scale, impacting human health and inducing a potential transfer to the aquatic and terrestrial ecosystems where they can cause hazardous effects.

This indicates that pesticides under study persist in the atmosphere once adsorbed on particles and can be considered as persistent organic compounds (POPs), if we do not consider photolysis and the presence of other oxidants in our calculation.

4. Conclusion

Heterogeneous degradation of pendimethalin, folpet, tebuconazole, and S-metolachlor adsorbed on hydrophobic silica particles by ozone and hydroxyl radicals were investigated at a relative humidity of 55 %. Studied pesticides are not or slowly degraded by ozone with half-lives ranging from a few weeks to several years. The pesticides are more reactive with hydroxyl radicals than with ozone, with a half-lives of 17 days for pendimethalin, folpet and S-metolachlor and of 4 days for tebuconazole. The four pesticides under study can be considered as persistent organic pollutants (POPs) regarding their heterogeneous degradation. Moreover, our study showed that the mixture does not significantly influence the degradation rate constants with OH radicals or ozone of pesticides. Indeed, the pendimethalin degradation rates were similar whether it was applied with folpet, tebuconazole, and S-metolachlor or with cyprodinil, deltamethrin, difenoconazole, fipronil, oxadiazon, permethrin and tetraconazole.

These findings validate the potential to investigate simultaneously the degradation kinetics of pesticide in the particulate phase when they are in mixture, providing advantages in terms of time and resource savings. More importantly, this study demonstrates that a kinetic constant measured for a specific compound within a given pesticide mixture, can be extrapolated to predict its degradation in another mixtures. This supports the strong transferability of results obtained in the laboratory to the actual environment, where pesticides are mostly found in mixture of nearly infinite variability.

CRedit authorship contribution statement

Boulos Samia: Writing – original draft, Investigation. **Loïc Della Puppa:** Investigation. **Coraline Mattei:** Writing – review & editing, Methodology, Conceptualization. **Amandine Durand:** Formal analysis,

Data curation. **Sylvain Ravier:** Software, Formal analysis. **Etienne Quivet:** Project administration, Methodology, Funding acquisition, Conceptualization. **Henri Wortham:** Writing – review & editing, Validation, Supervision, Project administration, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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Data availability

The authors are unable or have chosen not to specify which data has been used.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.envpol.2024.123351>.

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