



Atmospheric degradation of two pesticides mixed with volatile organic compounds emitted by citrus trees. Ozone and secondary organic aerosol production

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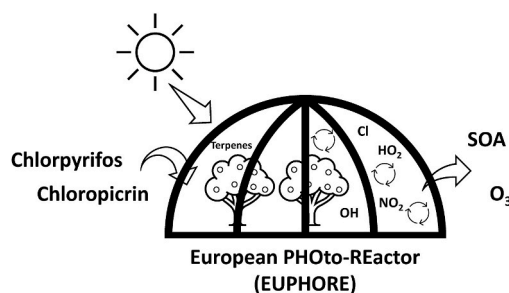
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HIGHLIGHTS

- Atmospheric oxidation study of terpenes and chloropicrin and chlorpyrifos.
- Pesticide degradation in the air leads to ozone and fine particle matter.
- BVOCS photolysis or ozonolysis enhances SOA formation with pesticides present.
- The plant protection products-BVOCS interaction produces high ozone and SOA levels.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Pesticides
Terpenes
Aerosol
 α -pinene
Chlorpyrifos
Chloropicrin

ABSTRACT

Once pesticides are released into the environment, their active ingredient and other formulation compounds, such as coadjuvants or solvents, may undergo biological and chemical degradation, and form a range of products that could be even more hazardous than their precursors. These degradation products may also interact with the natural biogenic compounds emitted by treated crops, which leads to secondary air pollutants, such as ozone (O_3) or fine particulate matter, which directly affect human health and climate warming. This research provides evidence for the atmospheric process influencing the atmospheric and environmental fate of pesticides, active substance chloropicrin and commercially formulated chlorpyrifos, which interact with biogenic volatile organic compounds (α -pinene and a mixture of monoterpenes) simulating mixtures of terpenes emitted by orange trees at the large outdoor European PHOto-REactor (EUPHORE). Significant SOA formations were observed during the photolysis and/or ozonolysis of both pesticides in the presence of biogenic volatile organic compounds. For the photolysis of chloropicrin in the presence of α -pinene, the aerosol and O_3 formation yields ranged from 6 to 16% and 167–338%, respectively, depending on the initial conditions. For the photolysis of commercial chlorpyrifos in the presence of a mixture of terpenes, the formed aerosol yield was 24%, higher than those obtained by the photolysis of the terpenes in the absence of pesticides. Both pesticides in combination with terpenes increased O_3 formation. O_3 reacted with those terpenes, which increased particulate matter formation and may pose atmospheric issues on local and global scales.

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1. Introduction

The use of pesticides, also called plant protection products (PPP), is widespread. Despite the relevant role of PPP in maintaining agricultural crop yields and their importance for the global economy, some of them promote serious problems for human health and the environment (Alavanja et al., 2004). Vast amounts of pesticide active ingredients are globally released, with values of more than 4 million tonnes per year (FAOSTAT, 2020). In Europe (EU-27), about 360,000 tonnes were sold annually during 2011–2018 (Eurostat, 2020). Around 500 active substances are currently authorised by the EU to be applied to various crops according to Regulation (EC) 1107/2009.

The intensive agricultural employment of PPP has led to the contamination of soil, water and air in exposed and remote areas (Atkinson et al., 1999; Espallardo et al., 2012; Degrendele et al., 2016). This has also given rise to concerns about their effects on the environment and/or human health (López et al., 2017; Fuentes et al., 2021; Degrendele et al., 2022).

In the atmosphere, pesticides are distributed in gas, particle and aqueous phases depending on their physico-chemical properties and environmental conditions (Tsa and Cohen, 1991). The amount of emitted PPP depends on the crop they are used to, the training of the applicators, and the recommended values (which might defer from one country to another). Once a PPP is applied to a field, the pesticide can be partitioned into the soil, water, biota and the atmosphere. Afterwards, the pesticide may undergo biological and chemical degradations, which lead to the formation of a range of different compounds, that could be even more hazardous than their precursors (Aly et al., 2022). The identification of the main degradation products formed is required to assess the potential danger to human health and to evaluate their potential for long-range atmospheric transport. Previous studies on atmospheric degradation of the gas phase pesticide-active substances have demonstrated that can form aerosols (Borrás et al., 2015a, b, Muñoz et al., 2012) and/or ozone (O_3) (Muñoz et al., 2011; Vera et al., 2010).

From the point of view of activity against pests, commercial pesticides include “inert” compounds such as solvents and adjuvants, which are compounds with a relatively short lifetime in the atmosphere. The atmospheric degradation of these considered “inert” compounds could lead to the formation of secondary contaminants, such as O_3 or fine particulate matter that directly affect health and climate warming (Chyacutelek and Coakley, 1974).

Aerosols can also directly affect human health in two ways: by short-term acute symptoms like asthma and bronchitis; by long-term chronic irritation and inflammation of the respiratory system, which can potentially lead to some cancer types (Mauderly and Chow, 2008), but can also be used by pathogens, such as viruses and bacteria, as transmission vectors to generate serious public health problems like the recent COVID-19 pandemic (Anderson et al., 2020).

Ozone (O_3) is considered the second most important gaseous pollutant in the environment (Cho et al., 2011), and is also one of the more important sources of the greenhouse effect (Hallquist et al., 2009; Newland et al., 2018). O_3 can also cause a variety of human health problems, especially for the elderly and children with lung diseases (Nuvolone et al., 2017). Also, O_3 is considered the most phototoxic air pollutant for some ecosystems like crops, forests and/or grasslands (Ainsworth et al., 2012).

In this work, the atmospheric behaviour of two different pesticides, namely active substance chloropicrin and commercial chlorpyrifos, was investigated in the presence of selected biogenic compounds: α -pinene and a mixture of similar monoterpenes to those emitted by orange trees, a very important crop globally, and particularly in the Mediterranean Basin. To investigate the formation of secondary organic aerosols (SOA) and O_3 , studies were carried out under atmospheric boundary layer conditions in the European Photochemical Reactor facility (EUPHORE).

Chloropicrin (trichloronitromethane, CCl_3NO_2) was selected because

is a pesticide that has been extensively used in agriculture as a pre-plant soil fumigant to control pathogens, parasitic nematodes, fungi and weeds. (Vera et al., 2010). This pesticide is not authorised for use in European agriculture, but it is commonly spread in China and the USA, two countries with major pesticide use globally (FAOSTAT, 2020). Chloropicrin has a relatively high vapour pressure (24 mmHg at 25 °C), and significant amounts are expected to be emitted to the atmosphere while being applied. Chloropicrin is usually applied by injecting it into the soil of crops and due to its high volatilization, much of it passes into the gas phase and thus into the atmosphere. In some studies, from 1000 $\mu\text{g m}^{-3}$ to finally about 60 $\mu\text{g m}^{-3}$ have been detected after a few minutes or away from the point of application due to the wind (Yates et al., 2015).

Chlorpyrifos is one of the organophosphorus most widespread insecticides used for agricultural crop protection worldwide. Recently in 2018 however, the European Commission withdrew all authorisations for PPP containing chlorpyrifos (EU Pesticides Database, 2020). Nevertheless, this PPP is still also commonly used globally. Chlorpyrifos concentrations up to 1.428 ng m^{-3} have been reported in ambient air in both gas and particle phases (Borrás et al., 2011; Degrendele et al., 2016; Desert et al., 2018). The atmospheric lifetime of chlorpyrifos related to OH reactions in the gas phase is approximately 2 h (Muñoz et al., 2014; Borrás et al., 2015b).

Citrus vegetation releases several gas-phase compounds into the atmosphere, such as CO_2 and several volatile organic compounds (VOCs) (Fares et al., 2011; Gentner et al., 2014). Oxygenated monoterpenes, monoterpenes and sesquiterpenes are the main biogenic VOCs emitted from citrus species. The reaction of these terpenes with O_3 and OH radicals may lead to the formation of SOA (Gentner et al., 2014). In spring, emissions of biogenic compounds frequently increase due to the high insolation and emission of those compounds by flowering (Calfapietra et al., 2013).

This research aims to study how pesticides interact with the organic compounds naturally emitted by crops to investigate their implication in the formation of SOA, O_3 and other compounds. Thus, understanding atmosphere reactions can help to estimate the expected formation of gas and/or particulate products in the troposphere for each pesticide.

2. Experimental part

2.1. Photoreactor and online instruments

The experiments were carried out at the EUPHORE high-volume atmospheric outdoor simulation chamber in Valencia, Spain (longitude = -0.5° , latitude = 39.5°N). This simulation chamber enables reactions to be carried out using natural sunlight, and minimises losses and wall-interaction effects, following similar procedures to those previously employed in this laboratory to investigate the atmospheric fate of several pesticides and other organic compounds (Borrás et al., 2017; Vera et al., 2015).

Technical information about the facility has been previously reported in the literature (Muñoz et al., 2011, 2018), and only the specific details related to the present work are herein explained. The chamber is a half-spherical fluoropolymer bag with a volume of 200 m^3 transparent to solar radiation. Pressure, humidity and temperature were measured by a pressure sensor (Air-DB-VOC, Sirsa, Madrid, Spain) and a dew point hydrometer (TS-2, Walz, Effeltrich, Germany). $J(\text{NO}_2)$ was measured by a calibrated JAZ Spectroradiometer (Ocean Optics Inc., Largo, FL, USA).

A TAPI NO_x monitor (T200UP, Teledyne, San Diego, USA) was used to measure NO , NO_2 and NO_x . Ozone was measured using a Serius 10 O_3 analyser (Echotec, Knoxville, Victoria, Australia). The concentrations of terpenes, chlorpyrifos (active substance), “inert” compounds and other degradation products were measured by automated-SPME (Solid-Phase MicroExtraction) online Gas Chromatograph – Mass Spectrometer (GC-MS). The automatic online SPME-GC-MS enclosed an adapted SPME module for automatic air sampling. The air from the chamber was

Table 1a

Initial experimental conditions. Concentrations of chloropicrin [CP] and α -pinene [α -PIN] in ppbV, ratio ([CP]/[α -PIN]), relative humidity (RH%), JNO₂ (solar reference value) in s⁻¹, and mass of aerosol formed (Δ M₀) in μ g m⁻³.

Exp	Type of experiment	[CP] ppbV	[α -PIN] ppbV	Ratio	RH (%)	JNO ₂ s ⁻¹	Δ M ₀ μ g m ⁻³
1	Photolysis of chloropicrin and α -pinene without scavenger, dry	31	145	0.21	0.7	7.8E-03	42
2	Photolysis of chloropicrin and α -pinene without scavenger, dry	131	150	0.87	1.1	7.9E-03	119
3	Photolysis of chloropicrin and α -pinene without scavenger, dry	63	35	1.81	1.4	8.4E-03	17
4	Photolysis of chloropicrin and α -pinene without scavenger, dry	62	72	0.86	1.7	8.0E-03	34
5	Photolysis of chloropicrin and α -pinene without scavenger, dry	73	188	0.39	0.7	8.2E-03	99
6	Photolysis of chloropicrin and α -pinene without scavenger, high RH	26	168	0.15	42.3	5.6E-03	44

sampled through an inert Silconert-coated steel tube heated to 80 °C and connected to a sampling cell, where the SPME fibre was exposed. Air was passed through a cell at 10 L min⁻¹ for 5 min. Finally, the sample was thermally desorbed in the injection port of an Agilent GC-MS (Santa Clara, CA, USA) equipped with an HP-5MS (Agilent) column (30 m \times 0.25 mm, i.d. \times 0.25 mm film thickness). The chromatography was programmed at 40 °C for 3 min, and then ramped at 5 °C min⁻¹ to 100 °C and ramped at 100 °C min⁻¹ to 200 °C. The injection port was set at 250 °C and the transfer line at 280 °C. Samples were injected in the splitless mode using helium as the carrier gas at a flow of 3 mL min⁻¹. The EI voltage was 70 eV, the ion source temperature was 200 °C, and the quadrupole temperature was 100 °C. The full-scan mode was applied (m/z 45–350).

A Proton-transfer-reaction mass spectrometry (PTR-MS) instrument (IoniconAnalytik GmbH, Innsbruck, Austria) was used for monitoring the VOCs in the gas phase. A 1/4" sulfonert® tube (4.0 mm i.d., 1 m long), covered by a warming blanket set at 80 °C, was used as a sampling line.

A Fourier-transform infrared spectroscopy (FTIR) spectrometer (NICOLET, 6700, resolution of 1 cm⁻¹, MCT/A detector) with a KBr beam splitter was employed for trace gas detection in combination with a long-path White-cell multireflection cell (616 m). Analyses were done by applying homemade software (Ródenas, 2018) to two spectral regions to detect parent compounds and degradation products as follows: chloropicrin, phosgene, sabinene and O₃ in the region 776–1148 cm⁻¹ and α -pinene, pinonaldehyde, α -terpinene, limonene, myrcene, d3-carene, formaldehyde, m-glyoxal and chloridric acid in the region 2625–2930 cm⁻¹. Dilution was measured following the decay of SF₆, an initially added inert tracer.

The aerosol mass concentration was measured by a scanning mobility particle sizer (SMPS), model 3080 (TSI, Shoreview, MN, USA). The sheath and aerosol sampling flows were 3 L min⁻¹ and 0.3 L min⁻¹, respectively.

2.2. Orange tree emissions. A mixture of monoterpenes

In a separate set of experiments, and before the experiments performed on commercial chlorpyrifos, the monoterpene emission

representative of citrus crops, in which this pesticide is widely used, was determined. For this purpose, a small chamber made of polycarbonate (14 m³ volume) was constructed and located on the rooftop of the CEAM Foundation building to obtain the fingerprint of the main terpenes emitted from orange trees in the spring season. Eighteen orange trees *Citrus sinensis* (L.), Osbeck, variety New Hallwere, were placed inside the chamber. The terpene emissions ratios were measured by SPME-GC-MS, while PTR-MS was used to confirm the total concentration of different isomers using the configurations and methods described in Section 2.1. Terpenes were measured during a very incipient flowering period.

2.3. Experiments carried out in the EUPHORE chamber

In this work, two different sets of experiments were run in the EUPHORE chamber as a case study of the interaction of pesticides and monoterpenes compounds. The first set (Set 1) was conducted to study how the interaction between one pesticide (active substance chloropicrin) and one single terpene (α -pinene) activated by direct photolysis could affect O₃ and SOA formation with different initial mixing ratios of both compounds.

Chloropicrin (99%, Sigma Aldrich Química, Spain) and α -pinene (99%, Sigma Aldrich Química, Spain) were injected into the EUPHORE chamber via a heated air stream (flow rate of 10 L min⁻¹) at different initial mixing ratios. After mixing reactants for 30 min, the chamber was exposed to natural sunlight. Experiments were carried out in late spring and in summer. The experimental conditions of Set 1 are shown in Table 1a.

The second set of experiments (Set 2) was applied to study the photolysis and ozonolysis of commercial chlorpyrifos and in dose applied on citrus crops, and a representative mixture of terpenes of those emitted by orange trees. SOA and other degradation products were measured. O₃ formation and consumption during photolysis or ozonolysis experiments were respectively determined. The experimental conditions of Set 2 are shown in Table 1b.

Firstly, 2.5 mL of commercial chlorpyrifos (Dow AgroScience Iberica, S.A; Clorpyrifos 48% p/v. EC) was prepared in 1 L of water and introduced into the chamber by sprayer. One hour later, a mixture of terpenes was also placed inside the chamber. After mixing the reactants for at least 40 min, either the chamber was exposed to sunlight or O₃ was added. Then the reaction started. Additional experiments in which only terpenes or commercial chlorpyrifos were introduced into the chamber were also carried out.

The errors associated with both the concentration of gaseous compounds (O₃, pesticide and terpenes) and particulate matter are less than 5%, their accuracy being determined as 1 σ .

The values of JNO₂ are measured because this value is therefore dependent on the solar zenith angle (SZA), the altitude, and other specific local environmental conditions and allows us to correlate our results in the Mediterranean region with different locations. As can be observed in experiments 4 and 5, they are replicated with the only difference being the conditions of solar radiation.

3. Results and discussion

3.1. Chloropicrin photolysis in the presence of α -pinene

A set of six experiments with different concentrations of α -pinene and chloropicrin were performed in the EUPHORE chamber, see Table 1a.

By way of example, a plot of the time-concentration profiles measured by FTIR for Exp.4 Photolysis of chloropicrin and α -pinene without OH scavenger, dry conditions is shown in Fig. 1. This figure displays the concentration of α -pinene and chloropicrin decay, while O₃, HCl, phosgene and pinonaldehyde (primary products) increase.

The yields and concentration variations of the detected products are summarised in Table 2. The generated products were O₃ and SOA, but

Table 1b

Initial experimental conditions. $J(\text{NO}_2)$ (solar reference value) in s^{-1} , maximum O_3 formed in ppbV, a mass of aerosol formed (ΔM_0) in $\mu\text{g m}^{-3}$, total precursors consumed in $\mu\text{g m}^{-3}$, and aerosol yield in %.

Exp	Type of Experiment	$J(\text{NO}_2)$ s^{-1}	$\text{O}_{3\text{max}}$ (ppbV)	ΔM_0 ($\mu\text{g m}^{-3}$)	ΔHC total ($\mu\text{g m}^{-3}$)	Yield (%)
1	Photolysis of orange trees terpenes without scavenger, dry	1.50E-02	8	79	864	9
2	Photolysis of commercial pesticide	1.28E-02	34	25	245	10
3	Photolysis of orange trees terpenes without scavenger, high RH	1.47E-02	14	112	842	13
4	Photolysis of orange trees terpenes without scavenger and commercial pesticide. Replicate 1	1.27E-02	6	145	1258	24
5	Photolysis of orange trees terpenes without scavenger and commercial pesticide. Replicate 2	1.61E-02	4	105	1463	16
6	Ozonolysis of orange trees terpenes without scavenger	–	563	564	1210	47
7	Ozonolysis of commercial pesticide	–	608	19	448	4
8	Ozonolysis of orange trees terpenes without scavenger and commercial pesticide	–	558	478	1814	26

Terpene mixture (ppbV) consisted on
 a-Pinene 7.5;
 Sabinene 83.3;
 β -Myrcene 13.1; a-Fellandrene 3.2; 3-Carene 3.8; a-Terpinene 22 and, Limonene 99.6
Commercial chlorpyrifos consisted on
 2.5 mL of commercial chlorpyrifos (Chlorpyrifos 48% p/v. EC) in 1 L of water and sprayed

also other substances like phosgene, which is a very poisonous gas at room temperature (20°C), and pinonaldehyde (PIN).

Chloropicrin photolysis leads to the formation of radical CCl_3 and NO_2 , as reported by Vera et al. (2010). The photolysis of NO_2 generates O_3 and NO . The further reaction of radical CCl_3 generates the corresponding peroxy, which would form phosgene (CCl_2O) in the presence of NO , another molecule of NO_2 , and the Cl radical. If no other processes are applied and considering that two NO_2 molecules can form, chloropicrin photolysis can, in principle, generate two O_3 molecules per consumed chloropicrin molecule according to Vera et al., (2010). Nevertheless, these authors observed a molar O_3 yield range from 50% to 167%. These high yield values were also observed in our experiments, with O_3 yields ranging from 167% to 338% concerning chloropicrin consumption (see Table 2).

Radical Cl can react fast in the presence of α -pinene, ($k_{\text{Cl}} = 4.7 \times 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$) (Renbaurn-Wolff and Smith, 2012). Moreover, during reactions, HO_2 is generated in the system which, in the presence of NO formed during NO_2 photolysis, it can lead to the formation of NO_2 and OH radicals, which can further react with α -pinene ($k_{\text{OH}} = 5.38 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$), (Renbaurn-Wolff and Smith, 2012). These OH

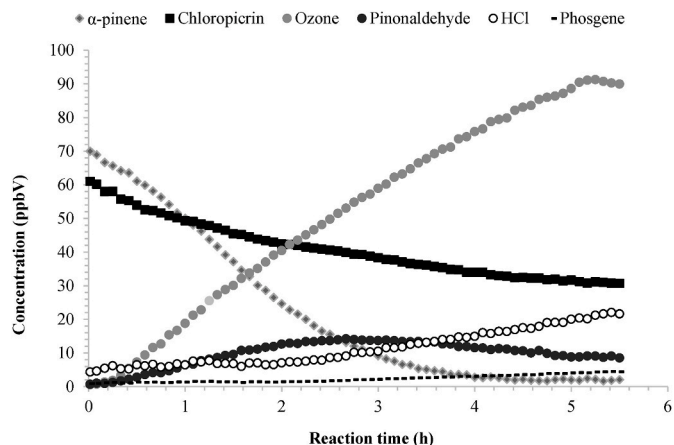


Fig. 1. Time-concentration profile for Exp. 4: chloropicrin + α -pinene reaction (concentration ratio = 0.86).

radicals may also react with α -pinene, which can generate HO_2 and OH -peroxyl-radicals ($\text{R-OH-OO}\cdot$). This reaction might decompose and contribute to the recycling of OH radicals. The additional OH formation route has been described in the literature (Asatryan et al., 2010; Da Silva, 2012; Peeters et al., 2014). At the same time, NO_2 can lead to the formation of additional O_3 in the system. O_3 can also react with α -pinene ($k_{\text{O}_3} = 1.07 \times 10^{-16} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ Stewart et al., 2013). But its net ozone formation would be almost negligible with what is produced for what is consumed and the positive balance of ozone formed would correspond only to the photolysis of chloropicrin.

Scheme 1 summarises possible mechanism pathways of photolysis of chloropicrin in the presence of α -pinene. The degradation chemistry of α -pinene is complicated given its complex structure and can lead to many possible products and reaction products (only some are indicated in our scheme).

The pinonaldehyde yields obtained in this work varied between 3% and 92%. The lowest (3%) and highest (92%) yields were obtained for Experiments 1 and 3, respectively, where the ratio $[\text{CP}]/[\alpha\text{-PN}]$ difference is maximum. Some literature data on the α -pinene OH photo-oxidation under different NO conditions reported pinonaldehyde yield values of around 30% (Rolletter et al., 2019). Other authors, such as Larsen et al. (2001) and Rolletter et al. (2019), report small yields ($\leq 5\%$). Hatakeyama et al. (1991) and Nozière et al. (1999) report higher values of 56% and 87%, respectively. Our system includes both OH and Cl radicals, which can react with α -pinene to form pinonaldehyde from two routes, but the absence of NO can explain the differences in pinonaldehyde formation.

A net O_3 formation was detected in all the experiments, and the maximum concentration ranged from 30 to 115 ppb. (Fig. S1 in the Supplementary Information), which shows the time-ozone concentration profile for Exp. 1–5 (dry conditions). As mentioned earlier, the O_3 yields obtained in these experiments were $>100\%$ because the photolysis of one chloropicrin molecule in the presence of oxygen may generate more than one ozone molecule.

The highest O_3 yields corresponded to the reaction with the chemical ratio within the 0.9–1.8 range, as seen in Experiments 2, 3 and 4 (See Fig. S2 in the Supplementary Information). The lowest O_3 levels were monitored for Experiments 1 and 6, in which low chloropicrin concentrations were employed. The humidity factor did not seem to affect O_3 formation because Experiments 1 and 6, performed under similar experimental conditions, but with different $\text{RH}\%$ values, led to almost the same O_3 formation.

It is well-established that α -pinene easily generates SOA when exposed to oxidants like OH radicals (Hatakeyama et al., 1991; Watne et al., 2017) or ozone (Inuma et al., 2004; Park et al., 2017). Therefore, the aerosol formation that took place in our experiments could be due to

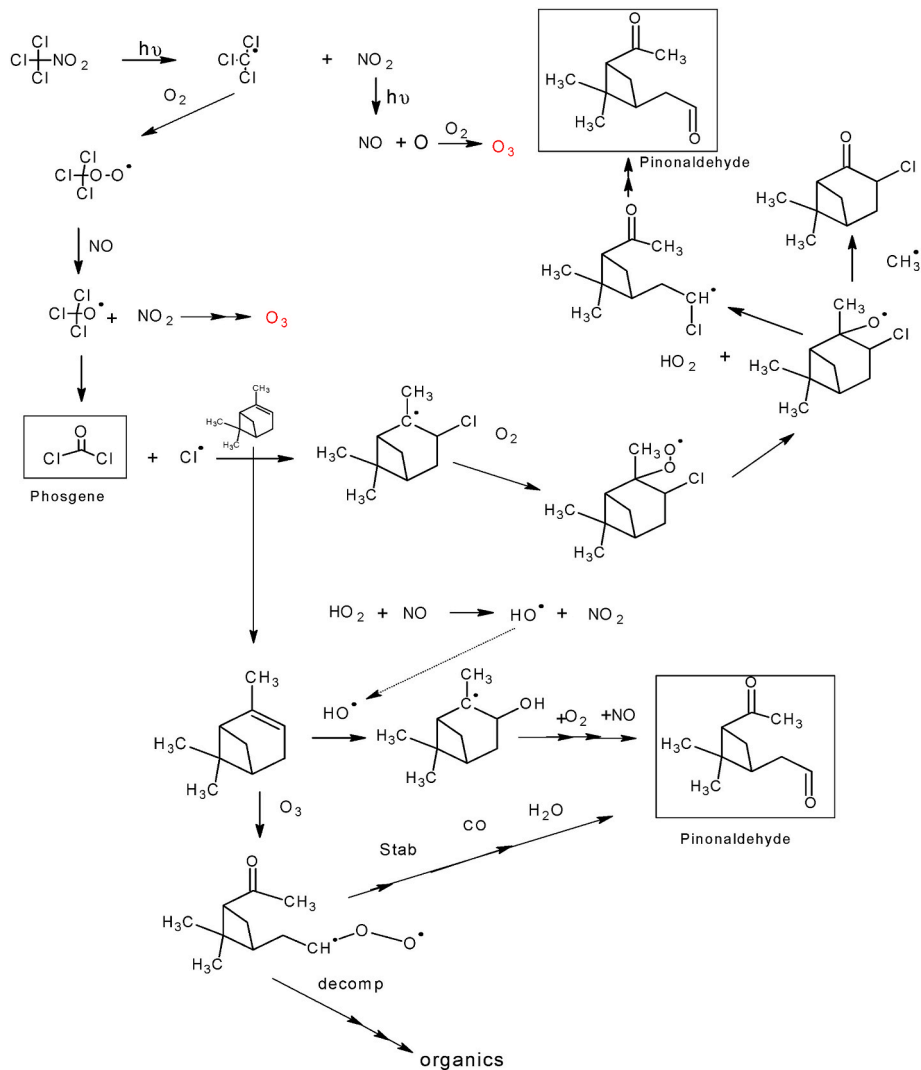
Table 2
The consumption formation yields of ozone (O_3), pinonaldehyde (PIN-al), phosgene and aerosol concerning chloropicrin (CP) and α -pinene (α -PIN) consumption.

Exp	*Ratio	$-\Delta[\alpha\text{-PIN}]$ ppb	$-\Delta[\text{CP}]$ ppb	ΔMo $\mu\text{g}/\text{m}^3$	$\Delta[O_3]$ ppb	$\Delta[\text{PIN-al}]$ ppb	$\Delta[\text{Phosgene}]$ ppb	Phosgene Y % ^(a)	α -PIN Y % ^(b)	O_3 Y % ^(a)	SOA Y % ^(b)
1	0.21	104	13	42	27	3	10	72	3	199	7
2	0.87	133	51	119	111	17	47	92	13	216	16
3	1.81	33	25	17	85	30	21	84	92	338	9
4	0.86	67	29	34	89	9	25	86	13	307	9
5	0.39	157	31	99	52	32	25	83	20	167	11
6	0.16	124	11	44	23	34	8	78	28	214	6

* Initial concentration ratio $[\text{CP}]/[\alpha\text{-PIN}]$.

^a Relative to chloropicrin consumption.

^b Relative to α -pinene consumption.



Scheme 1. The possible reaction pathways proposed for the studied photolysis of chloropicrin in the presence of α -pinene.

the reaction of α -pinene that can react with: chlorine atoms; the O_3 generated during chloropicrin photolysis (see Scheme 1); OH radicals, which can be produced during the photolysis process in air/ O_3 . The reaction of α -pinene with chlorine atoms is expected to be the first step in the formation of intermediate reaction products and is, therefore, important in the aerosol route because its rate coefficient is 1 and 6 orders of magnitude higher than OH radicals and O_3 , respectively (NIST Kinetics database, 2020). The Aerosol formation will, thus, depend on the concentrations of Cl, OH, and/or O_3 .

The aerosol yield (Y%), was calculated from the equation developed

by Odum et al. (1996):

$$Y = \frac{M_0}{\Delta[\text{HC}]} \quad [1]$$

where M_0 is the aerosol mass concentration that formed and ΔHC is the mass concentration of the reacted substrate, in this case, α -pinene.

Fig. 2 shows M_0 evolution vs. the reaction time. A significant amount of particulate matter between 17 and 119 $\mu\text{g}/\text{m}^3$ was obtained in the stationary stage, which was observed after more than 4 h of reaction in

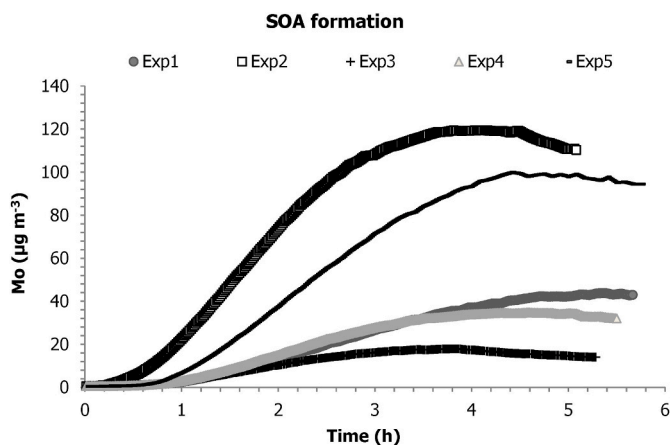


Fig. 2. Plot of the aerosol mass concentration versus time for the photolysis of α -pinene and chloropicrin at different initial mixing ratios under dry conditions.

all the experiments. As mentioned earlier, SOA formation was due to α -pinene consumption because the contribution of chloropicrin was experimentally demonstrated as being negligible. The main explanation for the increase of SOA formation can be the Cl radical formation that contributes to the photolysis reaction of α -pinene to increase de SOA formed.

The greatest aerosol formation ($Y = 16\%$) corresponded to the reaction run with approximately the same amount of α -pinene and CP (ratio ~ 1). Experiments 3, 4 and 5 provided similar aerosol yields (9–11%). However, lower aerosol yields were observed at both low $[CP]/[\alpha\text{-PIN}]$ ratios under dry or wet conditions (6–7%). These values agree with the literature (Spittler et al., 2005; Eddingsaas et al., 2012).

By comparing the formed aerosol yield (calculated regarding the α -pinene consumption), chloropicrin consumption and ozone formation, the correlation among aerosol yield, chloropicrin consumption and O_3 formation were significant (Fig. 3).

The combination of both species (chloropicrin and α -pinene) in the atmosphere determines ozone and SOA formation. The understanding of atmospheric reactions should help to estimate the expected formation of gas and particulate matter in the troposphere, which depends on each applied pesticide, the emitted biogenic compounds, and also on the concentration rates between them, as herein demonstrated.

3.2. Photolysis of commercial chlorpyrifos in the presence of orange terpenes mixture

In the first place, experiments to choose the mixture of terpenes to be used were carried out. The orange terpene mixing ratios (%) obtained in this work were compared to the data found in the literature and are shown in Table 3.

The terpenes detected at the highest concentration in this work were limonene and sabinene. However, in other studies, higher linalool and β -caryophyllene concentrations have been detected (Ciccioli et al., 1999; Hansen and Seufert, 1999; Fares et al., 2011). The non-commercial compound tentatively identified as Thujene in this work has also been detected in the literature as a commonly emitted compound by orange trees (Jabalpurwala et al., 2009; Gentner et al., 2014). Differences between our study and the bibliography are the orange variety, flowers' presence or absence and instrumental techniques to improve the identification of different terpenes isomers (PTRMS and SPME-GCMS). On the list of terpenes identified from orange tree emissions, a set of seven terpenes was chosen by taking into account their commercial availability and higher OH-reactivity (see Supplementary Information Table S1). They were introduced into the EUPHORE chamber to study their interaction with the commercial chlorpyrifos. The objective was to simulate the most realistic conditions in citrus

crops' atmosphere when commercial chlorpyrifos is sprayed in combination with a characteristic mixture of biogenic compounds emitted by orange trees.

Figures S3A and B in the Supplementary information show the chromatogram obtained for the orange tree emissions before and after being sprayed with commercial chlorpyrifos, respectively. Identifications were made based on considering their ion (m/z) fragments, chemical properties, retention time and expected polarity. They were compared to the standards and the NIST library. After applying the commercial chlorpyrifos (1h), no presence of chlorpyrifos (active substance) was found. However, several aromatic compounds (19) were detected.

A set of photolysis studies was used to investigate the interaction between the orange terpenes mixture and the commercial chlorpyrifos as regards SOA and O_3 formation and SOA formation at ozonolysis experiments. Aerosol yields ($Y\%$) were obtained by Equation [1] and the results are shown in Table 4.

For the ozonolysis experiments, the initial O_3 concentrations were between 550 and 600 ppbv. Figs. 4 and 5 show the time-concentration profile for O_3 consumption and SOA formation, respectively.

The greatest O_3 consumption was observed for the ozonolysis of commercial chlorpyrifos and orange terpenes mixture. For SOA formation, similar yields were obtained for the ozonolysis of the commercial chlorpyrifos (CFCHL) and orange terpenes mixture ($Y = 42\%$) and the ozonolysis of the orange terpenes mixture ($Y = 47\%$), where the yield of the latter was slightly higher. The ozonolysis of the commercially formulated chlorpyrifos generated a negligible amount of aerosol particles.

According to the results obtained in these experiments, it would seem that the presence of commercial pesticide in the orange terpene mixture leads to greater O_3 consumption, which would favour reactions in the gas phase, but this does not affect (significantly) the SOA formation generating lower levels of condensed particles (SOA).

As in dark conditions, the photolysis of orange terpenes mixture, the commercial chlorpyrifos combined with orange terpene mixture was investigated. The formation of both O_3 and aerosol was monitored during each studied reaction. Figs. 6 and 7 show the time-concentration profile for the generated O_3 and SOA, respectively.

The photolysis of the commercial chlorpyrifos produced O_3 as a result of the OH_2/RO reactions, which showed the highest O_3 concentration, between 2 and 8-folds higher than the other photolysis processes. This additional O_3 enhanced reactivity and O_3 could react with terpenes to form less volatile and more oxidised compounds, which would favour the formation of condensed particles and, therefore, higher SOA levels. As no OH scavengers were employed in our experiments, the formation of these hydroxyl radicals from O_3 degradation may also contribute to this process.

Moreover, the orange terpenes mixture photolysis under wet conditions led to higher SOA levels than for the dry conditions, possibly because water droplets may act as condensation nuclei and favour the formation of aerosols (Duan et al., 2019). Previous studies carried out at the EUPHORE facilities reveal that direct pure active substance chlorpyrifos photolysis does not generate particles (Borrás et al., 2015b) (see Fig. 7).

Different terpene degradation products were detected; for example, two ketones, limone ketone and sabinone ($C_9H_{14}O$), which were identified as the main gas-phase products in the photolysis of the orange terpenes and in the photolysis of commercial chlorpyrifos with orange terpenes mixture. Fig. 8 shows the time evolution of the area of the chromatographic peak for the ketones identified during the photolysis process. The PTR-MS data agree with the GC-MS data when considering the MW 138 attributable to the $C_9H_{14}O$ compounds. The normalisation data indicated the presence of some minor compounds with the same molecular weight (see Supplementary Information, Fig. S 4).

As for the formation of other gas products, the main products detected by PTR-MS were those with MW 152, attributable to the

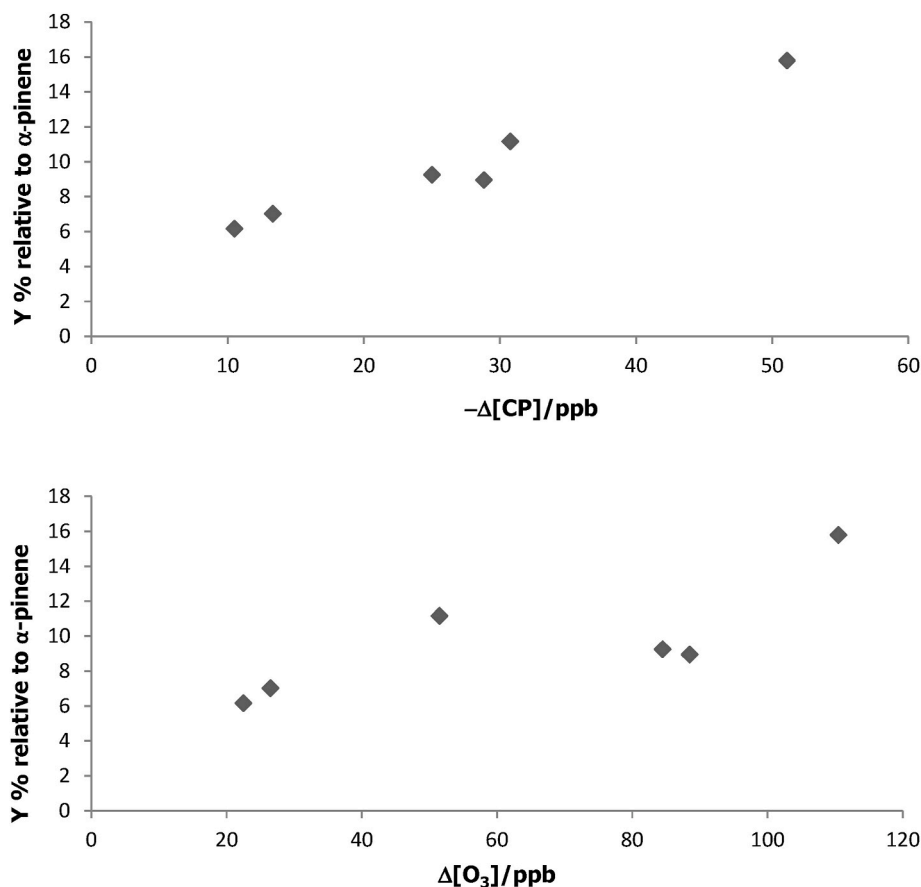


Fig. 3. The calculated aerosol yield with α -pinene degradation, versus A) chloropicrin reacted, B) ozone formed.

Table 3

Terpene mixing ratios (%) obtained in this work and the data found in the literature.

COMPOUND	Ratio % (measured directly) (flowers)	Ratio % simulated in this work (Flowers)	1Ratio % (No flowers)	1Ratio% (Flowers)	2Ratio% (No flowers)	2Ratio% (Flowers)	3Ratio% (No flowers)	3Ratio % (Flowers)
α -Pinene	3	3	1	–	–	–	–	–
Sabinene	17	33	3	1	7	4	–	–
β -Pinene	3	3	–	–	27	9	–	–
β -Myrcene	6	3	56	67	9	3	–	–
α -Fellandrene	1.5	1.5	–	–	–	–	–	–
3-Carene	1.9	1.7	–	–	–	–	–	–
γ -Terpinene	9	12	–	–	–	–	–	–
Limonene	40	40	7	2	7	8	–	–
Ocimene	–	–	31	30	–	–	37	38
Terp_unknown (Unconfirmed thujene)	17	3.*	–	–	–	–	–	–

¹ Parent Navel Orange. [Gentner et al. \(2014\)](#).

² Navel/Navel late Orange. [Ciccioli et al. \(1999\)](#). Average data in the daytime from the spring campaign.

³ *Citrus Sinensis* Orange. [Hansen and Seufert \(1999\)](#).

* Not commercially available, Sabine used as a surrogate. It was introduced as the impurity of the other terpenes.

general formula $\text{C}_9\text{H}_{12}\text{O}_2$ or $\text{C}_8\text{H}_8\text{O}_3$ (Figs. S5 and S6 are found in the Supplementary Information). These compounds seemed to be generated and consumed because, after a quick increase during the first reaction hour, the concentration reached a steady state.

As previously mentioned, the presence of commercial chlorpyrifos, together with the orange terpenes mixture, favoured SOA formation, and the formation of the gas-phase ketone was lower than the orange terpenes photolysis. One plausible explanation could be that it was due to the secondary reactions that would take place in these systems and

more oxidised compounds like carboxylic acids could form. Moreover, these compound types have lower pressure vapour and condense, which would explain greater SOA formation and the lower ketones concentration. This study is novel since is (in our knowledge) the first study ever reporting the atmospheric degradation of a commercially formulated pesticide and not only its active ingredient alone because the atmospheric degradation of an active substance would likely differ from one of its commercially formulated products. This could have large implications for the accuracy of the various atmospheric/environmental

Table 4

Summary of the results obtained in the experiments with the commercial chlorpyrifos (CFCHL) and orange terpenes mixture (TERP).

Exp	Experiment type	J(NO ₂) (s ⁻¹)	O ₃ max (ppbV)	ΔMo (μg m ⁻³)	Δ[TERP] (ppbV)	Y _{SOA} (%)
1	Photolysis of orange trees terpenes, dry	1.5E-02	8	79	155	9
2	CFCHL photolysis	1.3E-02	34	25	–	–
3	Photolysis of orange trees terpenes, high RH	1.5E-02	14	112	151	13
4	Photolysis of orange trees terpenes without scavenger and CFCHL	1.3E-02	6	145	109	24
5	Photolysis of orange trees terpenes and CFCHL	1.6E-02	4	105	114	16
6	Ozonolysis of orange trees terpenes without scavenger	–	563	564	217	47
7	CFCHL ozonolysis	–	608	19	–	–
8	Ozonolysis of orange trees terpenes without scavenger and CFCHL	–	558	510	217	42

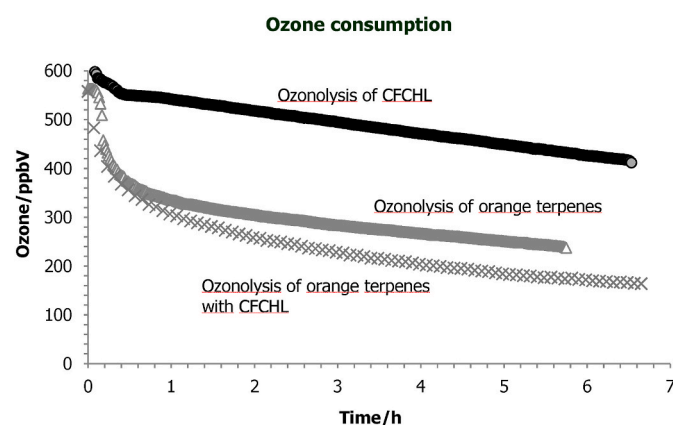


Fig. 4. Time-concentration profiles for the ozonolysis of the commercial chlorpyrifos (CFCHL) and orange terpenes mixture.

fate models used worldwide.

4. Conclusions

Atmospheric reactions of monoterpenes VOCs emitted by crops lead to the formation of secondary pollutants, such as organic aerosols and O₃. The formation of these compounds can be enhanced when pesticides are used.

For chlorpicrin photolysis, the first reaction steps lead to the formation of Cl radicals and NO₂ and, subsequently, NO₂ photolysis generates O₃. In addition, Cl can react with terpenes like α-pinene, which leads to the subsequent formation of HO₂, NO₂, OH and O₃ that can further react with α-pinene. Hence the final amount of O₃ generated in the system would very much depend on the initial chlorpicrin and α-pinene concentrations but, in all cases, yields would be higher than 160% concerning chlorpicrin consumption. A clear correlation

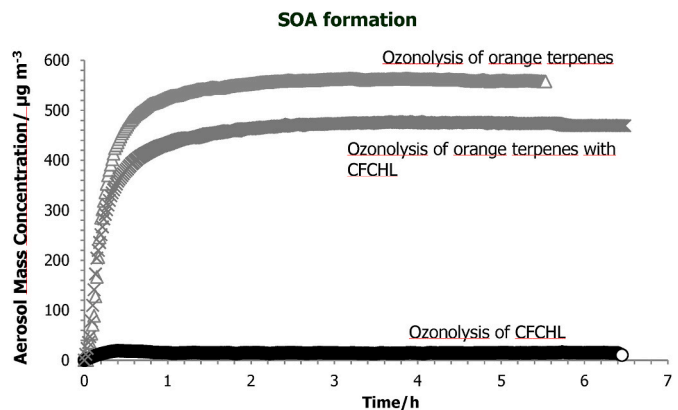


Fig. 5. Time-aerosol mass concentration profile for the ozonolysis of the commercial chlorpyrifos (CFCHL) and orange terpenes mixture.

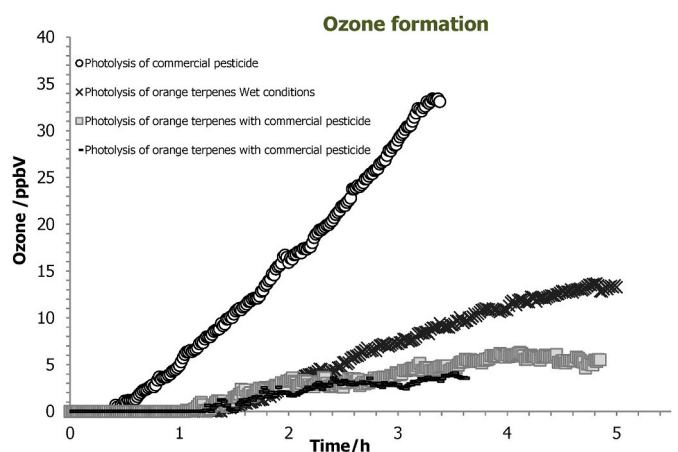


Fig. 6. Time-concentration profiles for the ozone generated during the photolysis reactions. To better visualise this figure, the photolysis of the orange trees' terpenes under dry conditions is not plotted.

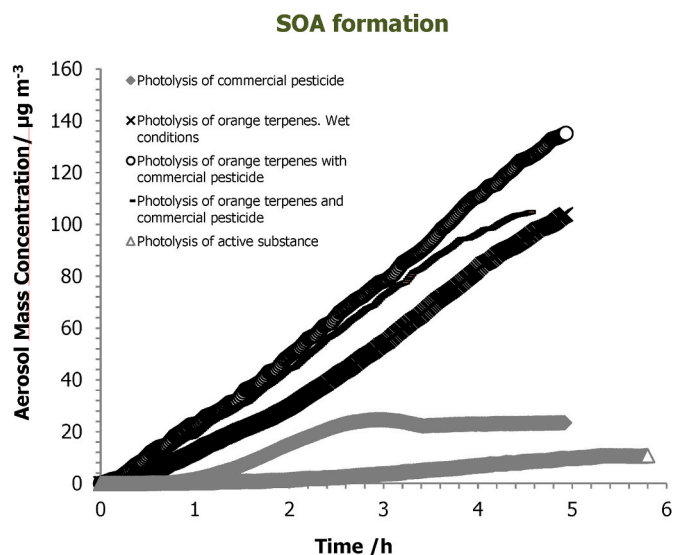


Fig. 7. Time-concentration profiles for the SOA generated in the photolysis reactions of commercial chlorpyrifos, pure active substance chlorpyrifos and/or orange terpenes mixture.

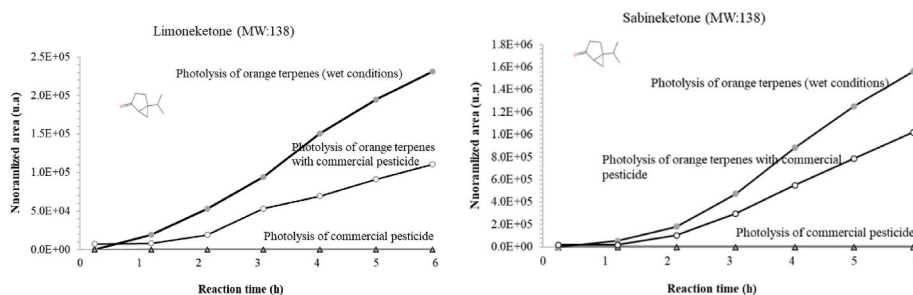


Fig. 8. Time evolution of a) limonene ketone, b) sabinene ketone.

between the aerosol yield, chloropicrin consumption, and therefore O_3 formation, was observed.

The presence of commercial chlorpyrifos in the presence of the orange terpenes mixture increases ozone formation, and O_3 may react with those terpenes increasing the particulate matter formation. As our previous studies have demonstrated that pure active coadjuvants and additives are responsible for this behaviour when they have added to the commercial pesticide product. The atmospheric fate and in this particular case, degradation of commercial pesticides would differ from the one for active substances alone. Therefore, there is a need to understand better this in the future and to incorporate it into environmental fate models. Similarly, the effect of formulation and adjuvants was found for another relevant environmental process which is the air-soil exchange (Das and Hageman, 2020).

Finally, the use of pesticides can play an important role in climate change because it has been pointed out that they can act as important SOA and ozone precursors. The combination of both commercial pesticides and terpenes emissions in the atmosphere determines the increase of secondary pollutants. Besides, high temperatures, such as those registered on summer days in the last few years in Mediterranean countries, can enhance pests, which would increase pesticide usage.

CRedit authorship contribution statement

Amalia Muñoz: Conceptualization, Writing – original draft, preparation, Writing – review & editing, Supervision. **Esther Borrás:** Investigation. **Teresa Vera:** Investigation. **Inmaculada Colmenar:** Writing – original draft, preparation. **Milagros Ródenas:** Investigation, Writing – review & editing. **Cristina Gimeno:** Investigation. **Esther Fuentes:** Investigation. **Clara Coscollá:** Investigation. **Héctor Calvete-Sogo:** Writing – original draft, preparation, All the authors have read and agreed to the published version of the manuscript.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgements

This research has been partially supported by the European Commission LIFE Programme (PERFECT LIFE grant number LIFE17 ENV/ES/000205), by the Spanish Ministry of Science and Innovation (CGL2013-49093-C2-1-R) and by the Generalitat Valenciana (PROM-ETEO/2019/110). Fundació CEAM is supported by the Generalitat Valenciana.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.atmosenv.2022.119541>.

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