OZONE AND SECONDARY ORGANIC AEROSOL PRODUCTION BY INTERACTION BETWEEN PESTICIDES AND BIOGENIC VOCs

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INTRODUCTION

Pesticides used for:

- ➢Agriculture

- ➢Gardening operations

- ➢House uses

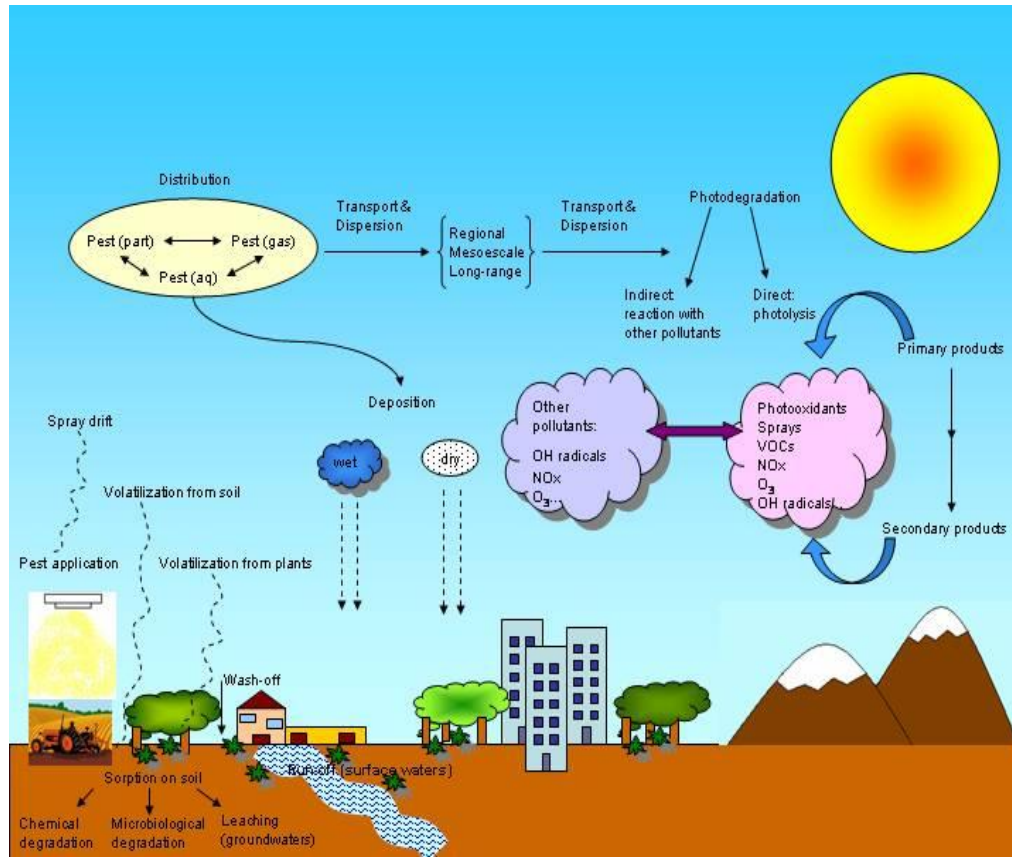
They can be emitted into the atmosphere by direct and indirect emisions

•through dispersion during spraying operations,

•volatilization from ground or leaf surfaces

•wind erosion

Once the pesticides are applied, they can be distributed among the different environmental compartments:



Source: "Pesticides: Evaluation of Environmental Pollution" (chapter 7: Pesticide Residues in the atmosphere; by T. V. Espallardo Vera, A Muñoz and JL Palau). 2012 by CRC Press (Taylor & Francis Books Inc).

ATMOSPHERIC DEGRADATION PATHWAYS

MAIN DEGRADATION PATHWAYS IN THE ATMOSPHERE

- **(Direct) Photolysis**: Chemical decomposition induced by light (absorption at wavelengths > 290 nm)

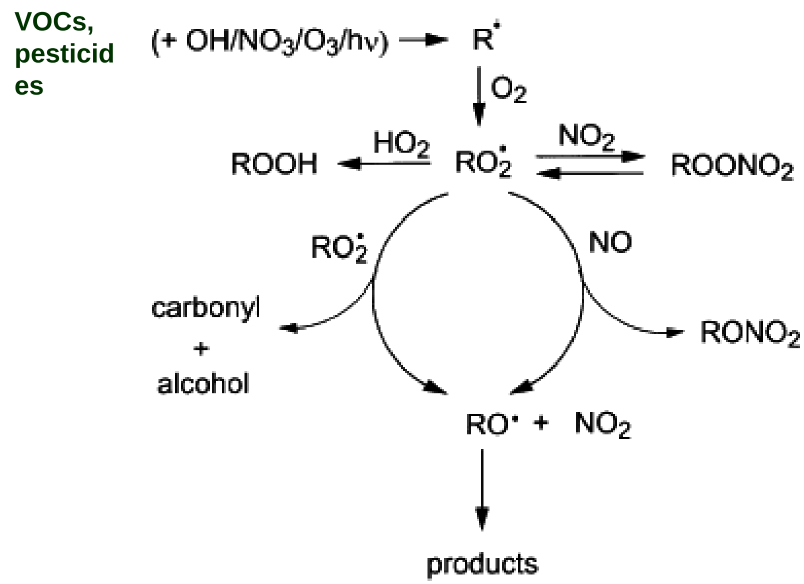
- **Indirect Photolysis or Photooxidation**: Reaction with hydroxyl radicals.
  OH radicals formed during the day mainly to the photolysis of O_3

- **Reaction with O_3:**
  Mainly reaction with unsaturated compounds
  (Ozone is not emitted directly but is a photochemical pollutant formed when VOCs interact with nitrogen oxides under the influence of sunlight)

- **Reaction with NO_3:**
  Important at night. NO_3 radicals are photolyzed rapidly so their concentration during the day is very low, but can be significant at night

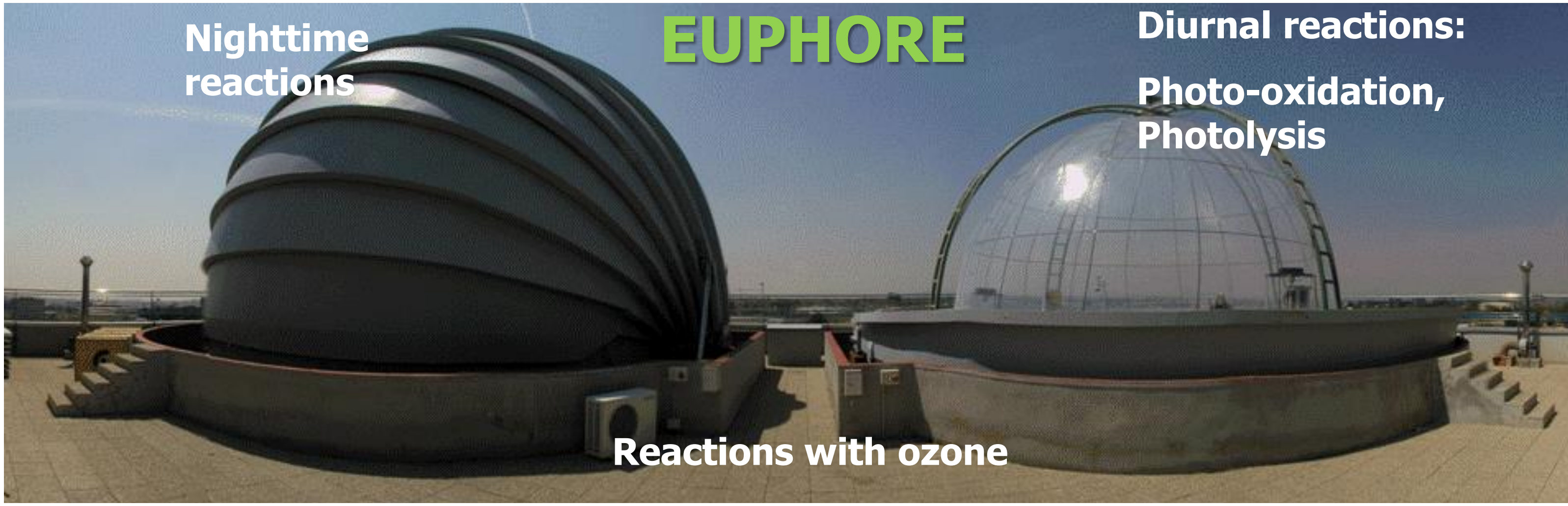
- **Reaction with Cl:**
  (usually fast reaction, but [Cl] in atmosphere is low)

Absorption of sunlight induces photochemistry and generates a variety of free radicals that drive the chemistry of the troposphere (also the stratosphere).









TO INVESTIGATE CHEMICAL PROCESSES RELATED TO TROPOSPHERIC CHEMISTRY:

- EUPHORE is one of the major research platforms in Europe and world-wide
- With outstanding analytical infrastructure
- Simulation of realistic conditions
- Several institutions (experts) were involved in its design
- Mechanism development under realistic conditions (sunlight, radical or NOx levels)
- Provide input parameters for numerical simulations: Kinetic data and product yields
- Perform product studies under realistic conditions
- Type of reactions: Product Studies with OH Radical in the presence or absence of NOx, Product Studies and Particle Formation from Ozonolysis, Particle Formation in Classical Photosmog Systems, Product Studies and Particle Formation at Ambient NOx Concentrations (Control NOx), Products Studies in Photolysis Processes, OH and NO_3 Kinetic Studies
- Scientific scope: Automobile Exhaust Emissions, Aromatic Compounds, Biogenic Compounds, Radicals Species, Aerosols, DMS and Sulphur Compounds, Organic Solvents, Fluorinated Compounds, Photocatalytic materials, **Pesticides**….

ATMOSPHERIC DEGRADATION OF PESTICIDES

OVERVIEW

COMPOUND	J $[s^{-1}]$	k_{OH} $[cm^3\ molec^{-1}\ s^{-1}]$	Lifetime /Main degradation pathway	Lifetime SAR method (only OH reaction)	Main degradation products
Chlorpyrifos [1,2]	1.4×10^{-5}	$(9.1 \pm 1.8)\times10^{-11}$	2 hours / Reaction with OH	2 hours	SO_2, 3,5,6-tricloro-2-pyridinol, SOA, chlorpyrifos oxon, dimethylphospahte, CH_3CHO, PAN (in the presence of NOx)
Chlorpyrifos oxon [1,2]	$< 4.8 \times 10^{-5}$	$(1.6 \pm 0.8)\times10^{-11}$	11 hours / Reaction with OH	4.6 hours	SOA, PAN (in the presence of NOx)
Chlorpyrifos-methyl [3,4]	$< 2\times10^{-5}$	$(4.1 \pm 0.4)\times10^{-11}$	3.5 hours / Reaction with OH	2 hours	SO_2, 3,5,6-tricloro-2-pyridinol, SOA, chlorpyrifos-methyl oxon
Diazinon [5, 6]	$< 1\times10^{-5}$	$(9.6 \pm 1.8)\times10^{-11}$	1.8 hours / Reaction with OH	1.5 hours	SO_2, PAN (in the presence of NOx), 2-Isopropyl-6-methyl-4-pyrimidinol 2-(1-hydroxy-1-methyl)-ethyl-4-methyl-6-hydroxypyrimidine,diethylphosphate, methylglyoxal, SOA
Diazoxon [6]	$< 4.8 \times 10^{-5}$	$(3.0 \pm 1.1)\times10^{-11}$	5.9 hours / Reaction with OH	4 hours	Hydroxydiazoxon, PAN (in the presence of NOx), SOA
Dichlorvos [7]	negligible	$(2.6\pm0.3)\times 10^{-11}$	5 hours / Reaction with OH	1.7 hours	Phosgene, CO

(1) Muñoz et al., 2014a, chemosphere. **(2)** Borras et al. Submitted. **(3)** Muñoz et al., 2011 a, EST. **(4)** Borrás et al, 2014 Chemosphere.
(5) Muñoz et al., 2011b, Chemosphere. **(6)** Muñoz et al., In Preparation. **(7)** Feigenbrugel et al., 2006, EST





ATMOSPHERIC DEGRADATION OF PESTICIDES

OVERVIEW

COMPOUND	J [s^{-1}]	k_{OH} [cm^3 $molec^{-1}$ s^{-1}]	k_{O3} [cm^3 $molec^{-1}$ s^{-1}]	Lifetime /Main degradation pathway	Lifetime SAR method (only OH reaction	Main degradation products
Lindane (12)	$<3.5 \times 10^{-5}$	6.4×10^{-13}	-	20 days / Reaction with OH	26 days	Hexhaclorocyclopentanone, HCl
Chloropicrin (13)	3.6×10^{-5}	-	4.8×10^{-18}	5.6 hours / Photolysis	115 days	Phosgene, NO_2, O_3
Hymexazol (14, 15)	$< 1.4 \times 10^{-5}$	4.9×10^{-12}	3.2×10^{-19}	20 hours / Reaction with OH	0.9 hours	3-Hydroxybutanoic acid, 2-Oxopropanoic acid, 3-Oxobutanal, 4,4-Dihydroxy-4-nitrosobutan-2-one, 3,4-Dioxobutanoic acid, 3-Oxobutanoic acid, 2-Oxobutanedioic acid

(12) Vera et al., 2015 Chemosphere.
(13) Vera et al., 2010, Zeitschrift für Physikalische Chemie
(14) Vera et al 2011 Atmospheric Environment
(15) Tortajada-Genaro et al. 2013. Chemosphere





PARTICULATE MATTER FORMATION FROM ATMOSPHERIC DEGRADATION OF ORGANOPHOSPHORUS PESTICIDES

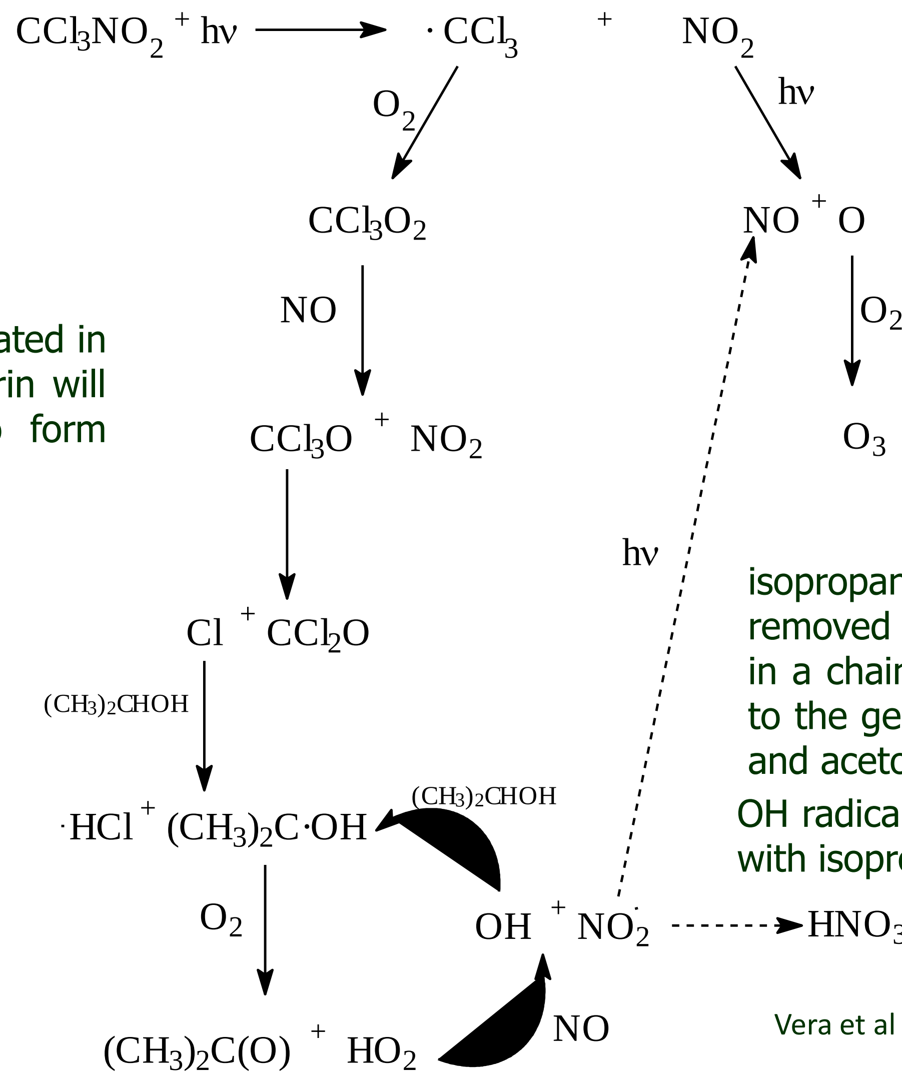
Pesticide	Type of experiment	Y(%)
Diazinon	Photolysis	<0.1
	Photo-oxidation in the presence of NO_x	44
Chlorpyrifos	Ozonolysis	<0.1
	Photolysis	6
	Photo-oxidation in the absence of No_x	-
	Photo-oxidation in the presence of NO_x	23
Chlorpyrifos-methyl	Ozonolysis	<0.1
	Photolysis	<0.1
	Photo-oxidation in the absence of No_x	8
	Photo-oxidation in the presence of NO_x	21
Pirimiphos-methyl	Ozonolysis	<0.1
	Photolysis	<0.1
	Photo-oxidation in the absence of No_x	5
	Photo-oxidation in the presence of NO_x	15
Chloropicrin	Photolysis	16

PM from pesticides can be considered a significant emerging pollutant, which formation from pesticide atmospheric degradation has been confirmed at the EUPHORE facilities.

CHLOROPICRIN REACTION MECHANISM IN GAS-PHASE

Reaction of Cl atoms generated in the photolysis of chloropicrin will react with isopropanol to form acetone.

The HO_2 radicals form OH radicals by conversion of the NO in the system to NO_2, and hence lead to the production of ozone.



isopropanol will be rapidly removed from the system in a chain reaction leading to the generation of ozone and acetone

OH radicals will also rapidly react with isopropanol

Vera et al 2010. Z. Phys. Chem.





PHOTOLYSIS OF CHLOROPICRIN IN GAS-PHASE WITH α-PINENE

	[α-pinene]/mg m^{-3}]	[chloropicrin]/mg m^{-3}]	RH (%)	JNO_2 /s^{-1}	ΔMo	Δ[pinene]	Δ[Chloropicrin]	Δ[O_3]	Y(%)
Exp1	779	197	0.7	7.82E-03	42	592	91	40	7
Exp2	806	852	1.1	7.92E-03	119	753	350	185	16
Exp3	187	403	1.4	8.43E-03	17	187	171	142	9
Exp4	389	410	1.7	8.03E-03	34	378	197	138	9
Exp5	1004	478	0.7	8.22E-03	99	889	211	80	11
Exp6	898	160	42.3	5.65E-03	44	706	72	36	6

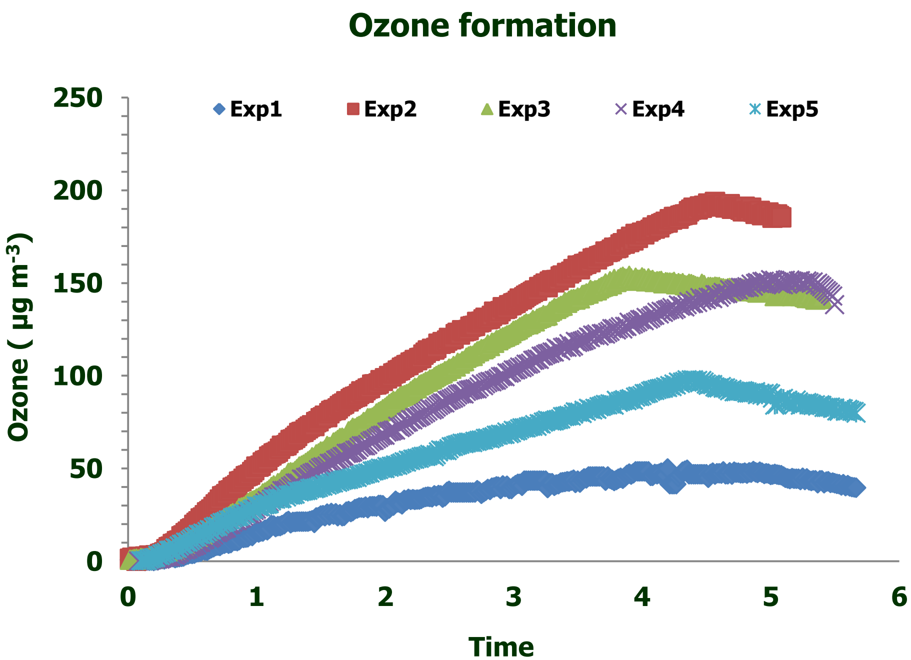
The extensive use of pesticides in combination to biogenic compounds presents an important environmental effect ➡ an important aerosol formation.

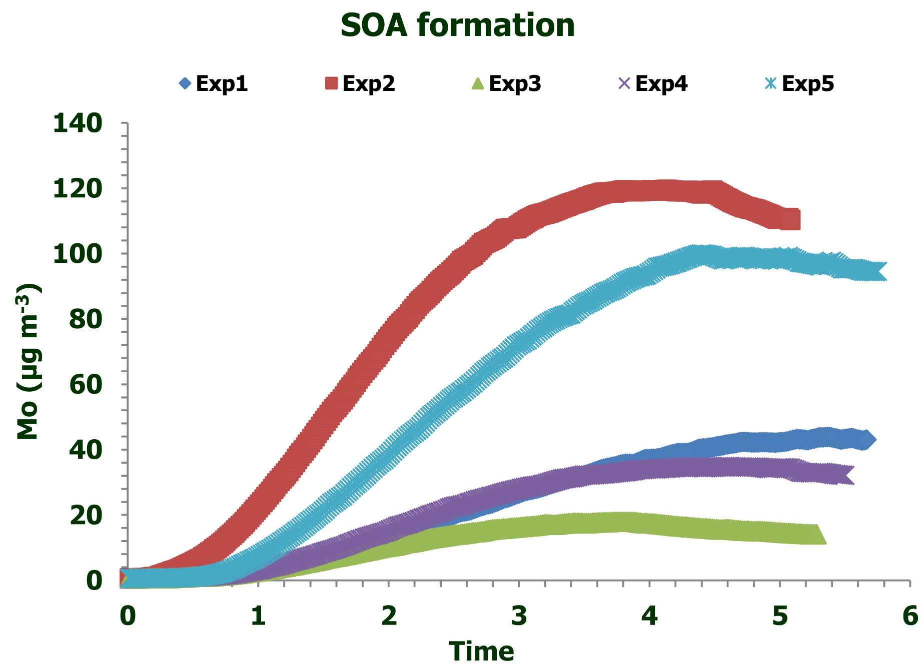
The highest aerosol yield and O_3 formation corresponds to the reaction with the same amount of each chemical ➡ the quid is the combination of both in the atmosphere.





PHOTOLYSIS OF CHLOROPICRIN IN GAS-PHASE





The highest aerosol yield and O_3 formation corresponds to the reaction with the same amount of each chemical → the quid is the combination of both in the atmosphere.

The understanding of atmospheric reactions should help to estimate the expected formation of gas and/or particulate matter in the troposphere, depending on each pesticide applied, and also, on the biogenic compounds emitted.





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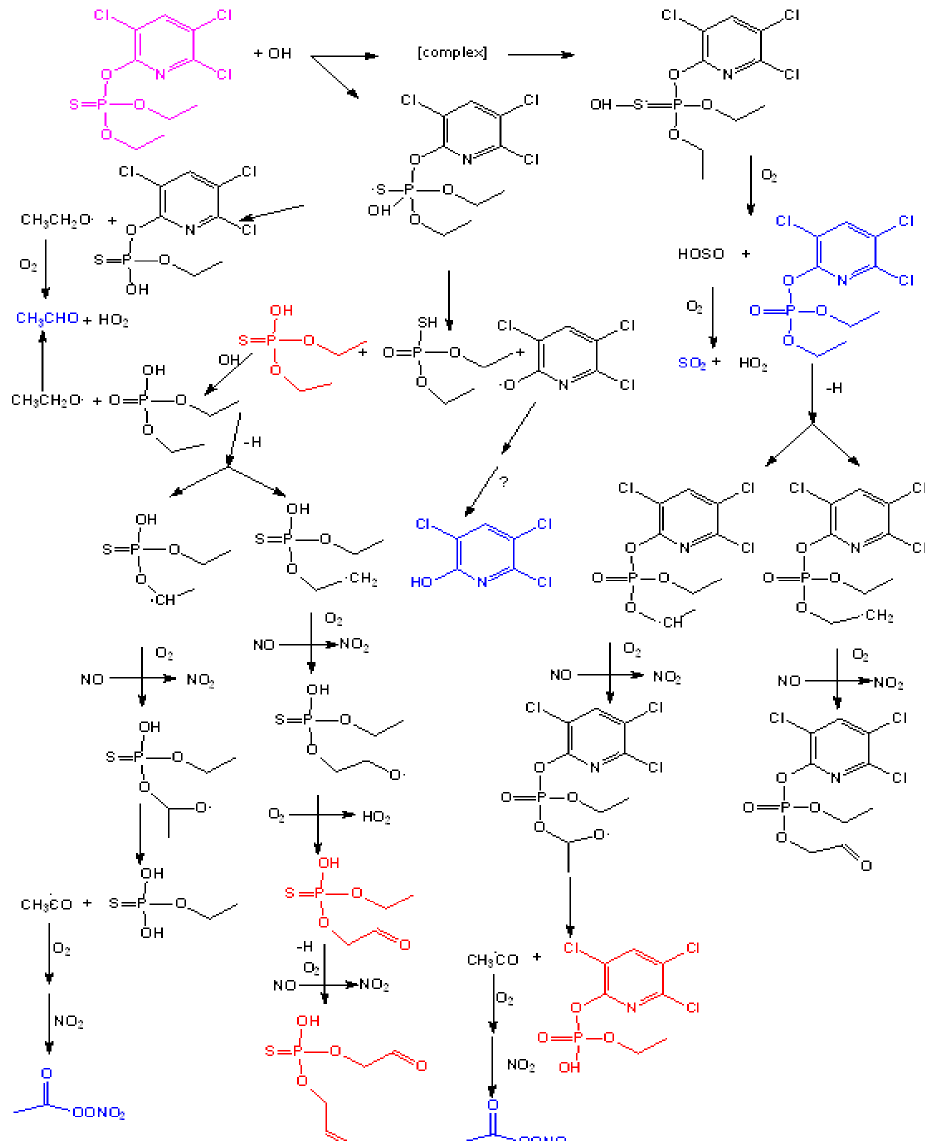
CLORPYRIPHOS MAIN DEGRADATION PATHWAY IN GAS-PHASE. REACTION WITH OH

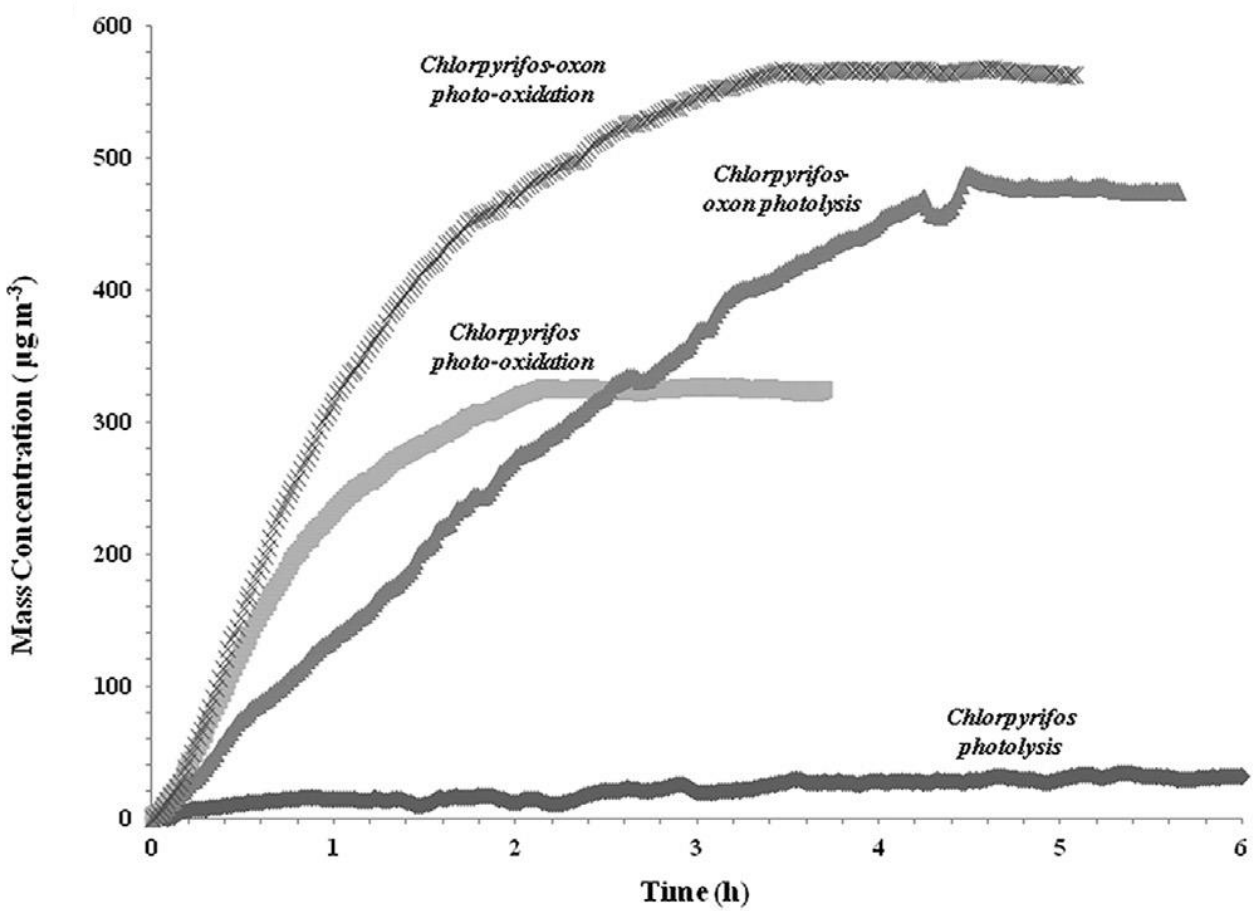
Pathway A: Addition of OH to the PS bond.

Structures in blue: identified and quantified compounds,
Structures in red: tentatively identified compounds by GCMS with derivatization, in gas and/or particle-phase



Muñoz et al., 2014, Chemosphere.

CLORPYRIPHOS AEROSOL FORMATION



No particle formation observed in the direct photolysis of Chlorpyrifos

Borras et al 2015. Atmos. Environm.

VOCs IMPLACAVELES

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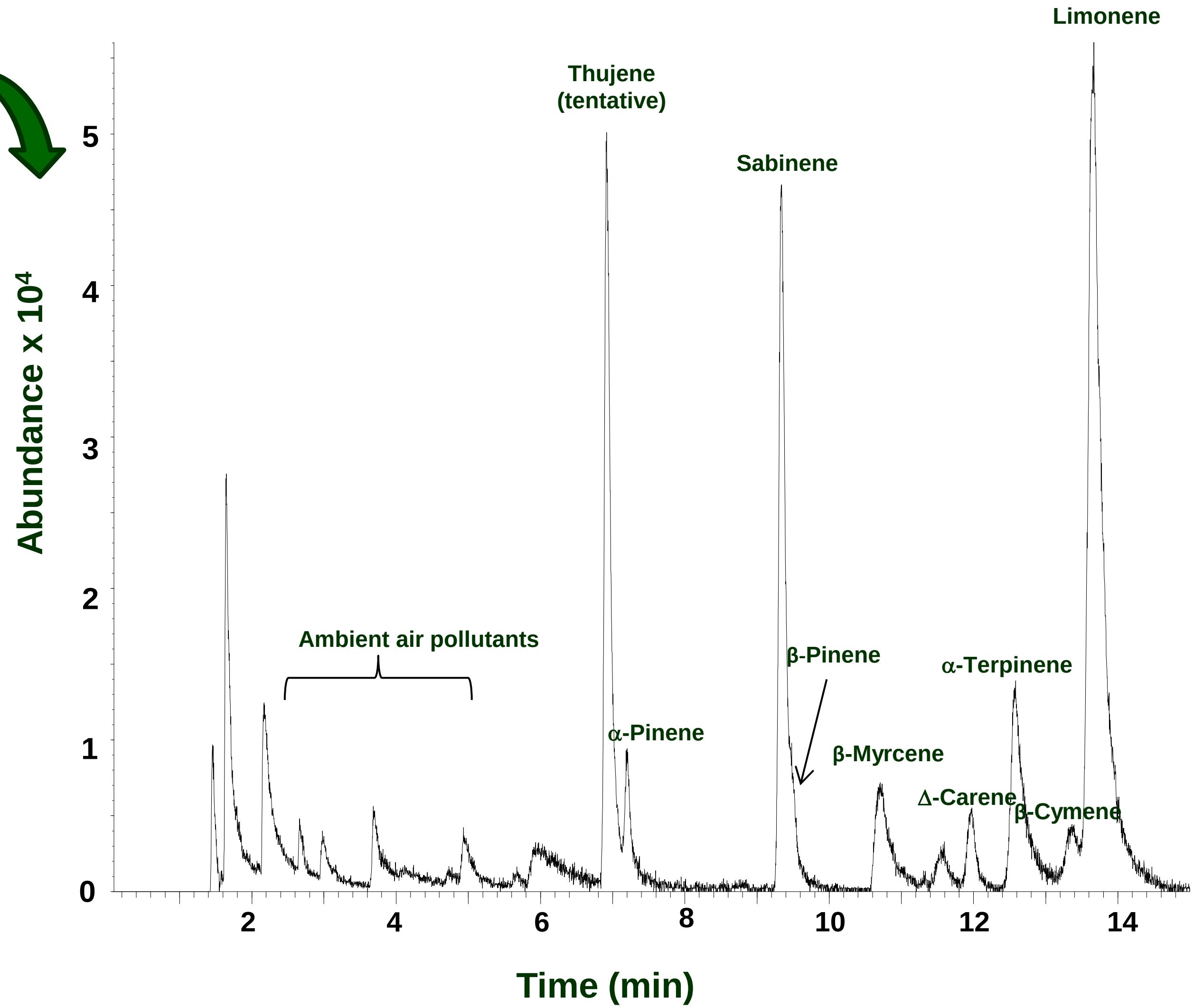
BVOCS: TERPENE EMISSIONS FROM ORANGE TREES

Orange trees direct emissions







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PHOTOLYIS AND OZONOLISIS STUDIES OF TERPENES WITH COMMERCIAL PESTICIDE

Type of Experiment	O_{3max} (ppbV)	SOA_{max} (mg m^{-3})	ΔHC (µg m^{-3})	Y (%)
Photolysis of orange trees terpenes without scavenger, dry	8.4	79.2	864.3	9.2
Photolysis of commercial pesticide	33.7	24.6	N.a.	N.a.
Photolysis of orange trees terpenes without scavenger, high RH	13.7	112.4	842.2	13.3
Photolysis of orange trees terpenes without scavenger and commercial pesticide	6.3	145.1	605.8	24.0
Photolysis of orange trees terpenes without scavenger and commercial pesticide	4.1	104.8	632.9	16.6
Ozonolysis of orange trees terpenes without scavenger	563.4	563.9	1209.5	46.6
Ozonolysis of commercial pesticide	608.0	19.3	N.a.	N.a.
Ozonolysis of orange trees terpenes without scavenger and commercial pesticide	558.0	509.7	1204.6	42.3

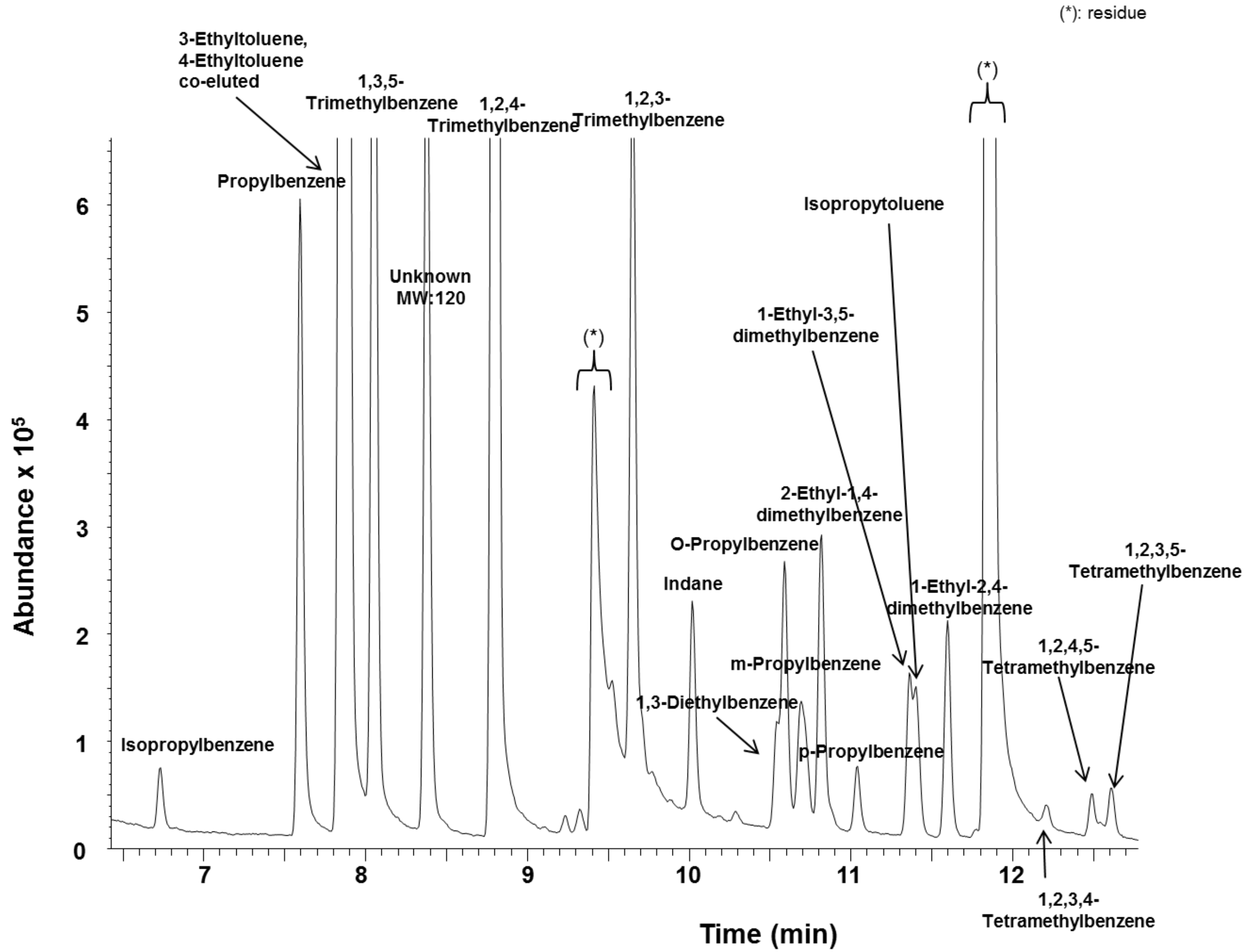
Terpene mixture (ppbV) consisted on

α-Pinene 7.5; Sabinene 83.3; β-Myrcene 13.1; α-Fellandrene 3.2; 3-Carene 3.8; α-Terpinene 22 and, Limonene 99.6

2.5 mL commercial solution in 1L water (active substance: chlorpyriphos)

Terpenes and concentrations selected looking for simulated the composition and proporcionalities found in our home-made greenhouse

GAS-PHASE ANALYSIS OF VOCS: TRIMETHYLBENZENES AND OTHER ADDITIVES ADDED TO COMMERCIAL PESTICIDES

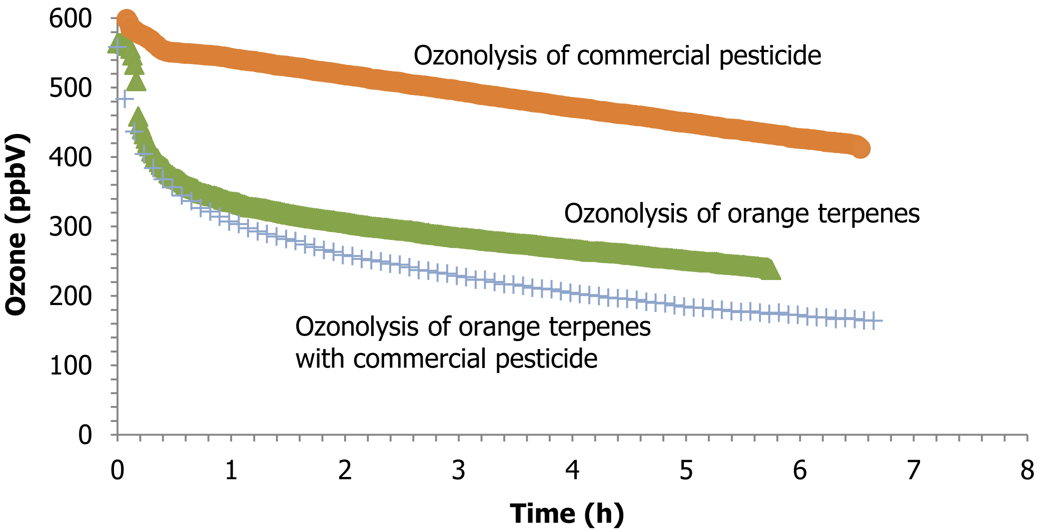






DARK CONDITIONS. REACTION WITH OZONE

Ozone consumption



Terpenes + commercial pesticide:

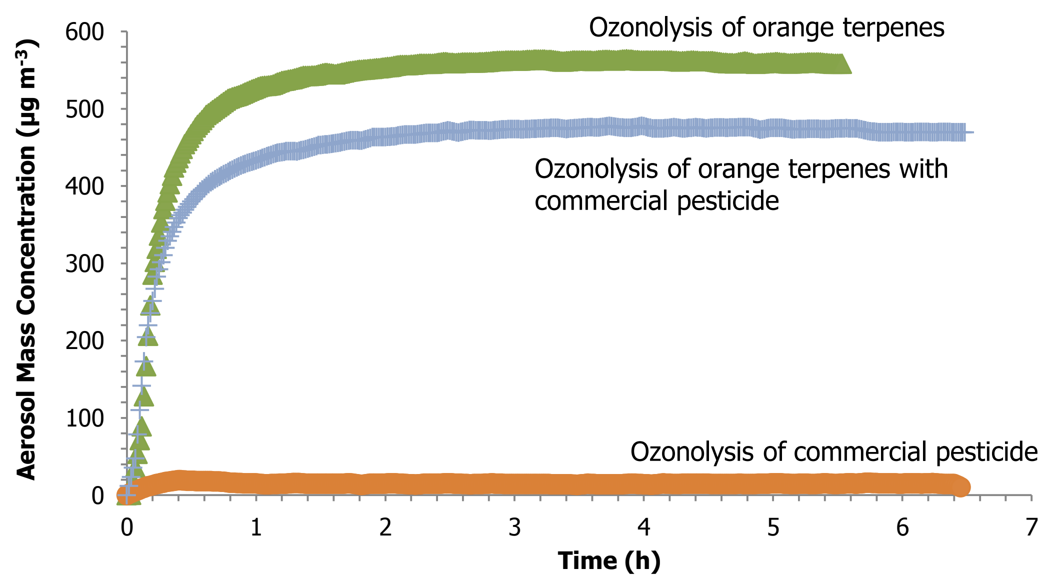
> Ozone consumption

< SOA formation

↓

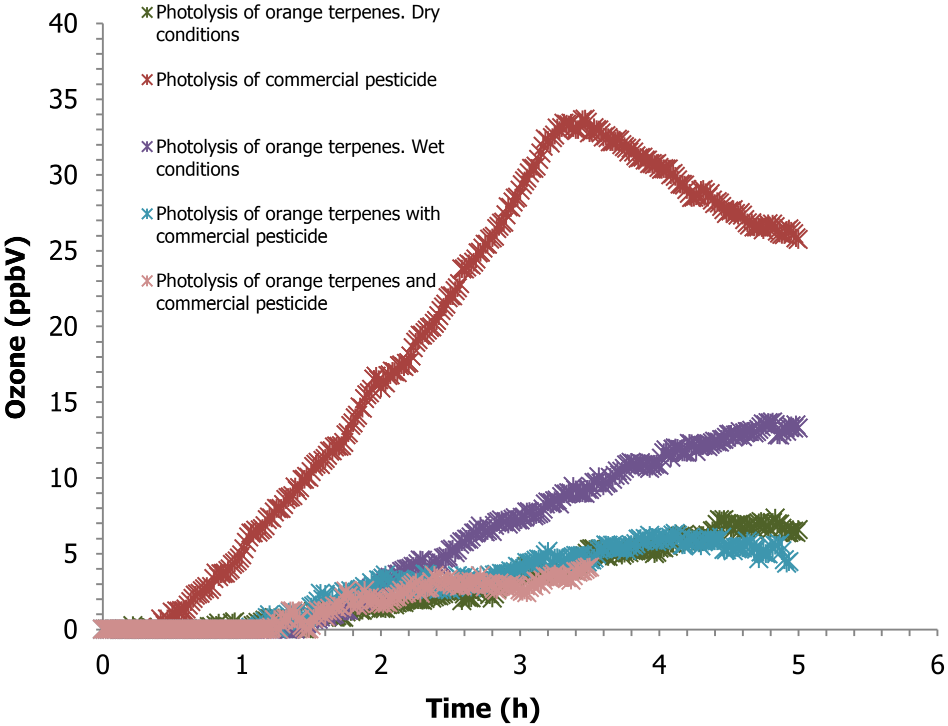
Reactions → gas-phase

SOA formation

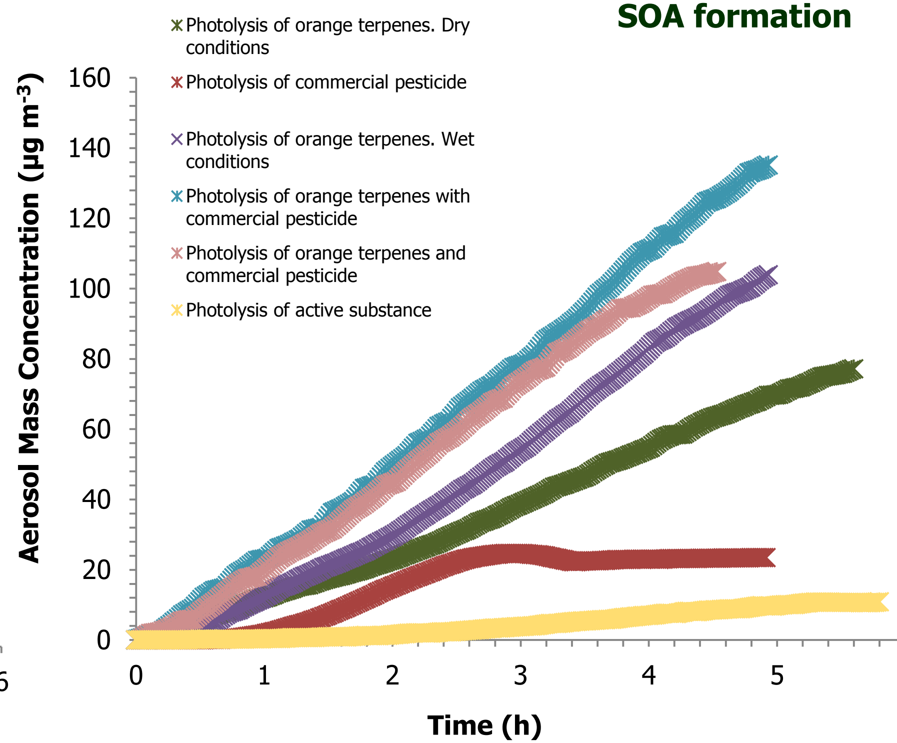


PHOTOLYSIS STUDIES

Ozone formation



SOA formation



Change RO_2 and HO_2 radical budget: Enhance reactivity.
Commercial pesticide increases ozone formed (as consequence of OH_2/RO), and this additional O_3 could react with terpenes, to form less volatile more oxidized compounds

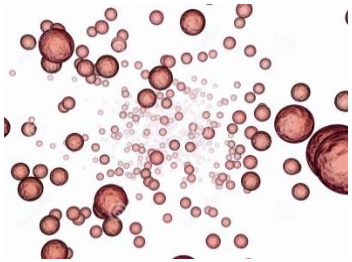




IMPACT ON CLIMATE CHANGE

Increased Secondary Organic Aerosol mass

Changes in Particle Size



Aerosols enriched in oligomers

Aerosols more CCN active

Cloud formation affected

Atmosphere-biosphere feedback.

Change in Environmental Conditions

Climate Change

Unfavorable environmental conditions and insect infestation (stresses) can induce more VOC emissions and change in composition

Higher temperatures enhance aerosol precursor emissions

Pesticide usage increase SOA formation

Higher temperatures could enhance plagues and increase pesticide usage

Based on **Zhao et al 2017**. Nature communications; **Kourtchev et al. 2016** Scientific Reports 6:35038 and **this work**





CONCLUSIONS

EUPHORE: sophisticated tool for studying pesticides under controlled atmospheric conditions with natural sunlight:

- Unique simulator chambers able to perform these studies worldwide

- **Very significant SOA formation** was observed during photolysis and ozonolysis experiments. The presence of a commercial pesticide solution in combination with terpenes, increased the ozone formation; then, O3 reacted with those terpenes, increasing the particulate matter formation. Since our previous studies demonstrated that chlorpyrifos does not photolize and does not react with ozone, our asumption is that solvents and additives added to the pesticide solution are the responsible for this behaviour

- The use of pesticides could play an important role on the climate change





ACKNOWLEDGEMENTS

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Thanks your for your attention