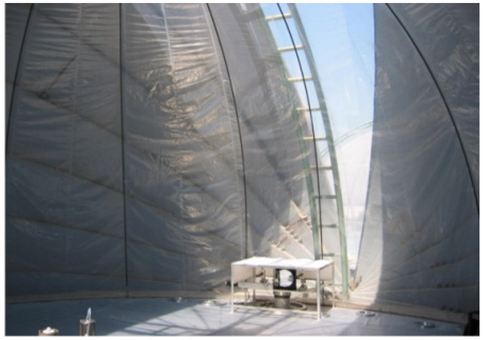
Atmospheric Degradation of Pesticides



Dr. Amalia Muñoz

amalia@ceam.es

European Workshop on Pesticides in Ambient Air, Valencia, 26-27th May 2014

INTRODUCTION

Pesticides used for:

- ➢Agriculture

- ➢Gardening operations

- ➢House uses

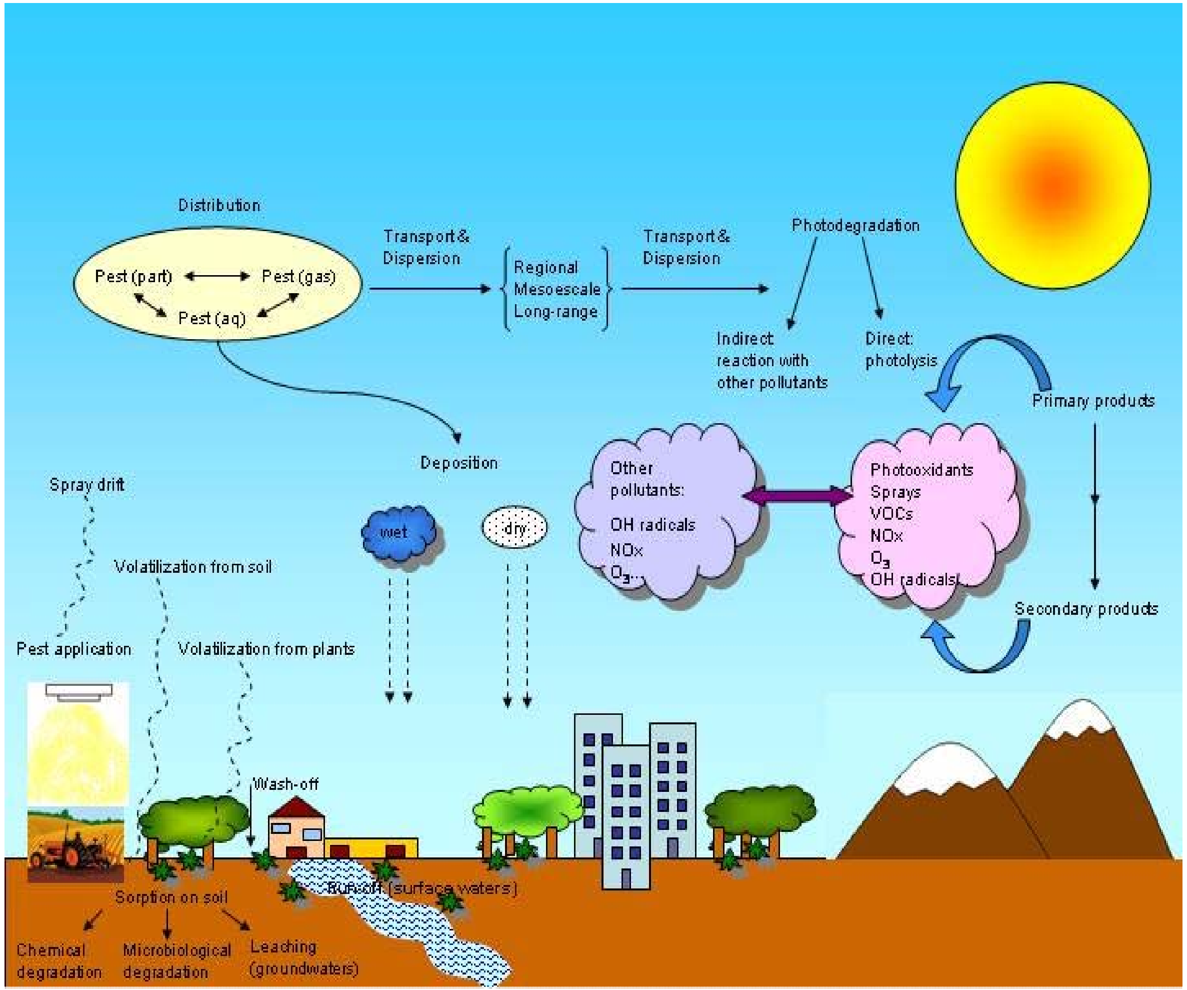
They can be emitted into the atmosphere by direct and indirect emisions

•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).

INTRODUCTION

Some references about (photo-)degradation of pesticides (under typical environmental conditions?):

In soils

Andreu, 2004, TrAC, 23, 772-789
Scholtz et al, 2007. Sci. Total Environ., 337, 61-80
Di Primo et al, 2003. Crop Prot. 22, 635-646
Gerstl et al, 1977. Soil Sci. Soc. Am. J., 41, 545-548
And MUCH MORE...

In water

Sakai, M., 2003. J. Health Sci., 49, 221-225
Comoretto, L. et al, 2007. Sci. Total Environ., 380, 124-132
Chiron et al, 1995. Environ. Roxicol. Chem., 14, 1287-1298
And MUCH MORE....

On aerosols

Palm et al, 1997. Environ. Sci. Technol., 31, 3389-3396
Palm et al, 1998. Ecotoxicol. Environ. Safety, 41, 36-43
Pflieger et al, 2011 Atmospheric Environment, 7127-7134
And FEW more...

In air (gas-phase)

Wade et al. 2006. J. Phys. Chem. A. 110, 4405-4412
LePerson et al, 2007. Chemosphere, 67, 376-383
Feigengrugel et al, 2006. Environ. Sci. Technol. , 40, 850-857
Carter et al, 1997. Atmos. Environ. 31, 1425-1439
And FEW more...

PESTICIDE HETEROGENEOUS STUDIES UNDER ATMOSPHERIC CONDITIONS, INCLUDING AEROSOLS

Table II.

Overview of published data on reaction rates of pesticides in the aerosol-borne state (reaction rate constants are in units of cm^3 $molecule^{-1}$ s^{-1}, at room temperature)

compound	k_{OH}	k_{O3}	Ref.
lindane	6.0×10^{-13}		Behnke and Zetzsch, 1989; Zetzsch, 1991
terbuthylazine	1.1×10^{-11}	$<5 \times 10^{-19}$	Palm *et al.*, 1997
pyrifenox[a]	1.8×10^{-11}	$<2 \times 10^{-19}$	Palm *et al.*, 1999

[a] Rate constant for the reaction with hydrogen peroxide was found to be negligible ($<< 1 \times 10^{-19}$)

Atkinson et al., 1999 Review

HETEROGENEOUS STUDIES UNDER ATMOSPHERIC CONDITIONS, INCLUDING AEROSOLS

Compound	Support	k_{OH} cm^3 molec^{-1} s^{-1}	τ_{OH}	k_{O3} cm^3 molec^{-1} s^{-1}	τ_{O3}	k_{NO3} cm^3 molec^{-1} s^{-1}	τ_{NO3}	Referencia
Alachlor	Silica particles				>8 months			Pflieger et al 2009
Terbuthylazine	Silica particles	1.5 x 10^{-13}	71 days	< 0.5 x 10^{-19}	>8 months			Pflieger et al 2009 Pflieger et al 2013
	Silicon dioxide	1.1 x 10^{-11}	1 day	< 5 x 10^{-19}				Palm et al 1997
Trifluralin	Silica particles			2.9 x 10^{-19}	40 days			Pflieger et al 2009
Dimetomorph	Quartz plaques			2 x 10^{-19}	60 days			Al Rashidi et al 2013
Fenthion	Suspended particles (azelaic acid)					3.3 x 10^{-3} s^{-1} (uptake) ($[NO_3]$= 10^{11}- 10^{12}		Liu et al, 2012
Malathion	Suspended particles (azelaic acid)					5.6 x 10^{-2} s^{-1} ($[NO_3]$= 10^{11}- 10^{12}		Liu et al, 2012
Parathion	Suspended particles (azelaic acid)					5.5 x 10^{-2} s^{-1} ($[NO_3]$= 10^{11}- 10^{12}		Liu et al, 2012
Resmethrin	Suspended particles (azelaic acid)					0.2 s^{-1} (uptake)	2.6 h	Wang et al, 2013
Pirimiphos-methyl	Suspended particles (azelaic acid)					9.9 x 10^{-12}		Wang et al, 2012

New references, use relative kinetic methods: terbutylazine

PESTICIDE GAS-PHASE STUDIES UNDER ATMOSPHERIC CONDITIONS, INCLUDING AEROSOLS

GAS-PHASE STUDIES UNDER ATMOSPHERIC CONDITIONS

Overview of published data on atmospheric reaction rates of pesticides
(reaction rate constants are in units of cm^3 $molecule^{-1}$ s^{-1}, at room temperature)

compound	k_{OH}	k_{NO3}	k_{O3}	k_{phot} (s^{-1})	Ref.
methyl bromide	2.9×10^{-14}				a
1,2-dibromo-3-chloropropane	4.3×10^{-13}		$<3 \times 10^{-20}$		b
cis-1,3-dichloropropene	8.4×10^{-12}		1.5×10^{-19}		c,d (L)
trans-1,3-dichloropropene	1.4×10^{-11}		6.7×10^{-19}		c,d (L)
EPTC	3.2×10^{-11}	9.2×10^{-15}	$<1.3 \times 10^{-19}$		e (L)
cycloate	3.5×10^{-11}	3.3×10^{-14}	$<3 \times 10^{-19}$		e (L)
α-hexachlorocyclohexane	1.4×10^{-13}				f (L)
γ -hexachlorocyclohexane	1.9×10^{-13}				f (L)
hexachlorobenzene	2.7×10^{-14}				f (L)
trifluralin				$\sim 3 \times 10^{-4}$	g (L)
				$\sim 6 \times 10^{-4}$	h (F)
phorate				$\sim 2 \times 10^{-3}$	i (L)
parathion				$\sim 6 \times 10^{-3}$	h (F)
phosphine	1.6×10^{-11}				j (L)
chloropicrin				5.7×10^{-5}	k (L)
methyl isothiocyanate				6.7×10^{-6}	l (L)
				see comment	m (L)

Atkinson et al., 1999 Review

EUPHORE

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….

EUPHORE

INSTITUTO UNIVERSITARIO CEAM CENTRO DE ESTUDIOS AMBIENTALES DEL MEDITERRÁNEO UNIVERSITAS Miguel Hernández

TECHNICAL DESCRIPTION

Half-spherical FEP covers

200 m³ volume

Well instrumented

Steel protection covers

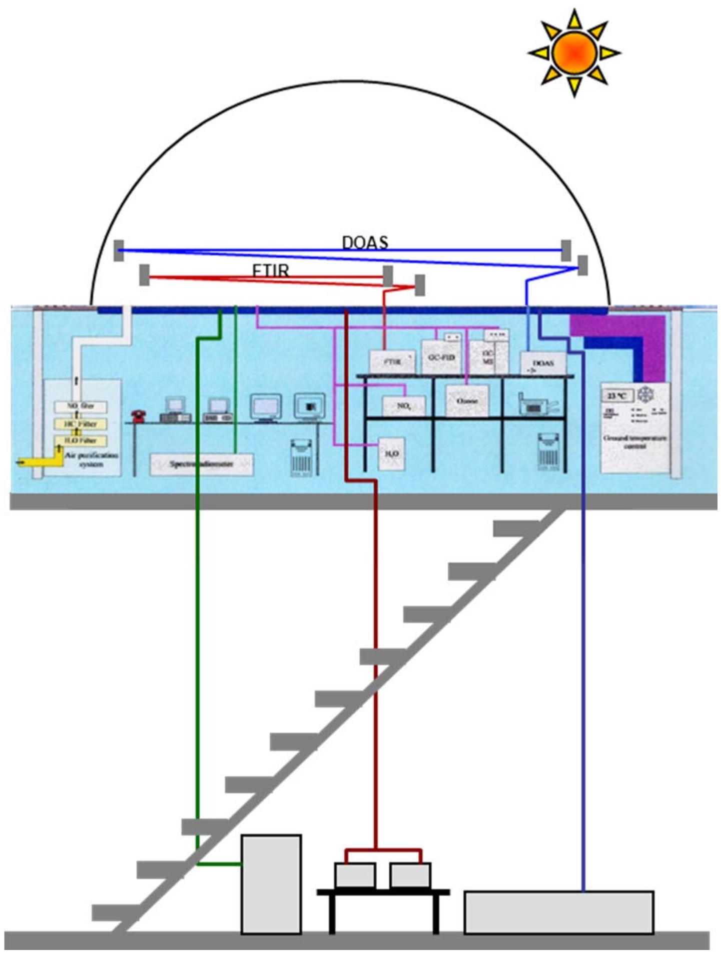
Air purification

Mechanical homogenisation

Meteorological tower

Cooled floor

Natural sunlight



Analytical Instrumentation

OPTICAL INSTRUMENTATION
- DOAS (UV-Vis)
- LIF (Laser)
- FTIR (IR)

MASS ESPECTROMETERS
- PTRMS

GAS MASS CHROMATOGRAPHS
- GC MS on-line
- GC MS off-line

GAS CHROMATOGRAPHS
- GC FID
- GC PAN
- GC FID/ECD
- GC FID+SPME
- GC PID/FID

LIQUID CHROMATOGRAPHS
- HPLC (UV/Fluorescence)
- LC-MS

MONITORS
- NO_x ECO ALPPT
- NO_x API 200AU
- NO_x TAPI200UP
- O_3
- CO
- SO_2
- HONO
- HCHO

AEROSOL INSTRUMENTATION
- SMPS
- TEOM

RADIOMETERS
- ACTINOMETERS
- SPECTRORADIOMETER

OTHERS
- BAROMETERS
- HYGROMETERS
- TEMPERATURE SENSORS
- AEROSOL GENERATOR
- DIESEL ENGINE

Studies of the Atmospheric Degradation of Pesticides at EUPHORE

Limiting factor for the atmospheric study of pesticides

↓

Vapour pressure of the pesticide

Considering the EUPHORE characteristics

↓

Pesticides with Pv higher than 0.1 mPa, to assure the presence of the compound in the gas phase

Almost all pesticides can be studied at EUPHORE regardless of their chemical family or type

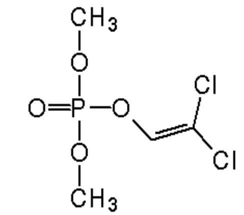
ATMOSPHERIC FATE OF SELECTED PESTICIDES

Examples of pesticides studied at EUPHORE chambers

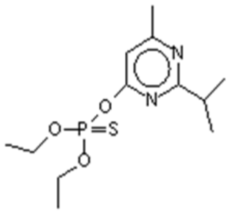
Organophosphorous insecticides and degradation products

Fungicides

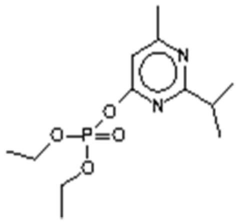
Chloroacetanilide and dinitroaniline herbicides



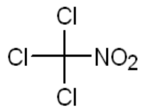
Dichlorvos



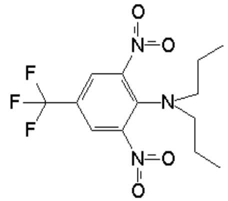
Diazinon



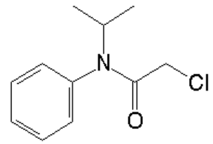
Diazoxon



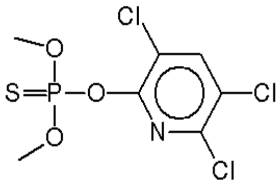
Chloropicrin



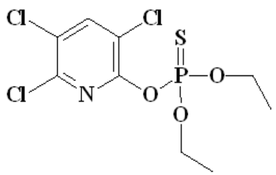
Trifluralin



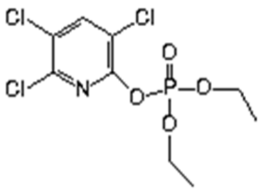
Propachlor



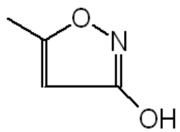
Chlorpyrifos-methyl



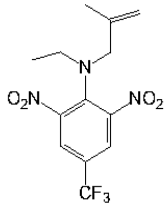
Chlorpyrifos



Chlorpyrifos-oxon



Hymexazol

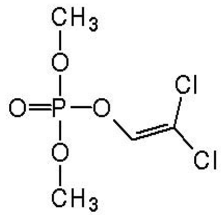


Ethalfluralin

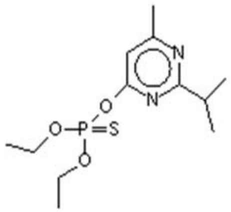
Main type of experiments

Type of experiment	Main objective	Usual conditions
Photolysis	Determination of **Photolysis rate constant** and **degradation products**	Experiments carried out in the presence of OH and/or Cl **scavenger** in order to prevent the reaction with those radicals.
Reaction with OH radical Determination of rate constants	Determination of the **rate constant** for the OH reaction with pesticides	**Relative kinetic method**. Depending on the compound and the estimated value of the OH constant 1,3,5-trimethylbenzene, cyclohexane, n-butyl ether, methylen dichloride, benzene or toluene have been used as references. When possible interferences from Cl radical could be derived, two references where used in the same experiment.
Reaction with OH radical Determination of reaction products	Determination of **degradation product**s of the reaction of OH. **Reaction mechanism**	Gas and particle phase analysis. Experiments carried out in the presence or in the absence of NOx.
Reaction with Ozone	Determination of Ozone **rate constant** and **degradation products**	Dark conditions. **Pseudo-first order conditions**. OH radical **scavenger** used.

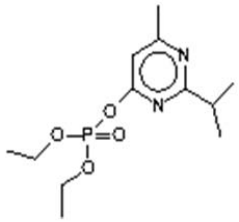
ATMOSPHERIC DEGRADATION OF ORGANOPHOSPHOROUS INSECTICIDES



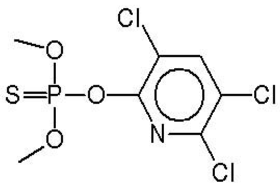
Dichlorvos



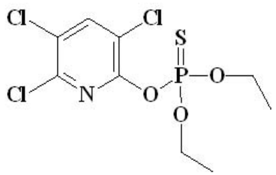
Diazinon



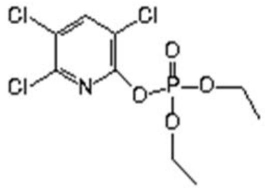
Diazoxon



Chlorpyrifos-methyl

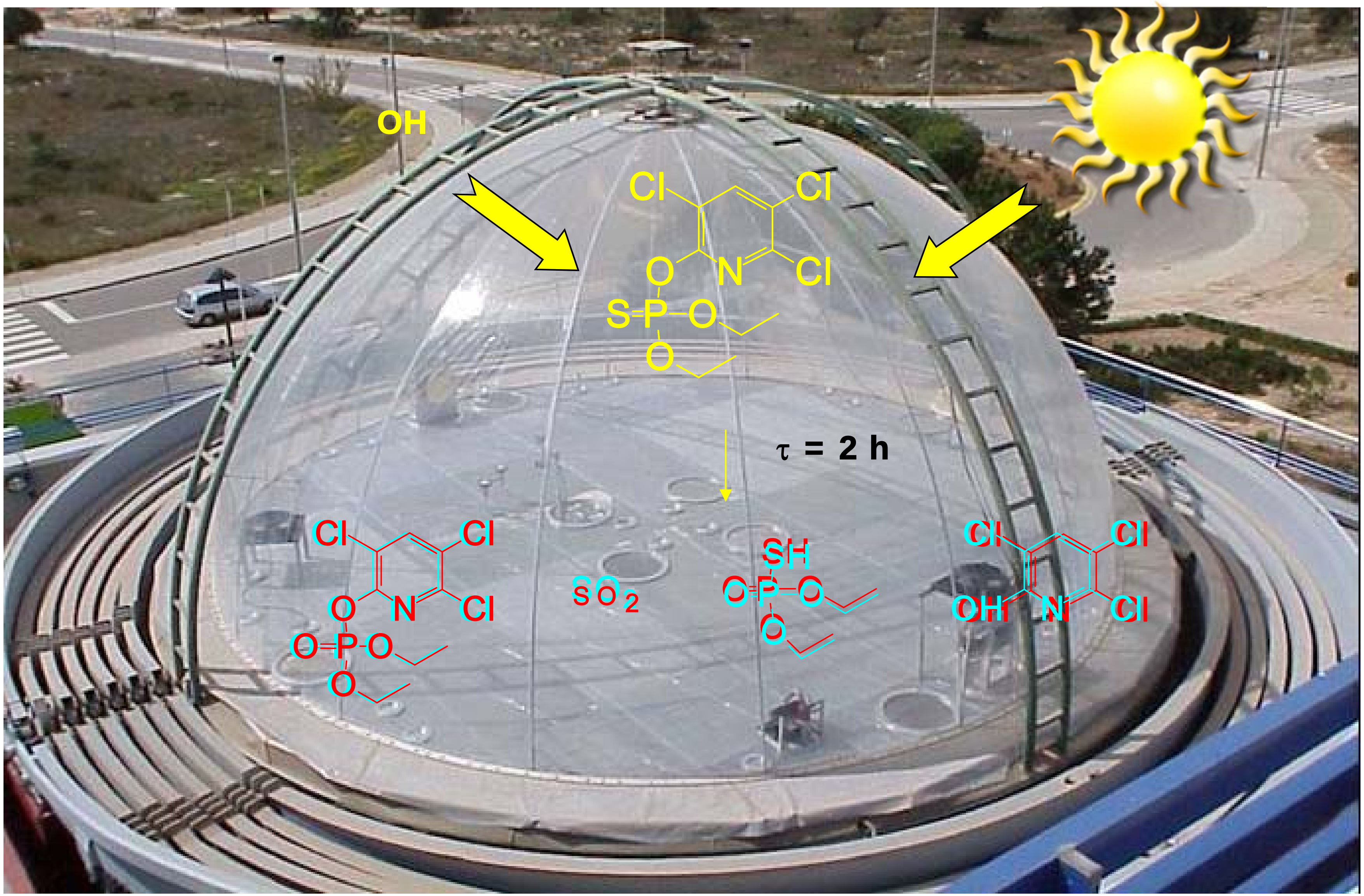


Chlorpyrifos



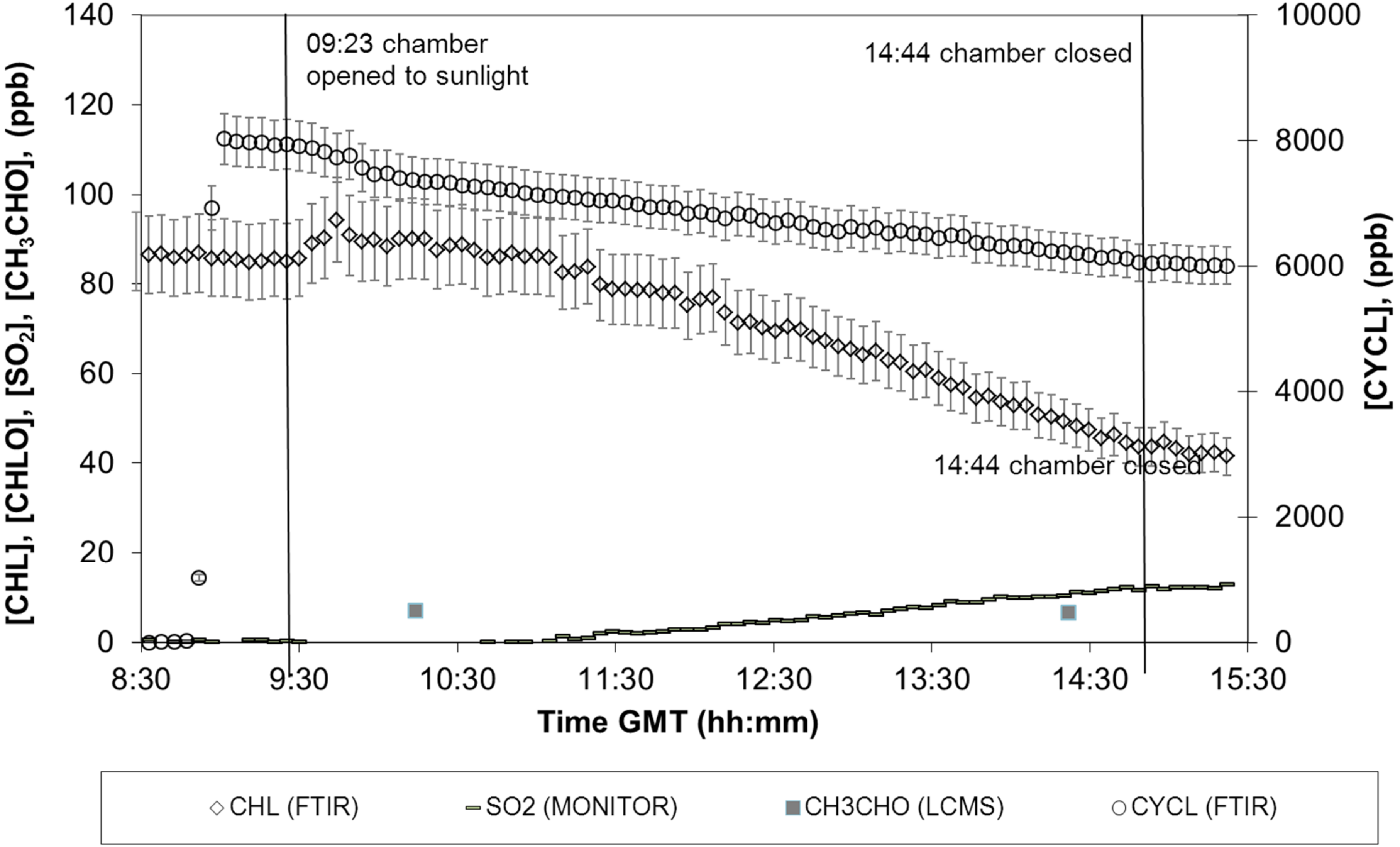
Chlorpyrifos-oxon

ATMOSPHERIC DEGRADATION OF CHLORPYRIFOS AND CHLORPYRIFOS-OXON



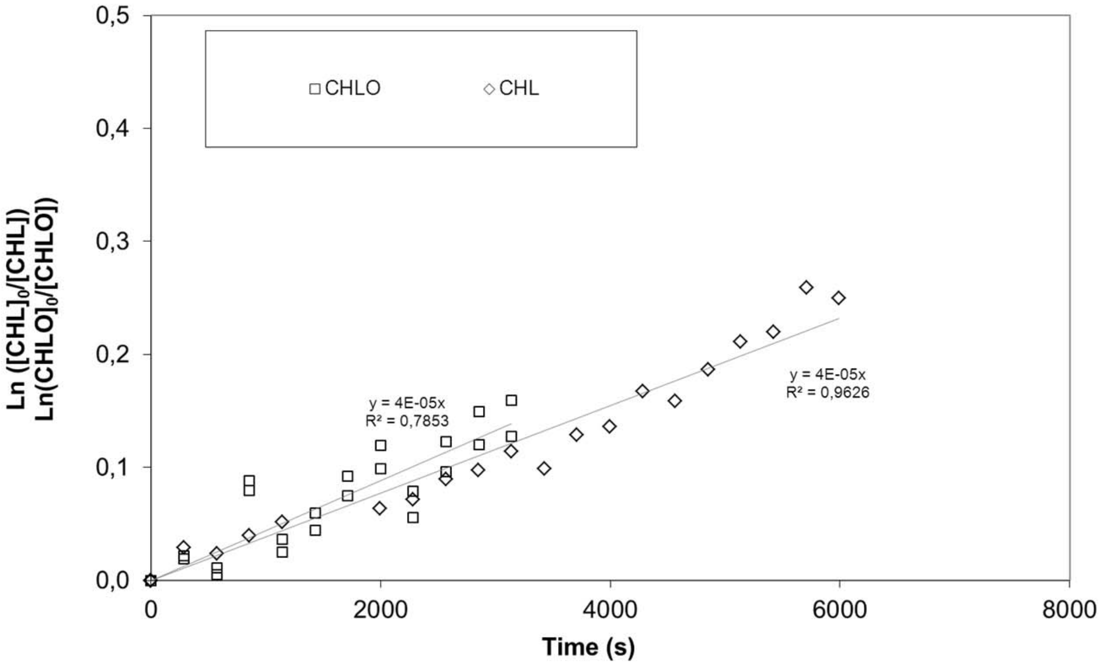
ATMOSPHERIC DEGRADATION OF CHLORPYRIFOS AND CHLORPYRIFOS-OXON

Photolysis (J)



Photolysis (J)

Kinetics



Pest + hν	→	Products	J(Pest)
Pest + Wall	→	Wall loss	k_{wall}(Pest)
Pest	→	Dilution	k_{dil}

$\ln([SF_6]_o/[SF_6]_t) = k_{dil}t$

The measured rate coefficient for the overall loss of a pesticide is given by:

$$\ln([Pest]_o/[Pest]_t) = (J_{meas})t$$

$$J_{meas} = J(Pest) + k_{dil} + k_{wall}(Pest)$$

$$t_{1/2\ (J)} = \ln(2)/(J_{PEST})$$

J(CHL) < $4.5 \times 10^{-5}\ s^{-1}$ (300 ± 5 K) → $t_{1/2\ (J\ (CHL))}$ > 4.3 hours
(JNO_2= 9.5 ± 1.7 x 10^{-3})

J(CHLO) < $4.4 \times 10^{-5}\ s^{-1}$ (305 ± 5 K) → $t_{1/2\ (J\ (CHLO))}$ > 4.4 hours
(JNO_2= 9.5 ± 1.7 x 10^{-3})

Photolysis (J)

Products

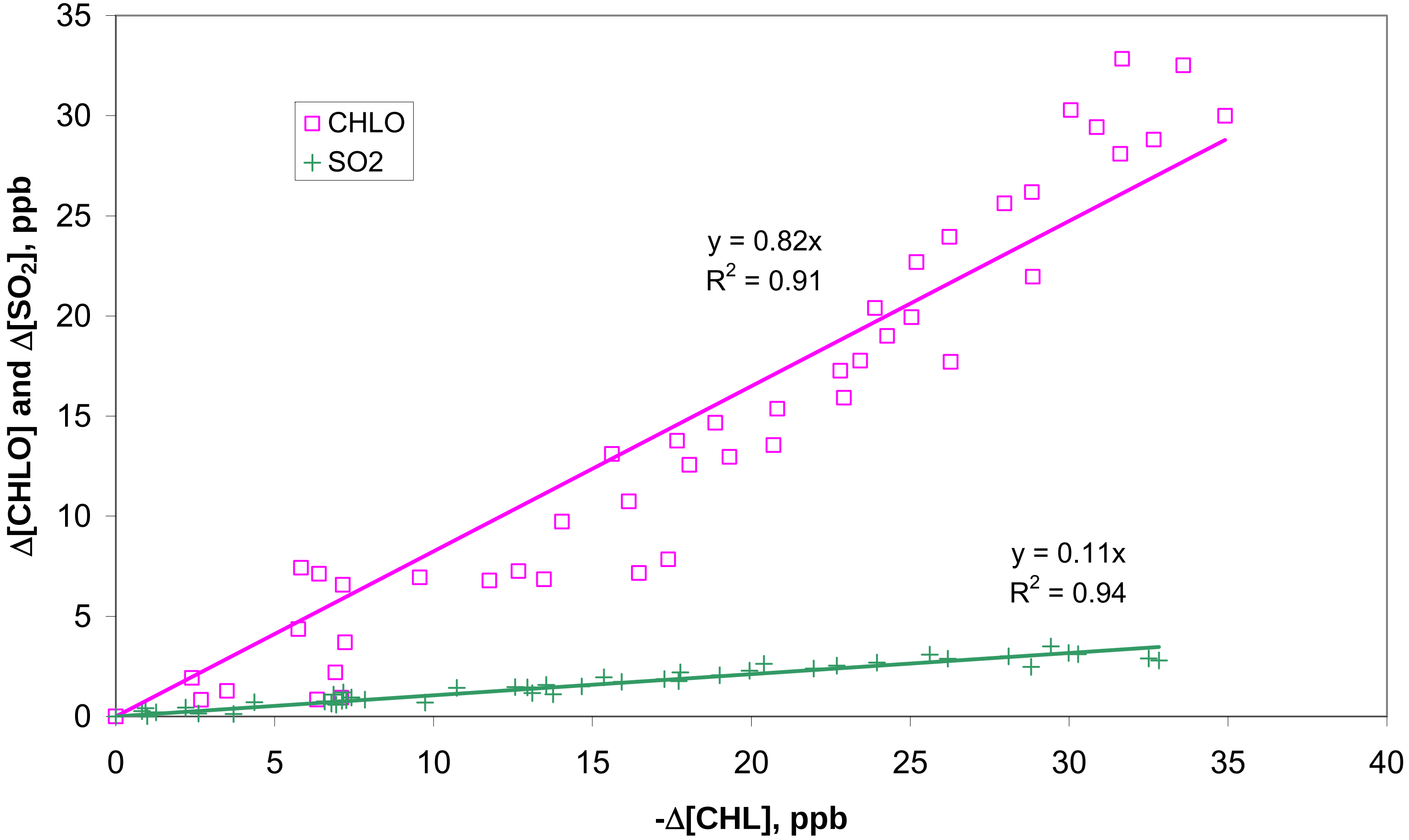
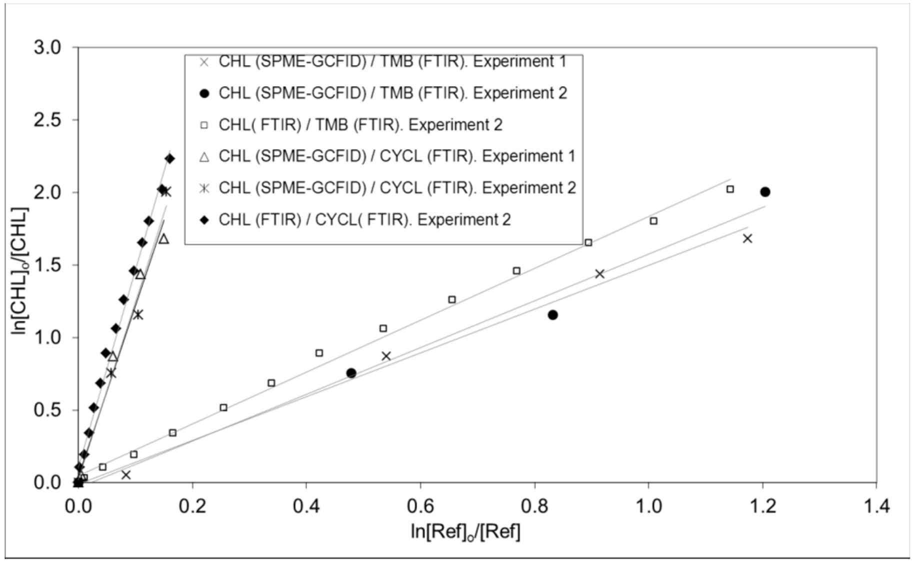
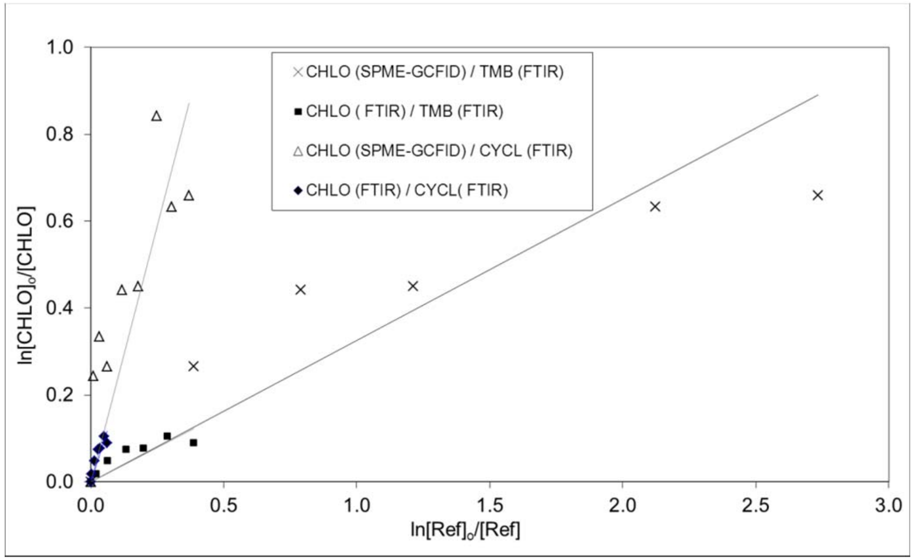


Photo-oxidation (k_{OH})

Kinetics





OH + Pest → Products k_{OH}(Pest)
PEST → Dilution k_{dil}
PEST → Wall loss k_{wall}

Reference → Products k_{OH}(Ref)
Reference → Dilution k_{dill}

$$\ln([Pest]_o/[Pest]_t) - (k_{dil}+k_{wall})t = k_{OH}(Pest)/k_{OH}(Ref)\ln([Ref]_o/[Ref]_t) - k_{dil}t$$

Half lifetime

$$t_{1/2(OH)} = \ln(2)/(k_{OH}(Pest)[OH])$$

$[OH] = 2\times10^{6}$ molecule cm^{-3}

$t_{1/2\,(CHL)}$ = 1.3 hours

$t_{1/2\,(CHLO)}$ = 7.8 hours

Photo-oxidation

Reaction Products

The gas-phase products observed by FTIR from the OH radical-initiated reaction of CHL and their molar formation yields

Compound	Formula	CAS Number	Detection Limit (ppb)	Accuracy Error	Analysis Region (cm^{-1})	Calibration Method
Chlorpyrifos (CHL)	$C_9H_{11}Cl_3NO_3PS$	2921-88-2	1.7	17%	760-1225	Regression
Chlorpyrifos-oxon (CHLO)	$C_9H_{11}Cl_3NO4P$	5598-15-2	3.0	15%	760-1225	Regression
3,5,6-trichloro-2-pyridinol (PYRIDOL)	$C_5H_2Cl_3NO$	6515-38-4	4.0	5%	760-1225	Regression
Cyclohexane	C_6H_{12}	110-82-7	0.70	4.9%	815 - 875	Regression
Cyclohexane	C_6H_{12}	110-82-7	0.70	4.9%		Regression
1,3,5-Trimethylbenzene	C_9H_{12}	108-67-8	1.30	2.0%	815 - 875	Regression
Methanol	CH_3OH	67-56-1	1.30	20.0%	950 - 1100	EPA Database
Formaldehyde	HCHO	50-00-0	3.00	3.3%	2700 - 2900	DOAS
Formic Acid	HCOOH	64-18-6	0.70	4.5%	1050 - 1150	Regression
Nitric Acid	HNO_3	7697-37-2	2.20	4.4%	825 - 950	Regression
Nitrous Acid	HONO	7782-77-6	2.50	7.0%	760 - 900	Regression
Glyoxal	$C_2H_2O_2$	107-22-2	2.5	8%	2750-2900	DOAS
Methylglyoxal	$C_3H_4O_2$	78-98-8	2.70	15.0%	2750 - 2900	DOAS
Ozone	O_3	10028-15-6	3.00	10.0%	950 - 1100	JPL NASA
Peroxyacetyl Nitrate	$C_2H_3NO_5$	2278-22-0	0.70	3.0%	775 - 1220	Regression
Sulfur Hexafluoride	SF_6	2551-62-4	0.10	10.0%	920 - 955	Regression
Chlorhidric acid	HCl	7647-01-0	2.7	30.0%	2700-2900	EPA Database

Photo-oxidation

Reaction Products

The gas-phase products observed by GC

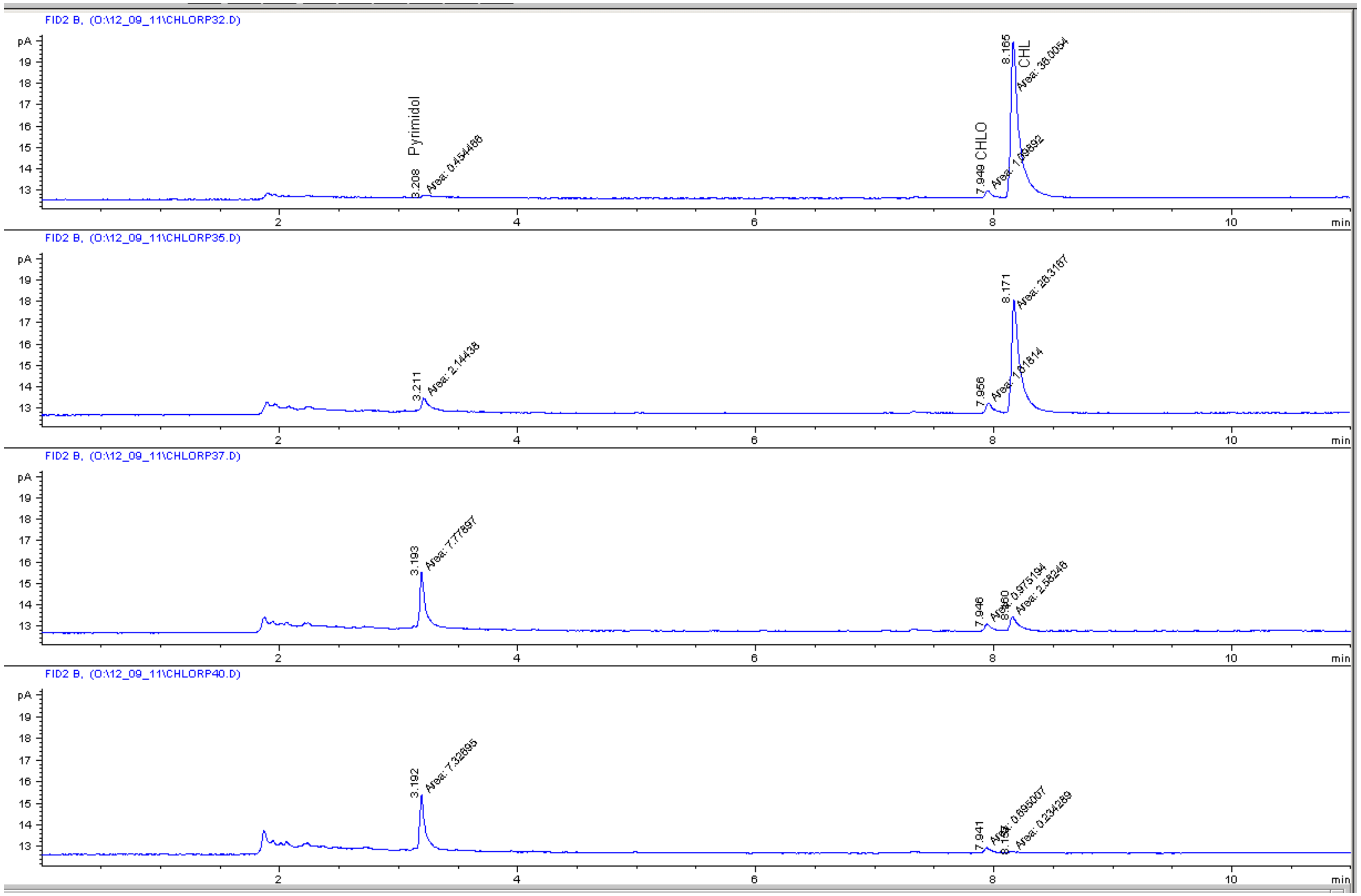


Photo-oxidation

Reaction Products

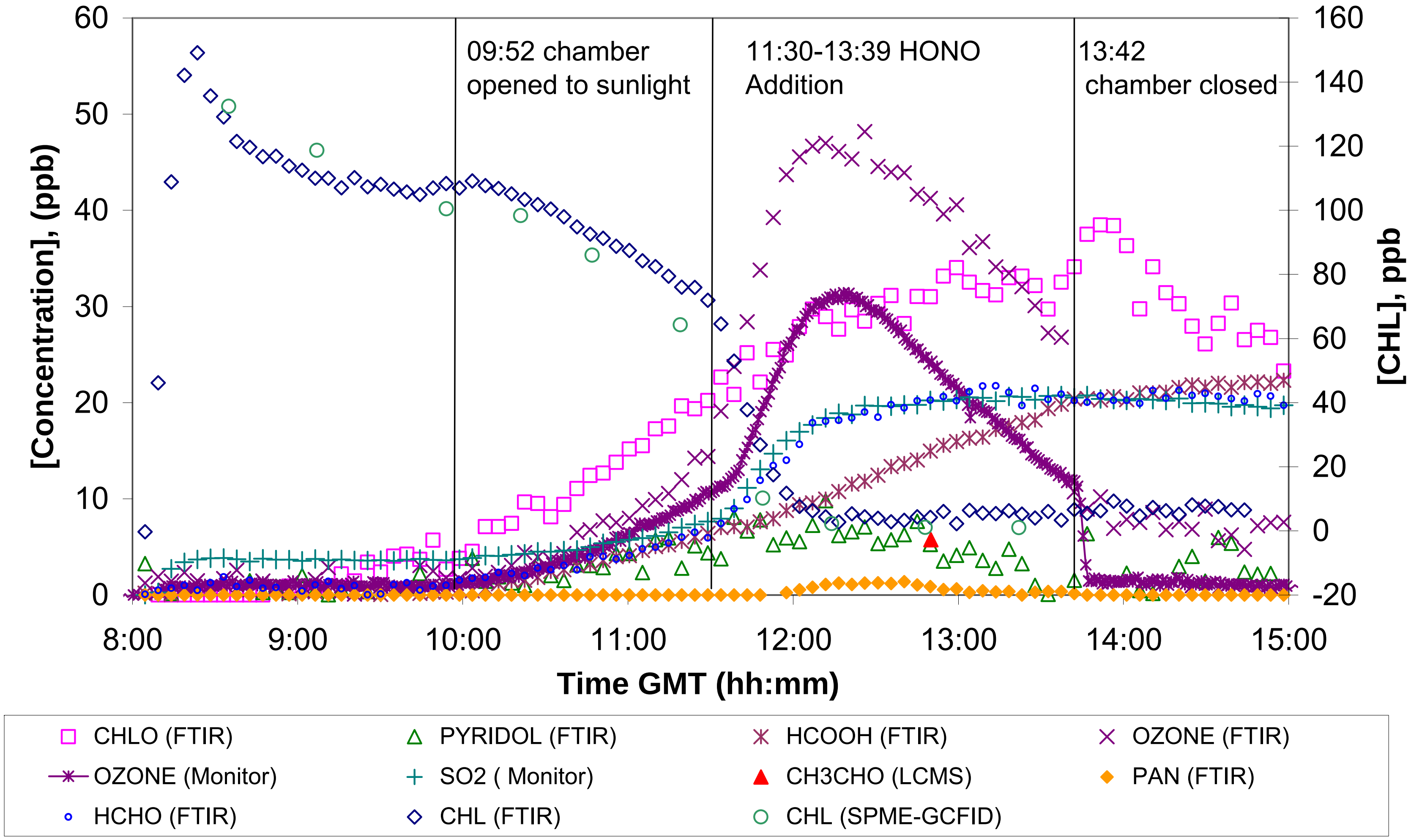
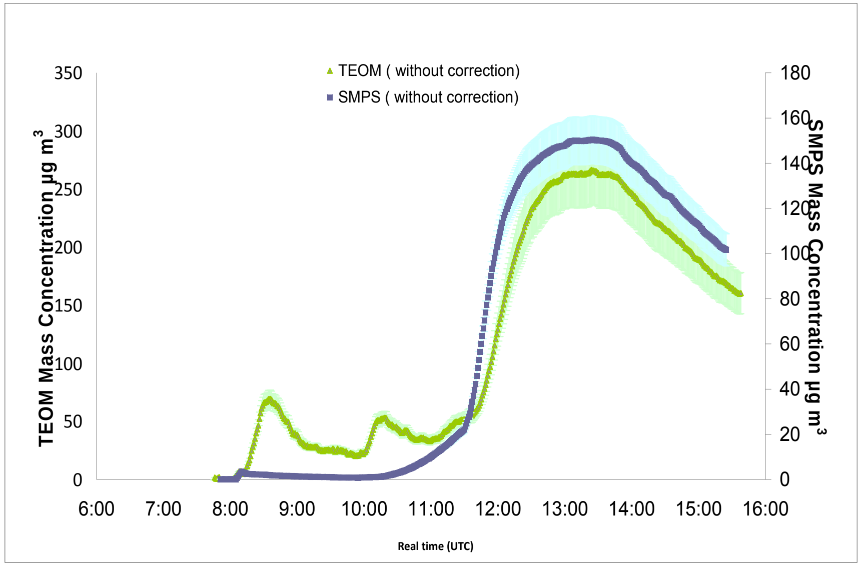
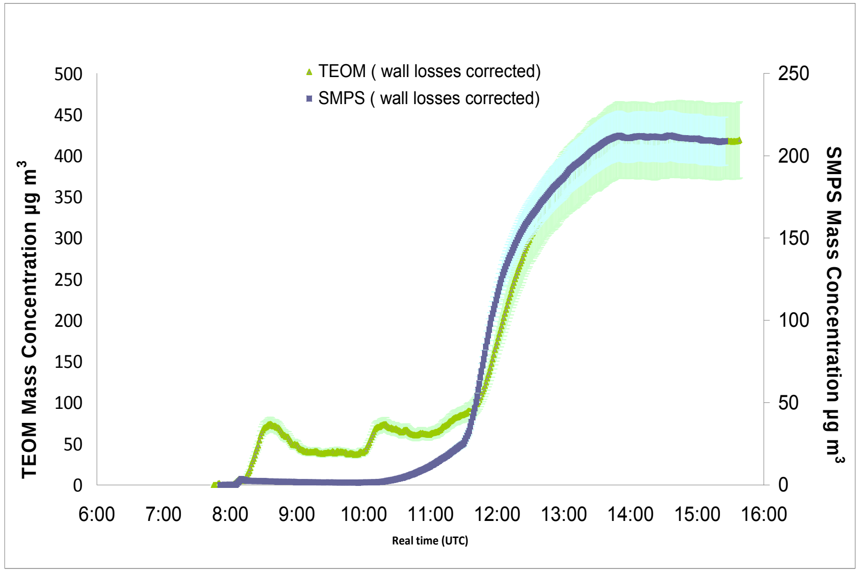


Photo-oxidation

Reaction Products

Aerosol formation





The aerosol concentration determined by TEOM and SMPS A) without wall losses correction, b) with wall losses correction

Photo-oxidation

Reaction Products

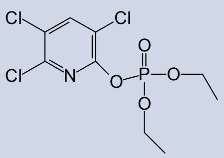
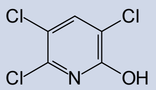
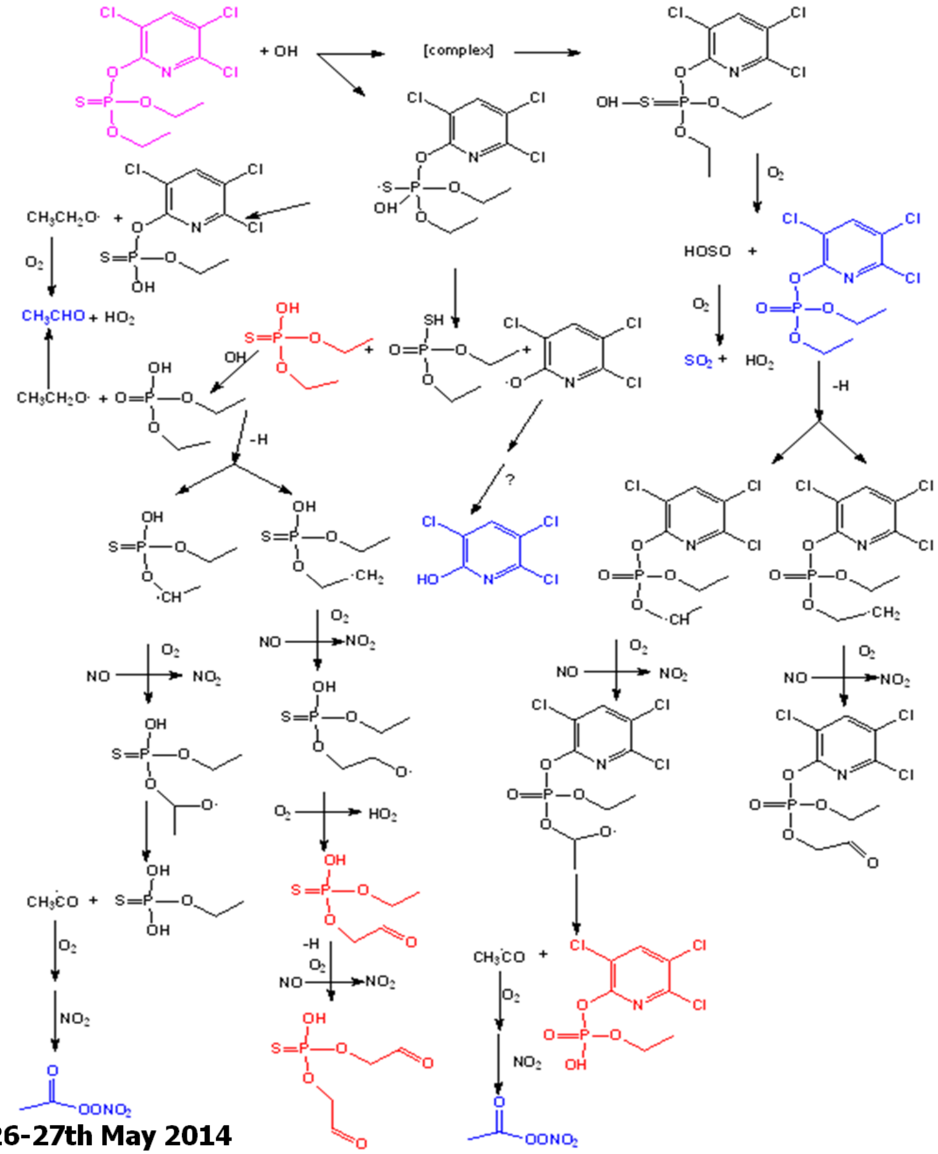
Product		% molar yield	Notes
CHLO		~10%	Corrected by the secondary losses with OH Where k_{OH}(CHLO)= 1.5 x 10^{-11} (this work) and $[OH]_{average}$=1.31 x 10^{7} (calculated from the losses of CHL considering k_{OH}(CHL)=9.10 x 10^{-11}). kdes was not taking into account
SO_2	SO_2	17 ± 5%	
PYRIDINOL		8 ± 4%	Corrected by the secondary losses with OH Where k_{OH}(PYRIDINOL)= 1.8 x 10^{-13} (EPIWEB) and $[OH]_{average}$=1.31 x 10^{7} (calculated from the losses of CHL considering k_{OH}(CHL)=9.10 x 10^{-11})
Peroxyacetylnitrate	$CH_3C(O)OONO_2$	< 10%	Secondary product. Yield depending on the NO_{2}/NO concentration ratio and not expected to be constant throughout the reaction. Corrected by the thermal losses of PAN at 303k, k = 3.3 x 10^{-4} s^{-1}
Formaldehyde	HCHO	< 17%	This is the maximum yield as HCHO can also be formed by the auxiliary mechanism of the chamber
$(C_2H_5O)_2P(S)OH$		Observed	
Other compound/s containing the P=O group		Observed	

Photo-oxidation

Reaction Products

Pathway A: Addition of OH to the PS bond.

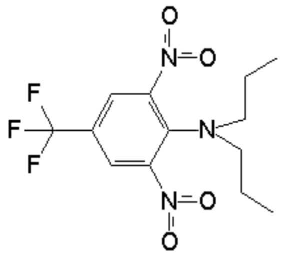
Structures in blue: identified and quantified compounds,
Structures in red: tentatively identified compounds by GCMS with derivatization



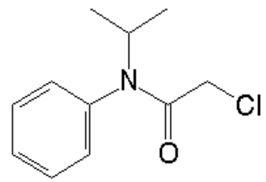
COMPOUND	J [s^{-1}]	k_{OH} [cm^3 $molec^{-1}$ s^{-1}]	Lifetime /Main degradation pathway	Main degradation products
Chlorpyrifos (1)	1.4 × 10^{-5}	(9.1 ± 1.8)×10^{-11}	2 hours / Reaction with OH	SO_2, 3,5,6-tricloro-2-pyridinol, SOA, chlorpyrifos oxon, dimethylphospahte, CH_3CHO, PAN (in the presence of NOx)
Chlorpyrifos oxon (1)	< 4.8 × 10^{-5}	(1.6 ± 0.8)×10^{-11}	11 hours / Reaction with OH	SOA, PAN (in the presence of NOx)
Chlorpyrifos-methyl (2)	< 2×10^{-5}	(4.1 ± 0.4)×10^{-11}	3.5 hours / Reaction with OH	SO_2, 3,5,6-tricloro-2-pyridinol, SOA, chlorpyrifos-methyl oxon
Diazinon (3, 4)	< 1×10^{-5}	(9.6 ± 1.8)×10^{-11}	1.8 hours / Reaction with OH	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 (4)	< 4.8 × 10^{-5}	(3.0 ± 1.1)×10^{-11}	5.9 hours / Reaction with OH	Hydroxydiazoxon, PAN (in the presence of NOx), SOA
Dichlorvos (5)	negligible	(2.6±0.3)× 10^{-11}	5 hours / Reaction with OH	Phosgene, CO

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

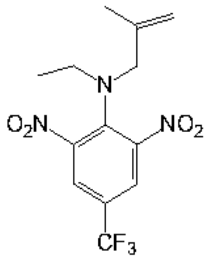
ATMOSPHERIC DEGRADATION OF CHLOROACETANILIDE AND DINITROANILINE HERBICIDES



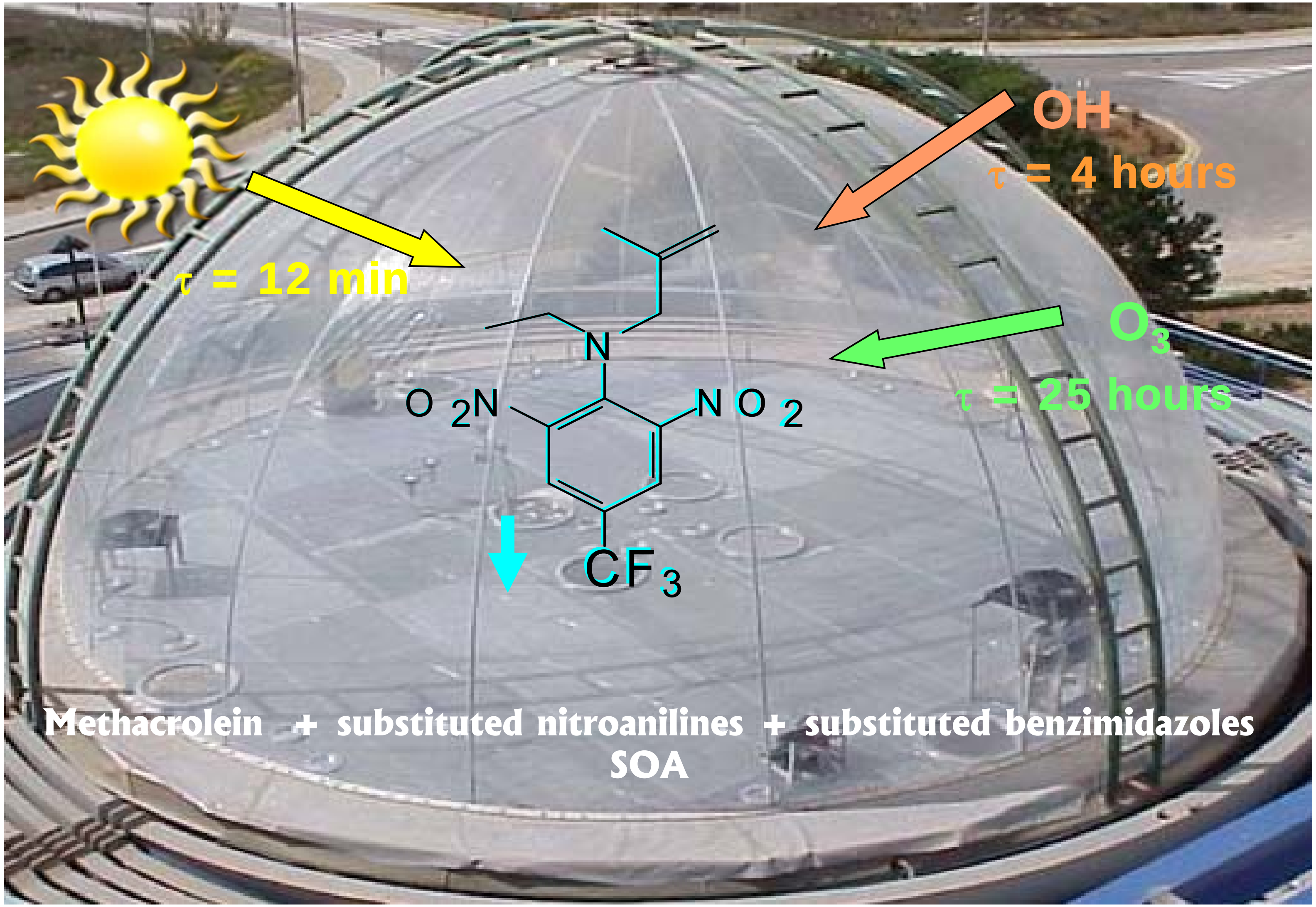
Trifluralin



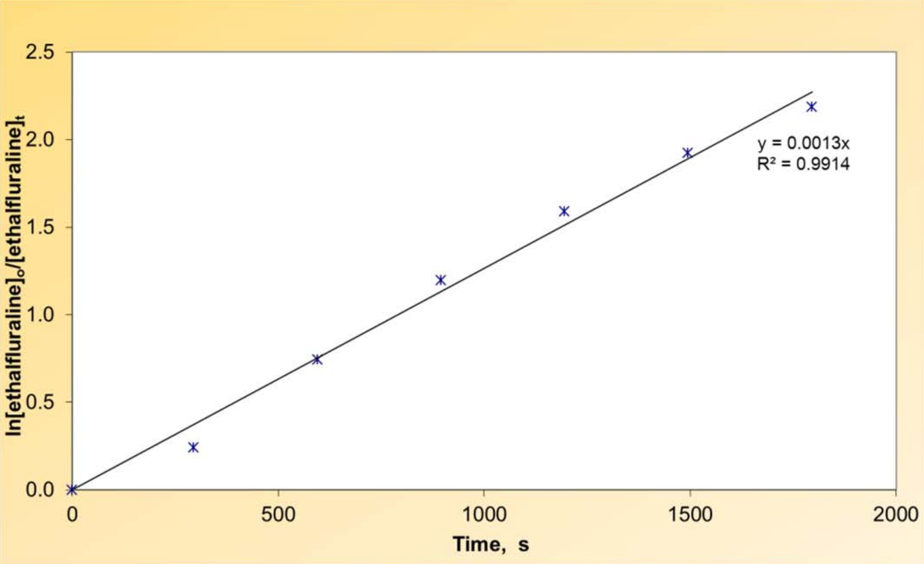
Propachlor

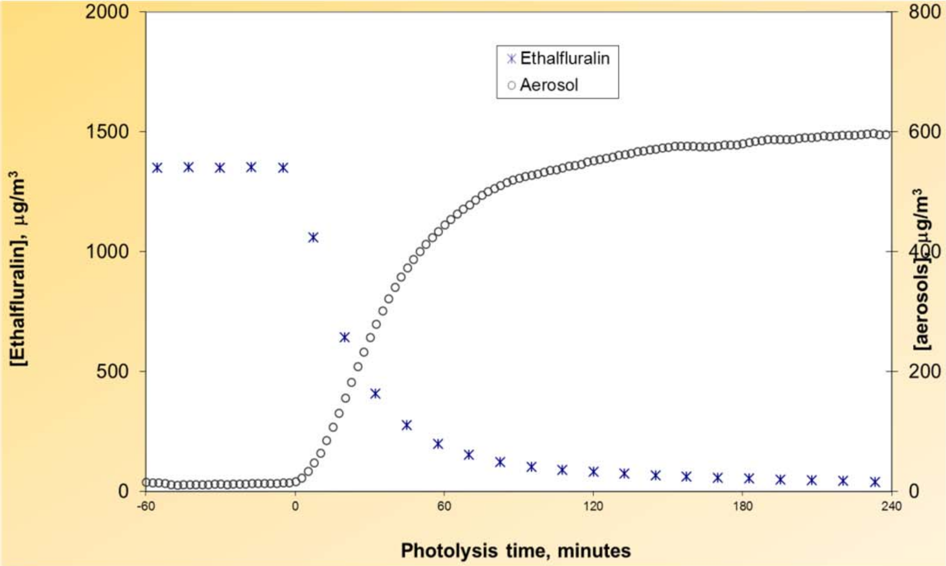


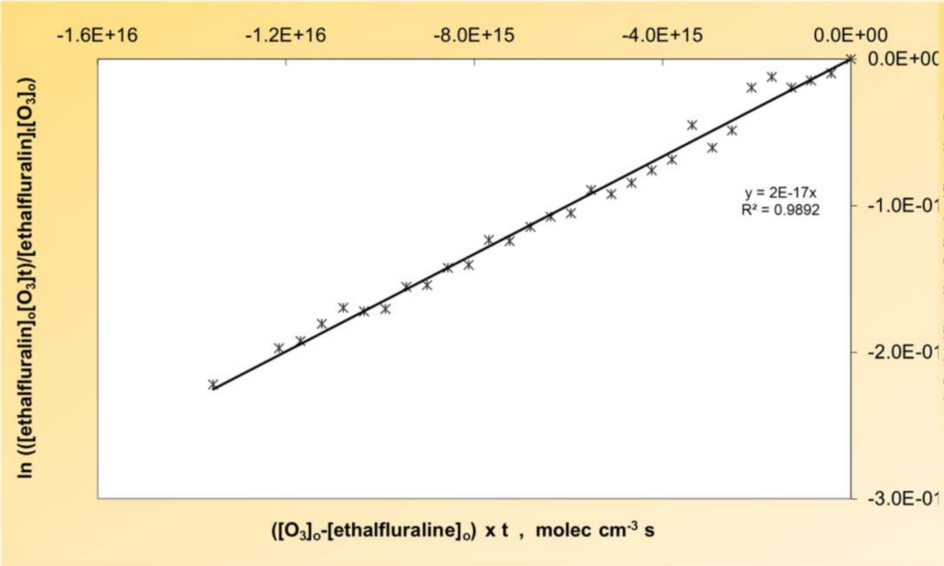
Ethalfluralin

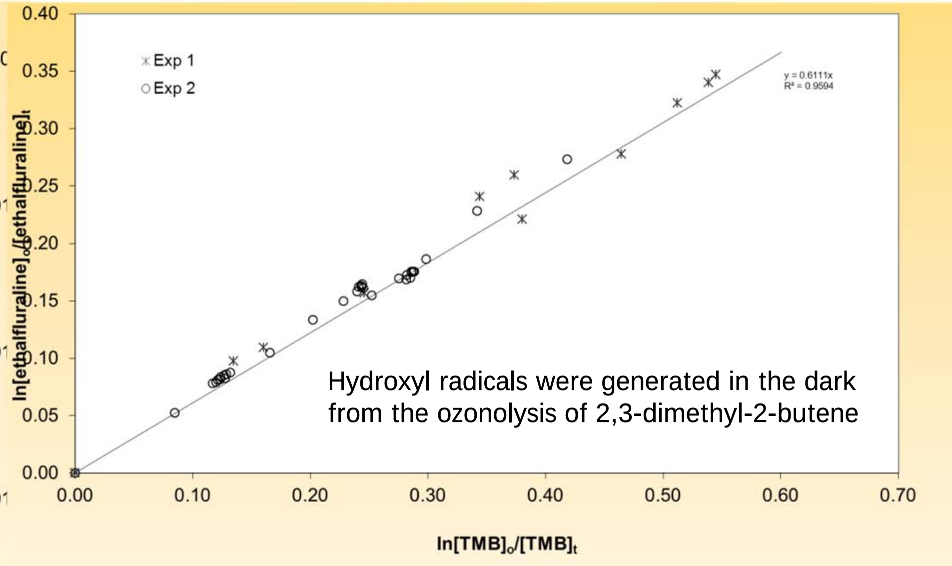

OH
τ = 4 hours
τ = 12 min
O3
τ = 25 hours
N
O2N
NO2
CF3
Methacrolein + substituted nitroanilines + substituted benzimidazoles
SOA

ATMOSPHERIC FATE OF ETHALFLURALIN





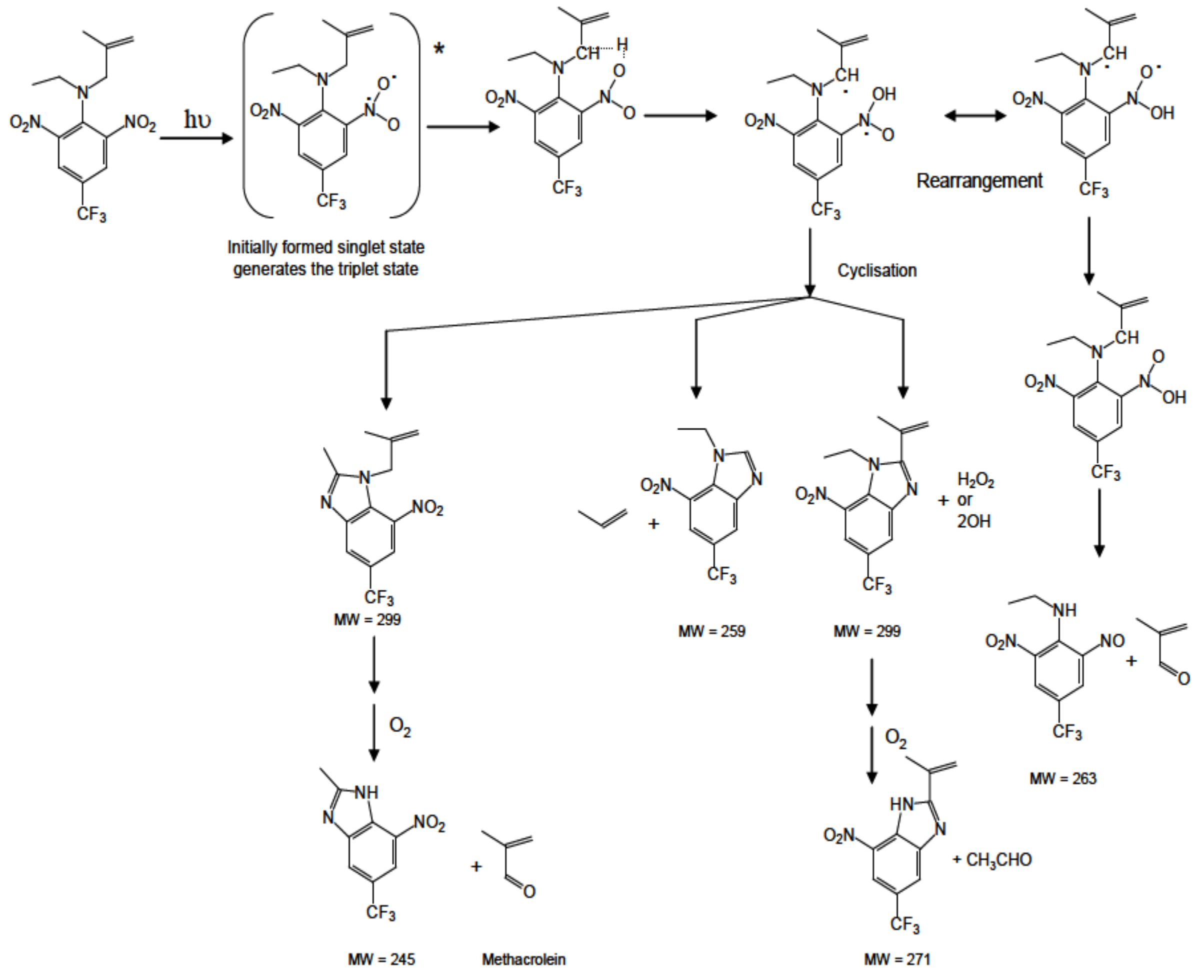




Compound	Main Fragments	MW	Losses	Phase
Unk1	69,85,112,140,141	?		gas
Unk2	101,111,129,184,186	?		gas
Unk3	120,143,176,199, 211, 227,257 (281/288)?	257	$211=[M-46]^+$	gas/particle
Unk4	131,135,184,185, 231,259	259	$185=[M-74]^+$	gas
Unk5	69, 131, 152, 187, 199, 245	245	$199=[M-46]^+$	gas
Unk6	271	271		gas/particle
Unk7	225	?		gas
Unk8	299	299		gas/particle
Unk9	299	299		particle

Nitroaniline and benzimidazol type compounds

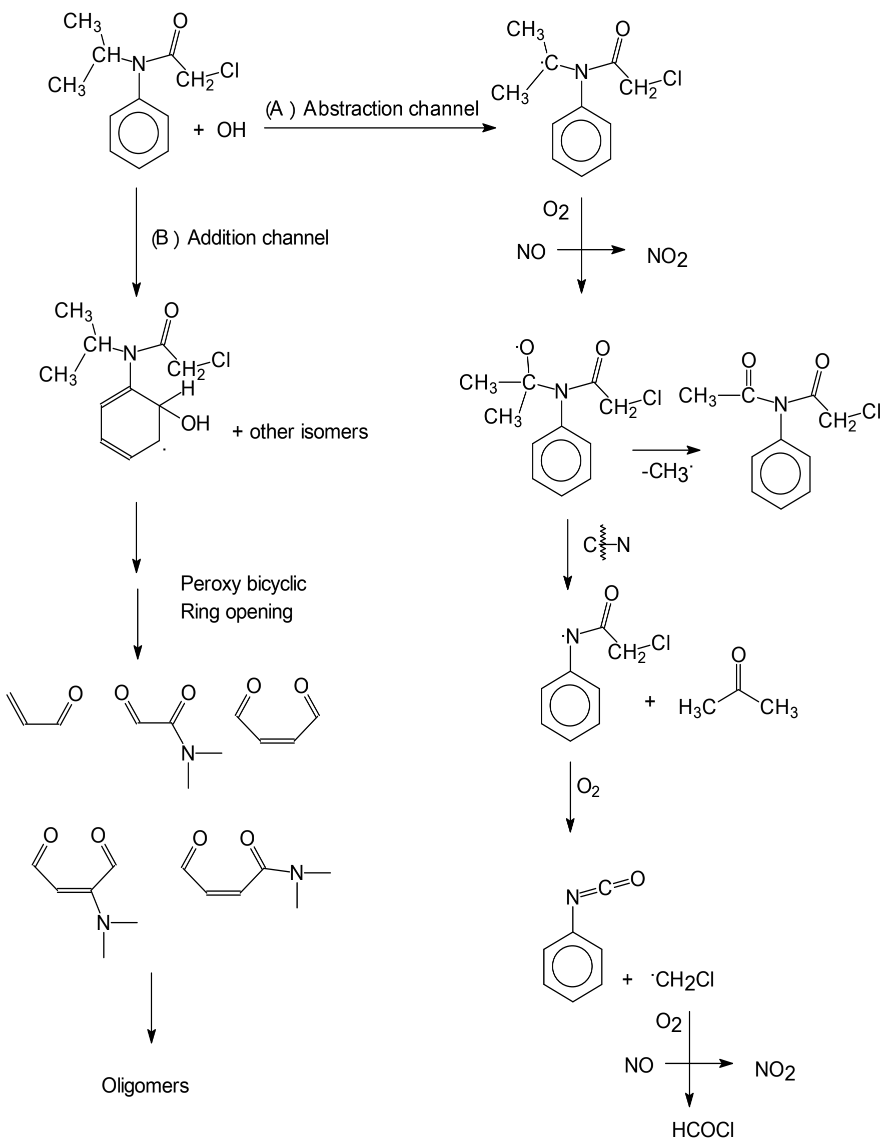
ATMOSPHERIC FATE OF ETHALFLURALIN

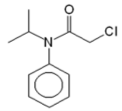
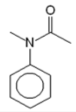
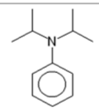


Photolysis of ethalfluralin by solar radiation can result in either **intramolecular hydrogen abstraction** by an electronically excited ortho-NO_2 group from the –NCH_2CH_3 and –$NCH_2C(CH_3)=CH_2$ groups or intramolecular addition of the oxygen atoms of electronically excited NO_2 to the double bond in the side chain. Intramolecular H-atom abstraction in ethalfluralin is likely to be from the allylic –CH_2- group in –$NCH_2C(CH_3)=CH_2$, or from –CH_2- in the –NCH_2CH_3 substituent.

Nitroaniline and benzimidazol type compounds

ATMOSPHERIC FATE OF PROPACHLOR



		k_{OH} $cm^3\ molec^{-1}\ s^{-1}$	Reference compounds
Propachlor		1.3×10^{-11}	1,3,5-TMB, *n*-octane, toluene
N- methylacetamide		2.7×10^{-11}	*n*-octane, isoprene
N, N-diisopropilaniline		4.4×10^{-11}	*n*-octane, isoprene

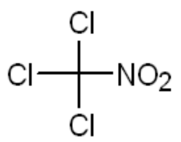
- A relatively large number of reaction products were observed.
- The infrared and mass spectra of the main products suggest that the primary reaction products were unsaturated dicarbonyl compounds, which rapidly polymerized to form carbonyl group-containing oligomers with molecular weights in the region of approximately 280-500.
- It was not possible to unambiguously identify the products, although the absence of products arising from the abstraction channel suggests that **the major reaction pathway for the reaction of OH radicals with propachlor is probably addition to the aromatic ring**.
- The major fate of the adduct radical formed by addition to the ring is likely to be ring opening to produce a number of unsaturated dicarbonyl compounds as reported for the reaction of OH radicals with other substituted aromatic compounds.

COMPOUND	J $[s^{-1}]$	k_{OH} $[cm^3\ molec^{-1}\ s^{-1}]$	k_{O3} $[cm^3\ molec^{-1}\ s^{-1}]$	Lifetime /Main degradation pathway	Main degradation products
Ethalfluralin [6]	$(1.3\pm0.2)\times10^{-3}$	$(9.6\pm1.8)\times10^{-11}$	$(1.6\pm0.4)\times10^{-17}$	12 minutes / Photolysis	Methacrolein, Acetaldehyde, SOA, nitroaniline and benzimidazol type compounds
Propachlor [7]	$<(2\pm0.5)\times10^{-5}$	$(1.5\pm0.3)\times10^{-11}$	$<1.5\pm0.4)\times10^{-19}$	20 hours / Reaction with OH	carbonyl group-containing oligomers with molecular weights in the region of 280-500 (SOA)
Trifluralin [8]	$(1.2\pm0.5)\times10^{-3}$	$(1.7\pm0.4)\times 10^{-11}$	-	15 minutes / Photolysis	2-ethyl-4-nitro-6-(trifluoromethyl)-1H-benzimidazole, Propanal, acetaldehyde, formaldehyde, SOA

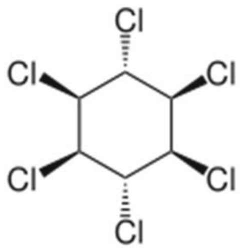
(6) Muñoz et al., 2014b, chemosphere.
(7) Muñoz et al., 2012, Atmospheric Environment
(8) Le Person et al., 2007, Chemosphere.

ATMOSPHERIC DEGRADATION OF

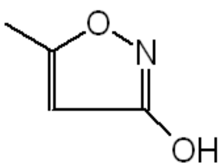
FUNGICIDES AND CHLORINATED INSECTICIDES



Chloropicrin



Lindane



Hymexazol

Comparison with other studies:

- ($t_{1/2}$) ~ **20 days** (Moylanen et al, 1978)
- ($t_{1/2}$) ~ **18 hours** J = $(6.3\pm0.2)\times10^{-4}$ min^{-1} (Carter 1997, experimental)

} Artificial light

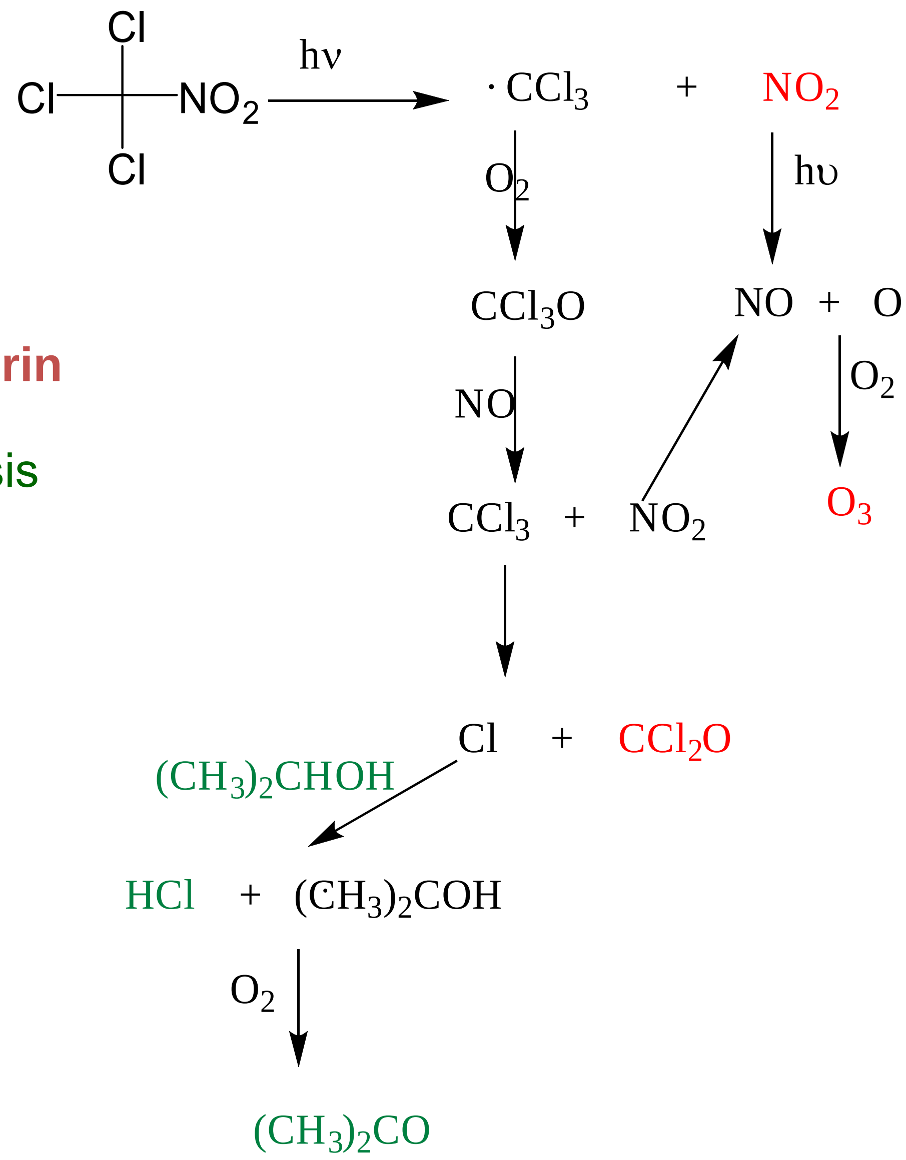
- ($t_{1/2}$) from **3.4 h to 7.6 hours** (Carter 1997, teoric, using actinic fluxes calculated by Peterson, 1976)
- ($t_{1/2}$) ~ **5.4 hours** (our work).

K_{O3} ~ $(4.8\pm2.3)\times10^{-19}$ cm^3 $molec^{-1}$ s^{-1}

K_{OH} Calculation not possible

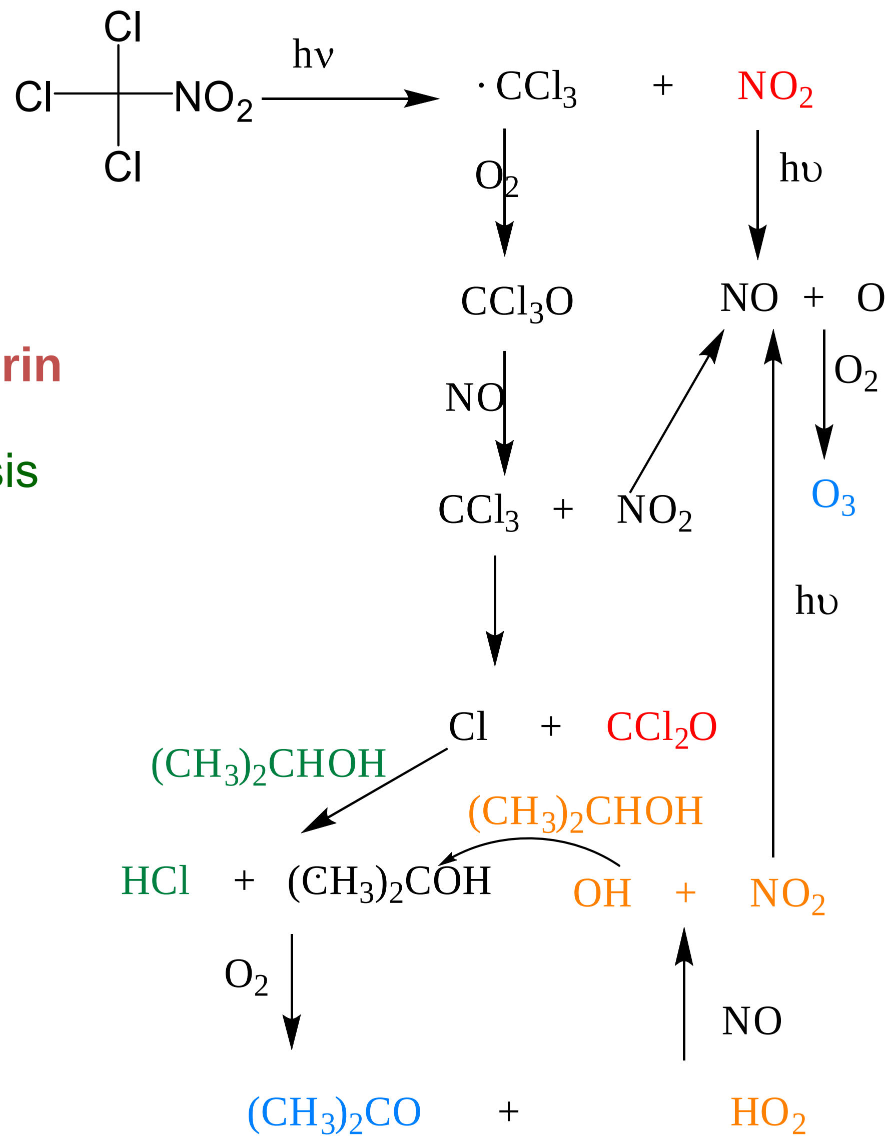
Examples: Chloropicrin

Photolysis



Examples: Chloropicrin

Photolysis



ATMOSPHERIC DEGRADATION OF FUNGICIDES AND CHLORINATED INSECTICIDES

COMPOUND	J [s^{-1}]	k_{OH} [cm^3 $molec^{-1}$ s^{-1}]	k_{O3} [cm^3 $molec^{-1}$ s^{-1}]	Lifetime /Main degradation pathway	Main degradation products
Lindane (7)	<3.5 × 10-5	6.4× 10-13	-	20 days / Reaction with OH	Hexhaclorocyclopentanone, HCl
Chloropicrin (8)	3.6 x 10-5	-	4.8 x 10-18	5.6 hours / Photolysis	Phosgene, NO_2, O_3
Hymexazol (9, 10)	< 1.4 x 10-5	4.9 x 10-12	3.2 x 10-19	20 hours / Reaction with OH	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

(7) Vera et al., In preparation.
(8) Vera et al., 2010,
(9) Vera et al 2011 Atmospheric Environment
(10) Tortajada-Genaro et al. 2013. Chemosphere

Conclusions

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

- Products information useful for proposing mechanisms of reaction
- Results useful to introduce in the models
- Rate coefficients important to assess the impact of the pesticides on air quality and on human health with the product information

Acknowledgements

- Spanish Ministry of Economy and Innovation
  - GRACCIE (Consolider-Ingenio 2010)
  - IMPESTAT (CGL2010-18474/CLI)
  - ECOPEST (CGL2007-65223/CLI)
  - INNPLANTA project: PCT-440000-2010-003
- European Community's 7th FP. GA 228335 (Eurochamp2)
- Generalitat Valenciana
- FEEDBACKS (Prometeo - Generalitat Valenciana)
- Dow AgroSciences
- Makhteshim Chemical Works Ltd
- LSR Associates
- Huntingdon Life Sciences
- Abdelwahid Mellouki from CNRS-ICARE
- Howard Sidebottom from University College Dublin

Thanks your for your attention