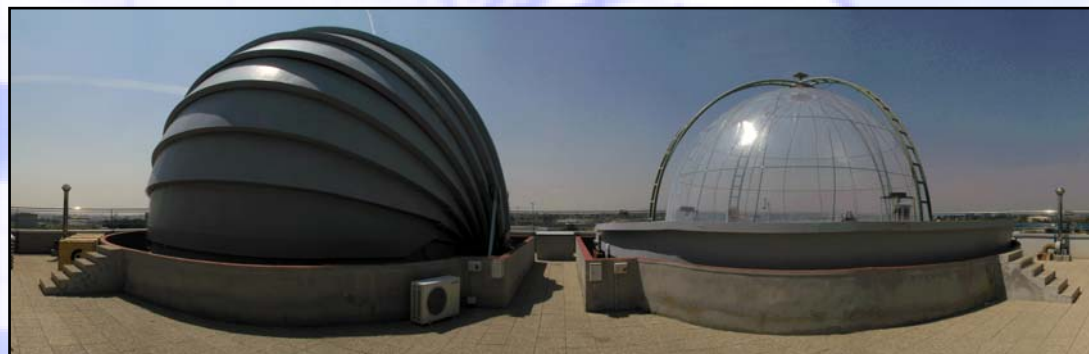


ATMOSPHERIC FATE OF PESTICIDES: STUDIES OF THE ATMOSPHERIC DEGRADATION OF PESTICIDES AT EUPHORE CHAMBERS

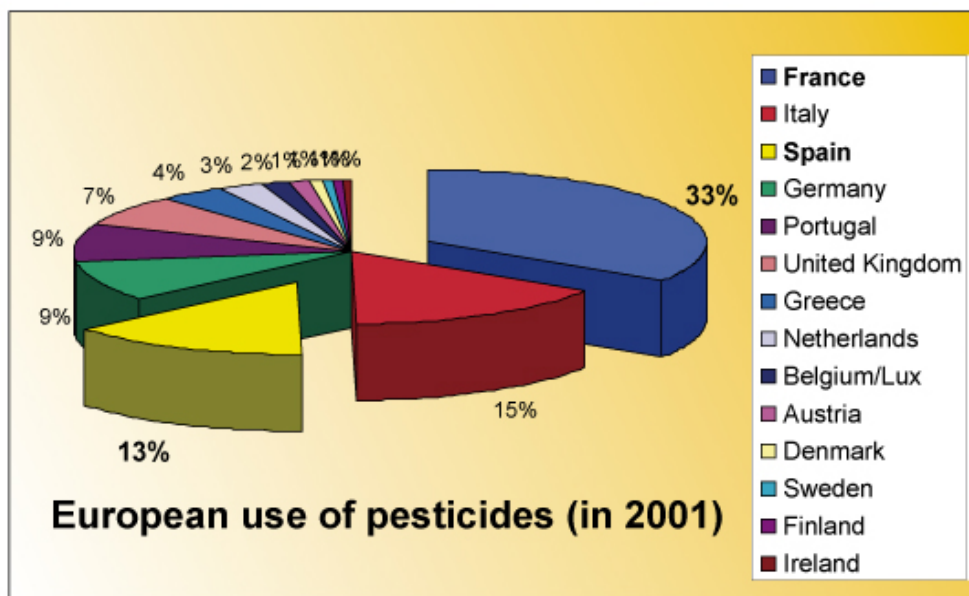
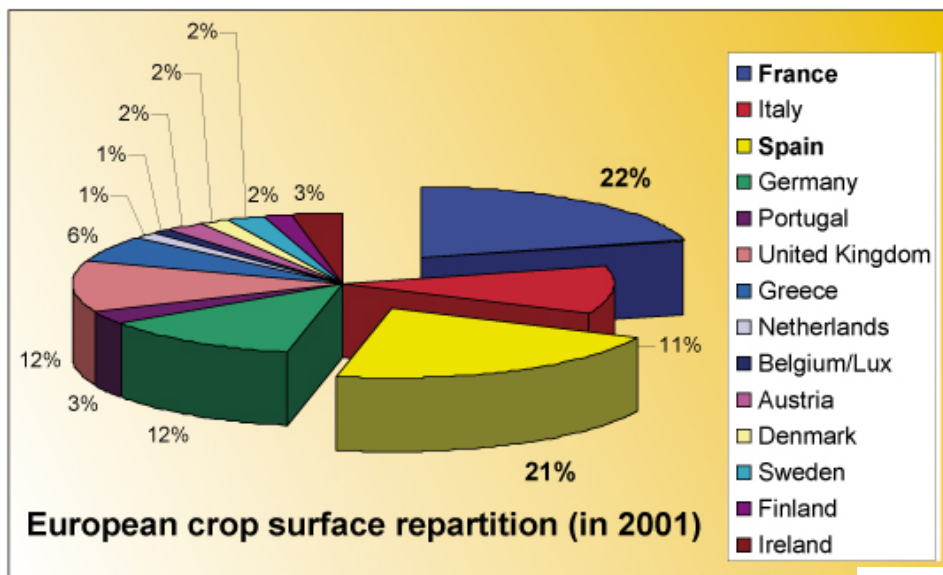


Amalia Muñoz, Teresa Vera, A. Mellouki, Esther Borrás, Milagros Rodenas, Mónica Vázquez, and María Marqués.

Fundación CEAM, EUPHORE Laboratories, 46980 Paterna, Valencia, Spain
e-mail: amalia@ceam.es

ATMOSPHERIC FATE OF PESTICIDES: STUDIES OF THE ATMOSPHERIC DEGRADATION OF PESTICIDES AT EUPHORE CHAMBERS

Use of Pesticides in Europe



Source: <http://www.era-orleans.org/AFIP/portail.html> AFIP project

ATMOSPHERIC FATE OF PESTICIDES: STUDIES OF THE ATMOSPHERIC DEGRADATION OF PESTICIDES AT EUPHORE CHAMBERS

Pesticides used for:

➤ Agriculture



➤ Gardening operations



➤ House use

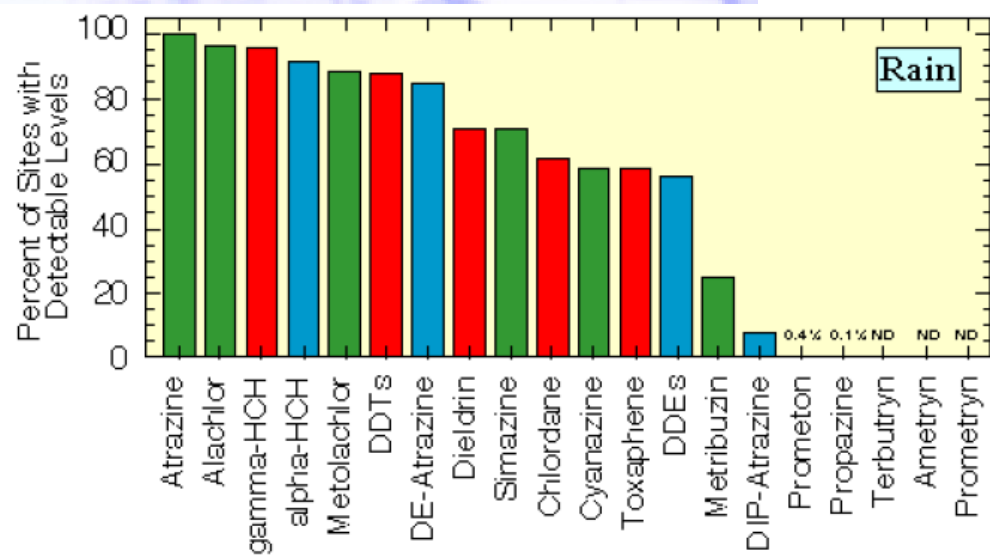
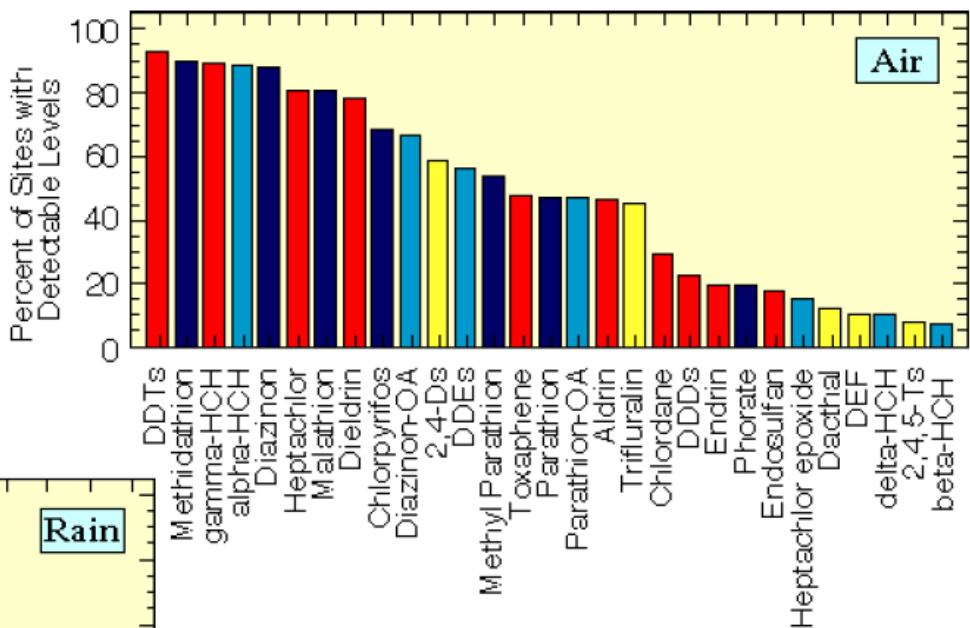
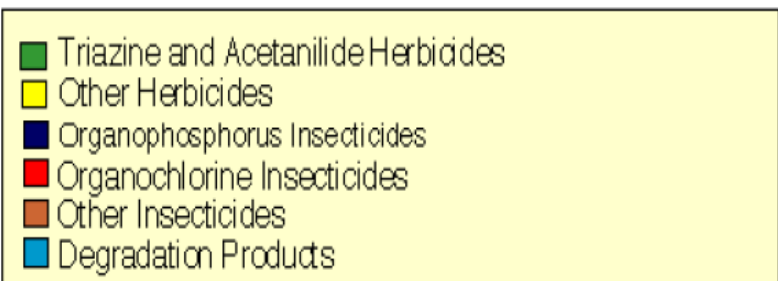


They can be emitted into the atmosphere by Direct and Indirect Emissions

- through dispersion during spraying operations,
- volatilization from ground or leaf surfaces
- wind erosion

ATMOSPHERIC FATE OF PESTICIDES: STUDIES OF THE ATMOSPHERIC DEGRADATION OF PESTICIDES AT EUPHORE CHAMBERS

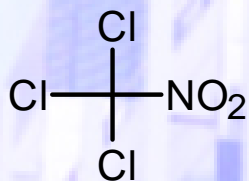
Some pesticides found in the atmosphere



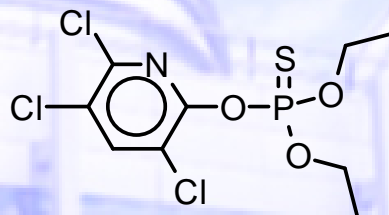
Source: Lig d'air and CNRS-ICARE.
 PACT project.
 France

ATMOSPHERIC FATE OF PESTICIDES: STUDIES OF THE ATMOSPHERIC DEGRADATION OF PESTICIDES AT EUPHORE CHAMBERS

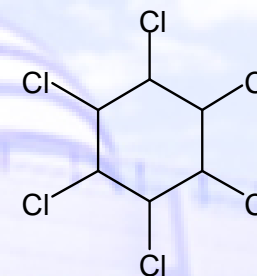
Examples of pesticides



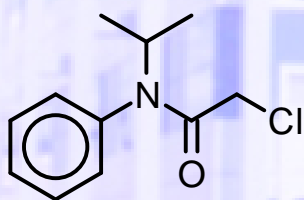
Chloropicrin



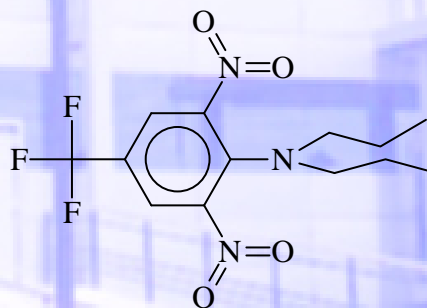
Chlorpiriphos



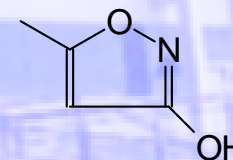
Lindane



Propachlor



Trifluralin



Hymexazol

They also can be simple: CH_3Br

ATMOSPHERIC FATE OF PESTICIDES: STUDIES OF THE ATMOSPHERIC DEGRADATION OF PESTICIDES AT EUPHORE CHAMBERS

Some references about studies of pesticides:

In soils

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. Toxicol. Chem., 14, 1287-1298
 And **MUCH MORE**....

In air

Lammel et al, 2007. Atmos. Environ., 41, 452-464.
 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...

On aerosols

Krüger et al, 2001. Fraunhofer-Institut für toxikologie and Aerosolforschung, Hannover, Ufoplan- Nr 200 67 406/73
 Palm et al, 1997. Environ. Sci. Technol., 31, 3389-3396
 Palm et al, 1998. Ecotoxicol. Environ. Safety, 41, 36-43
 And **FEW** more...

ATMOSPHERIC FATE OF PESTICIDES: STUDIES OF THE ATMOSPHERIC DEGRADATION OF PESTICIDES AT EUPHORE CHAMBERS

Limiting factor for the atmospheric study of pesticides



Vapour pressure of the pesticide

Considering the EUPHORE characteristics



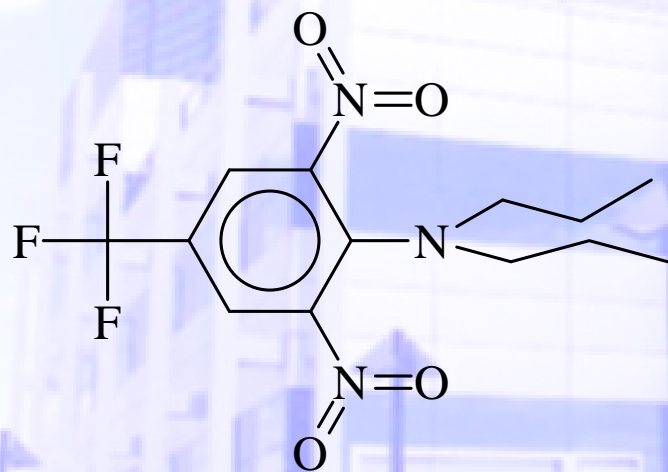
Pesticides with P_v higher than 5 mPa, to assure the presence of the compound in the gas phase

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

ATMOSPHERIC FATE OF PESTICIDES: STUDIES OF THE ATMOSPHERIC DEGRADATION OF PESTICIDES AT EUPHORE CHAMBERS

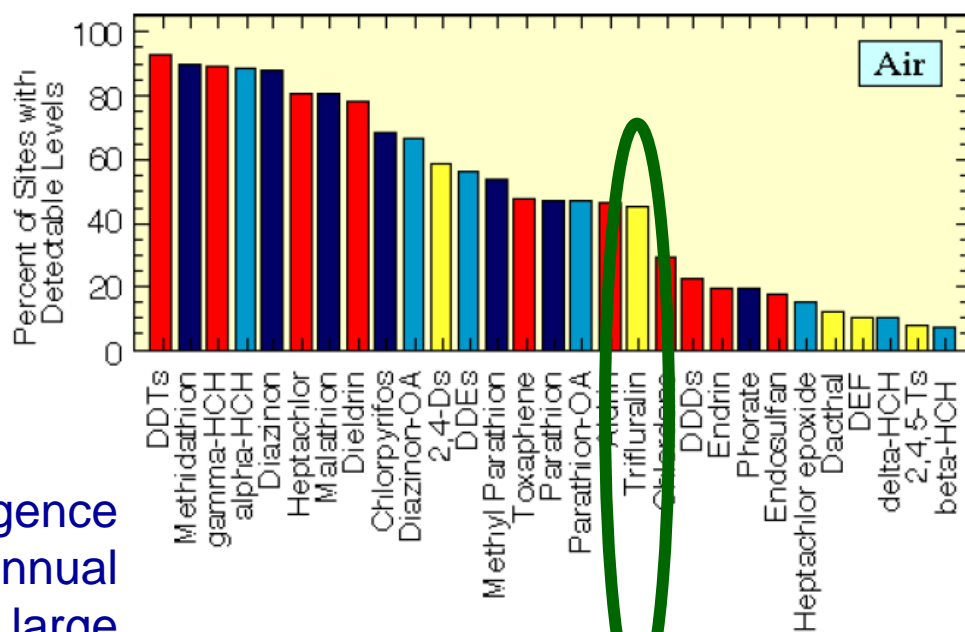
Examples: Trifluralin

Le Person, A., Mellouki, A., Muñoz, A., Borrás, E., Martín-Reviejo, M. Wirtz, W.
Chemosphere, 2007, 67, 376-383



a selective, pre-sowing or pre-emergence herbicide used to control many annual grasses and broadleaf weeds in a large variety of arable and horticultural crops

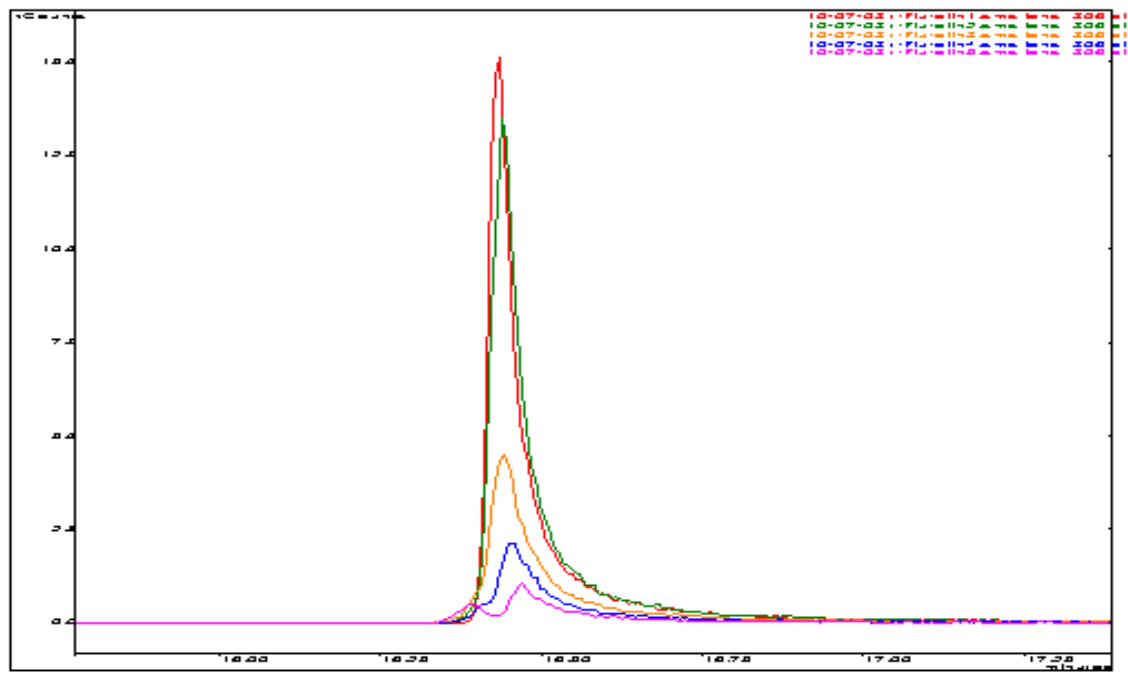
widely used herbicide ⇒ suspected carcinogen



Detected in air

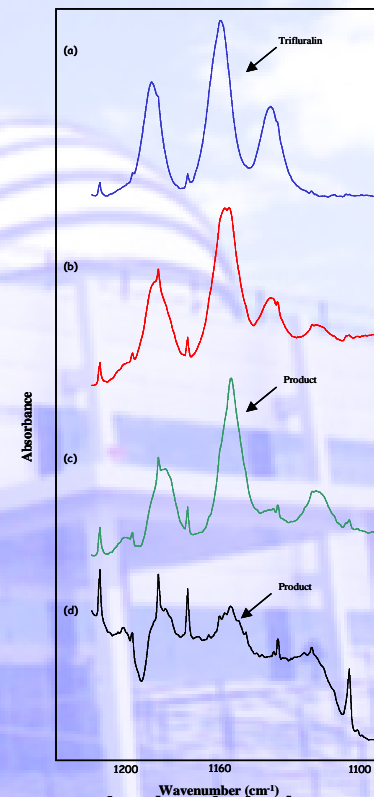
ATMOSPHERIC FATE OF PESTICIDES: STUDIES OF THE ATMOSPHERIC DEGRADATION OF PESTICIDES AT EUPHORE CHAMBERS

Photolysis experiments **Examples: Trifluralin**



GC-MS chromatograms obtained during a photolysis experiment of the trifluralin. Ion 306 .

- a) Chromatogram corresponding to the trifluralin;
- b) Chromatogram corresponding to the trifluralin
- c) Chromatogram after 27 min of irradiation;
- d) Chromatogram after 1h13 min of irradiation;
- e) Chromatogram after 1h58 of irradiation.

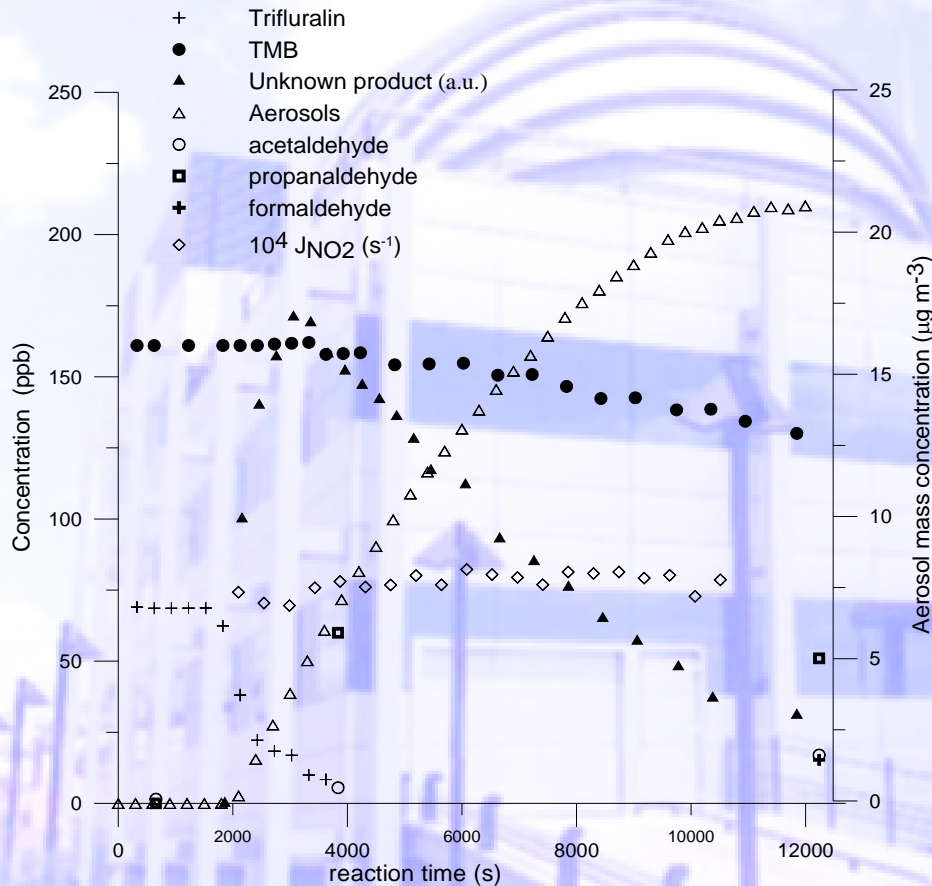


IR spectra obtained during a photolysis experiment of the trifluralin

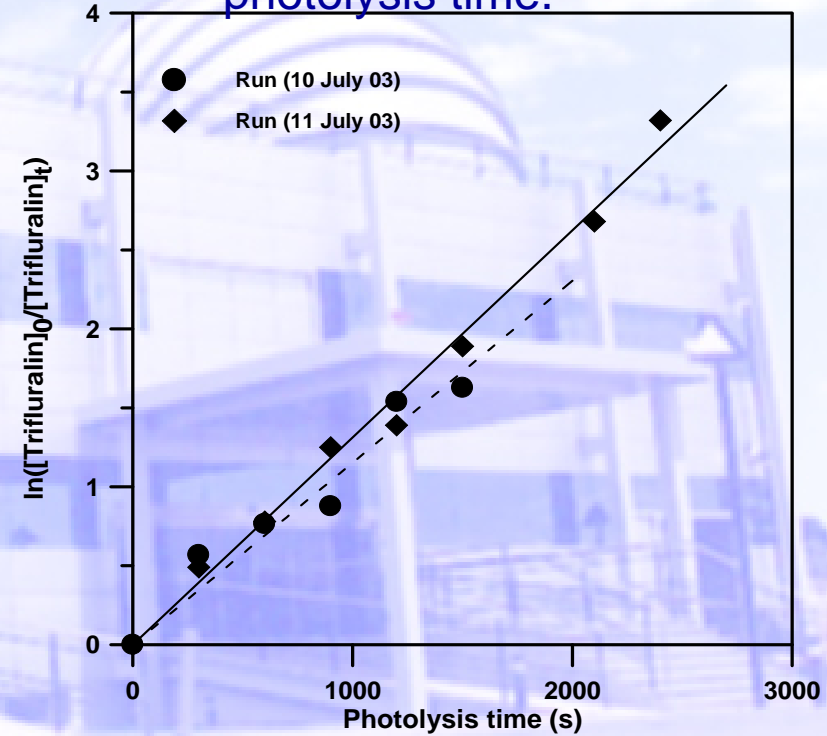
- a) IR spectrum corresponding to the trifluralin;
- b) IR spectrum of the mixture after 5 min of irradiation;
- c) IR spectrum after 20 min of irradiation;
- d) IR spectrum after 1h40 of irradiation.

ATMOSPHERIC FATE OF PESTICIDES: STUDIES OF THE ATMOSPHERIC DEGRADATION OF PESTICIDES AT EUPHORE CHAMBERS

Examples: Trifluralin



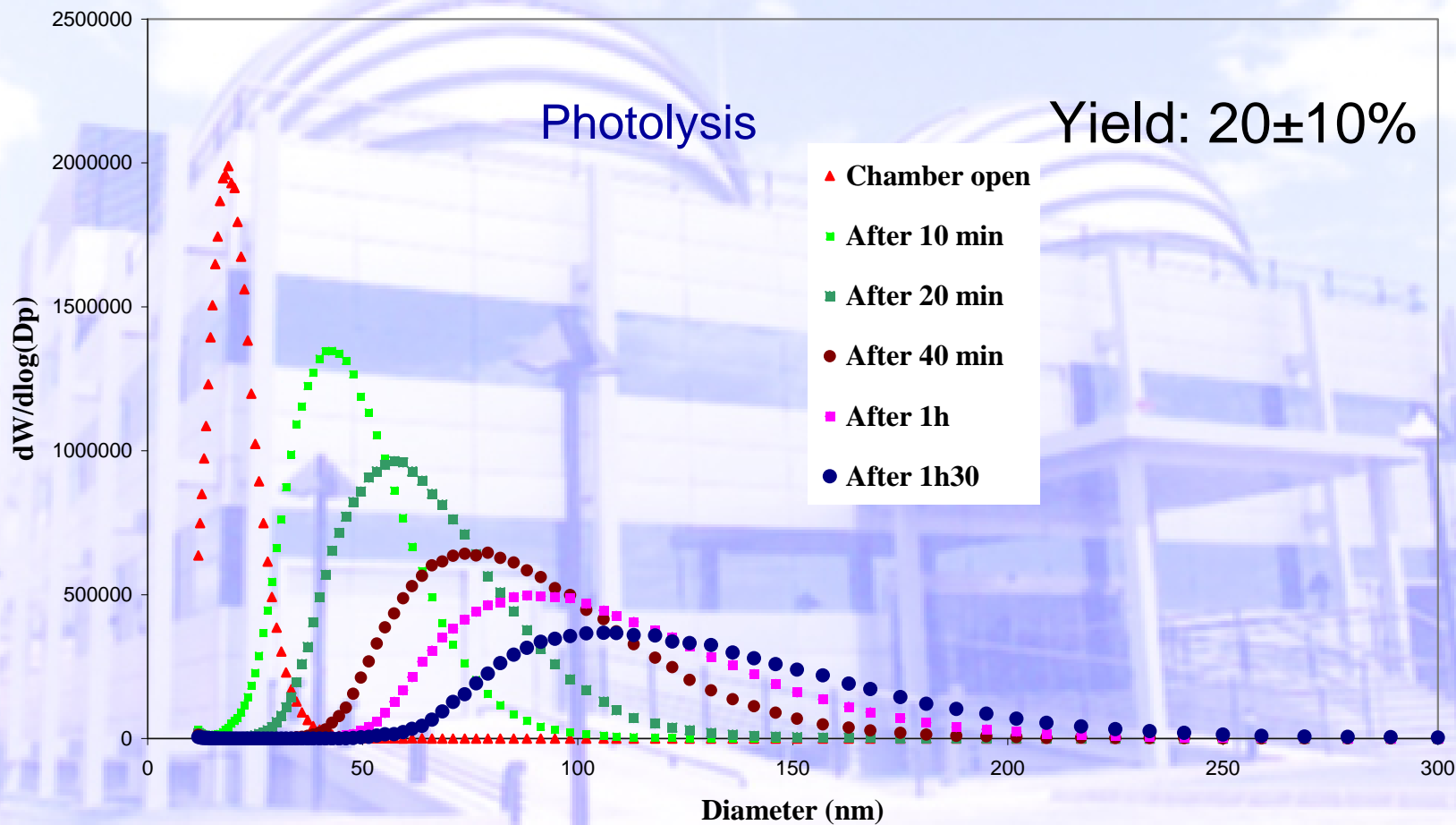
Plots of $\ln([Trifluralin]_0/[Trifluralin]_t)$ vs photolysis time.



$$J_{trifluralin} = 1.2 \times 10^{-3} \text{ s}^{-1}$$

Time-Concentrations profiles of trifluralin, 1,3,5-Trimethylbenzene (TMB), aldehydes and aerosols

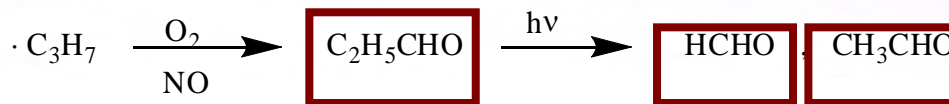
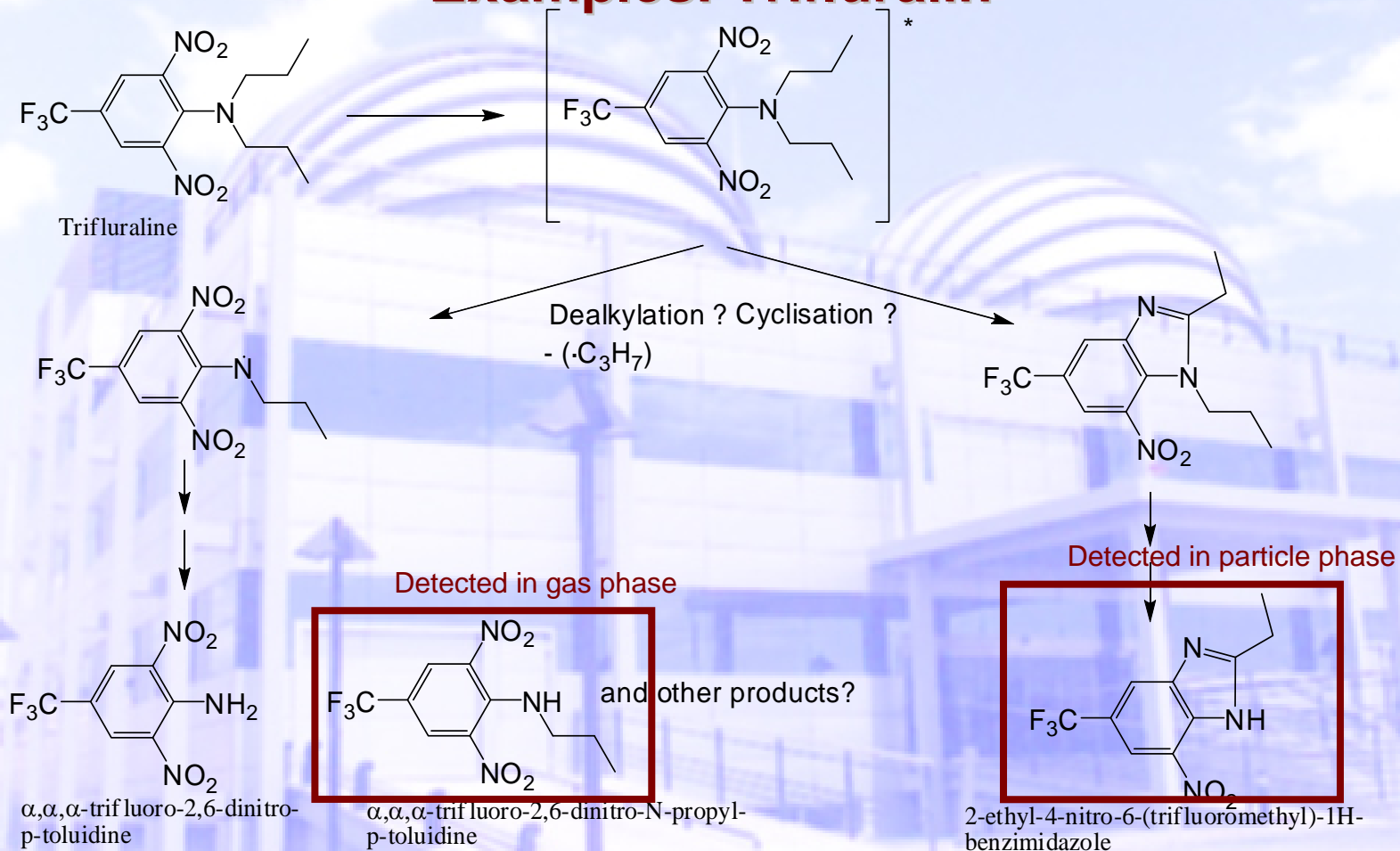
Examples: Trifluralin



Aerosol distribution

ATMOSPHERIC FATE OF PESTICIDES: STUDIES OF THE ATMOSPHERIC DEGRADATION OF PESTICIDES AT EUPHORE CHAMBERS

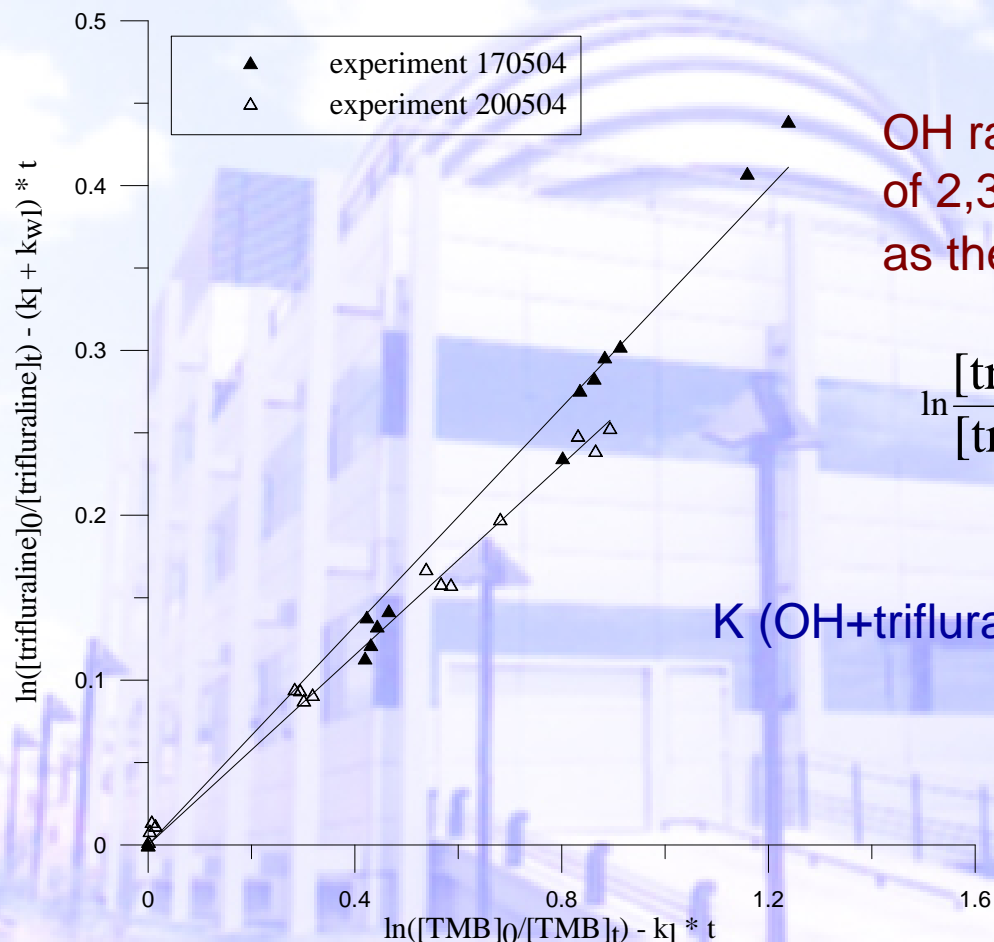
Examples: Trifluralin



Examples: Trifluralin

Reaction with OH radicals

OH radicals generated in the dark: ozonolysis of 2,3-dimethyl-2-butene ((CH₃)₂C=C(CH₃)₂) as the OH radicals source.



$$\ln \frac{[\text{trifluralin}]_0}{[\text{trifluralin}]_t} - (k_l + k_{wl}) * t = \frac{k}{k_{\text{TMB}}} \ln \frac{[\text{TMB}]_0}{[\text{TMB}]_t} - k_l * t$$

$$K (\text{OH} + \text{trifluralin}) = (1.7 \pm 0.4) \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$$

Plots of $\ln([\text{trifluralin}]_0/[\text{trifluralin}]_t) - (k_l + k_{wl}) \times t$ vs $\ln([\text{TMB}]_0/[\text{TMB}]_t) - k_l \times t$ during kinetic experiments of trifluralin with OH.

Examples: Trifluralin

$$K(\text{OH} + \text{trifluralin}) = (1.7 \pm 0.4) \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$$

$$[\text{OH}]_{\text{average}} = 2 \times 10^6 \text{ molec cm}^{-3}$$

$$t_{\text{OH}} \sim 8.5 \text{ h}$$

$$K(\text{O}_3) \text{ upper limit} < 1 \times 10^{-17} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$$

$$[\text{O}_3]_{\text{average}} = 7 \times 10^{11} \text{ molec cm}^{-3}$$

$$t_{\text{O}_3} > 40 \text{ h}$$

$$J_{\text{trifluralin}} = 1.2 \times 10^{-3} \text{ s}^{-1}$$

$$t_{\text{photolysis}} \sim 15 \text{ min.}$$

Atmospheric implications

Tropospheric degradation of trifluralin is controlled by photolysis with a non negligible contribution of OH reaction



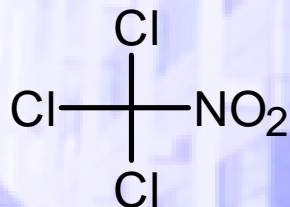
These degradation processes generate organic aerosols

Examples: Chloropicrin

Partially presented in GK-Orleans 2006

Vera, T., Muñoz, A., Rodenas, M., Vazquez, M., Ismael, I., Sidebottom, H., Mellouki, A.

Application: injection into soil as pure liquid or applied in combination with other compounds (methyl bromide)



$P_v = 2400 \text{ Pa (20}^\circ\text{C)}$; solubility in water 2.27 gL^{-1}
 (Worthington et al., 2007, Atmos Environ, 41, 5510)



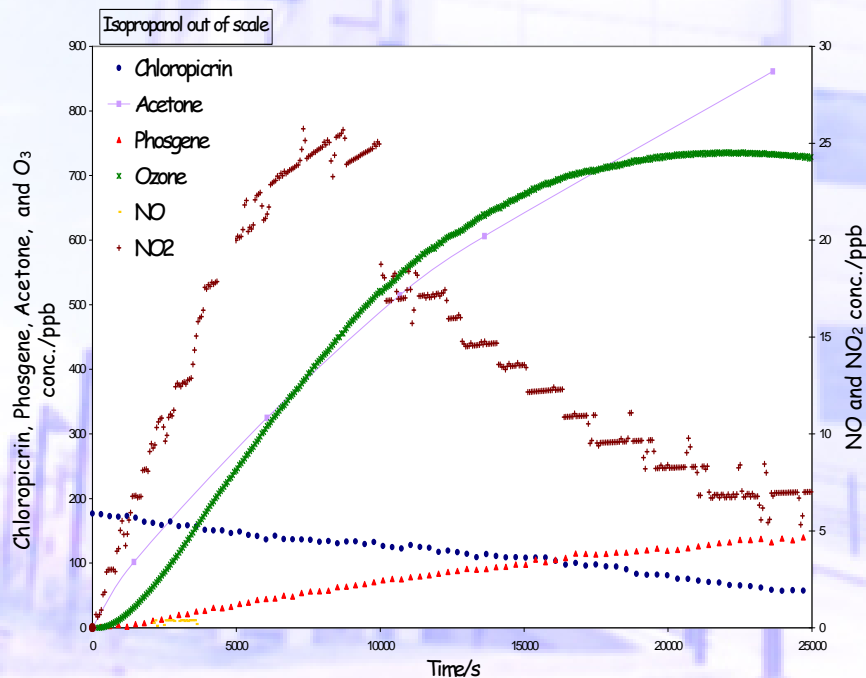
It can be found in soil, water and the atmosphere

ATMOSPHERIC FATE OF PESTICIDES: STUDIES OF THE ATMOSPHERIC DEGRADATION OF PESTICIDES AT EUFORE CHAMBERS

Examples: Chloropicrin

Photolysis

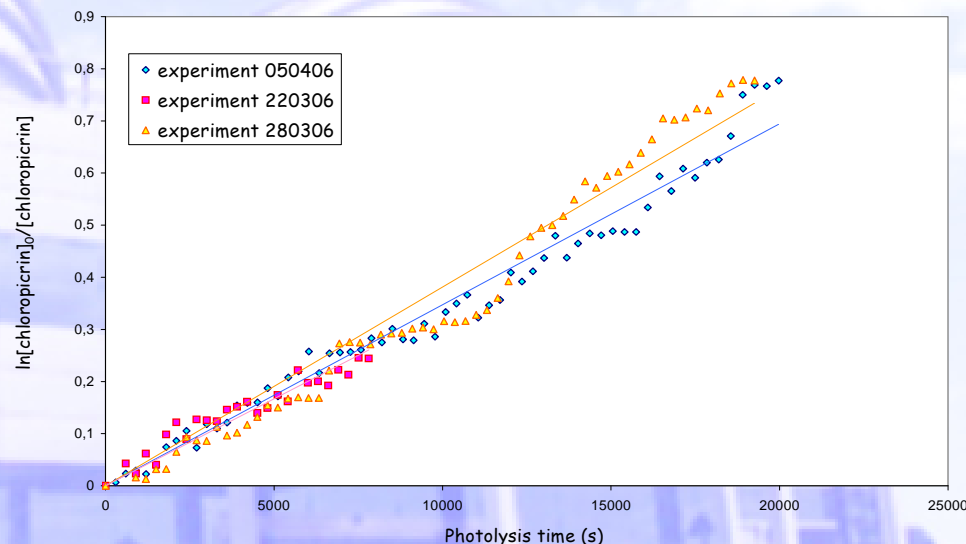
$[\text{Chloropicrin}]_0 = 177 \text{ ppb}$
 $[\text{Isopropanol}]_0 = 15000 \text{ ppb}$



$J_{\text{Photolysis with scavenger}} = (3.6 \pm 0.7) \times 10^{-5} \text{ s}^{-1}$



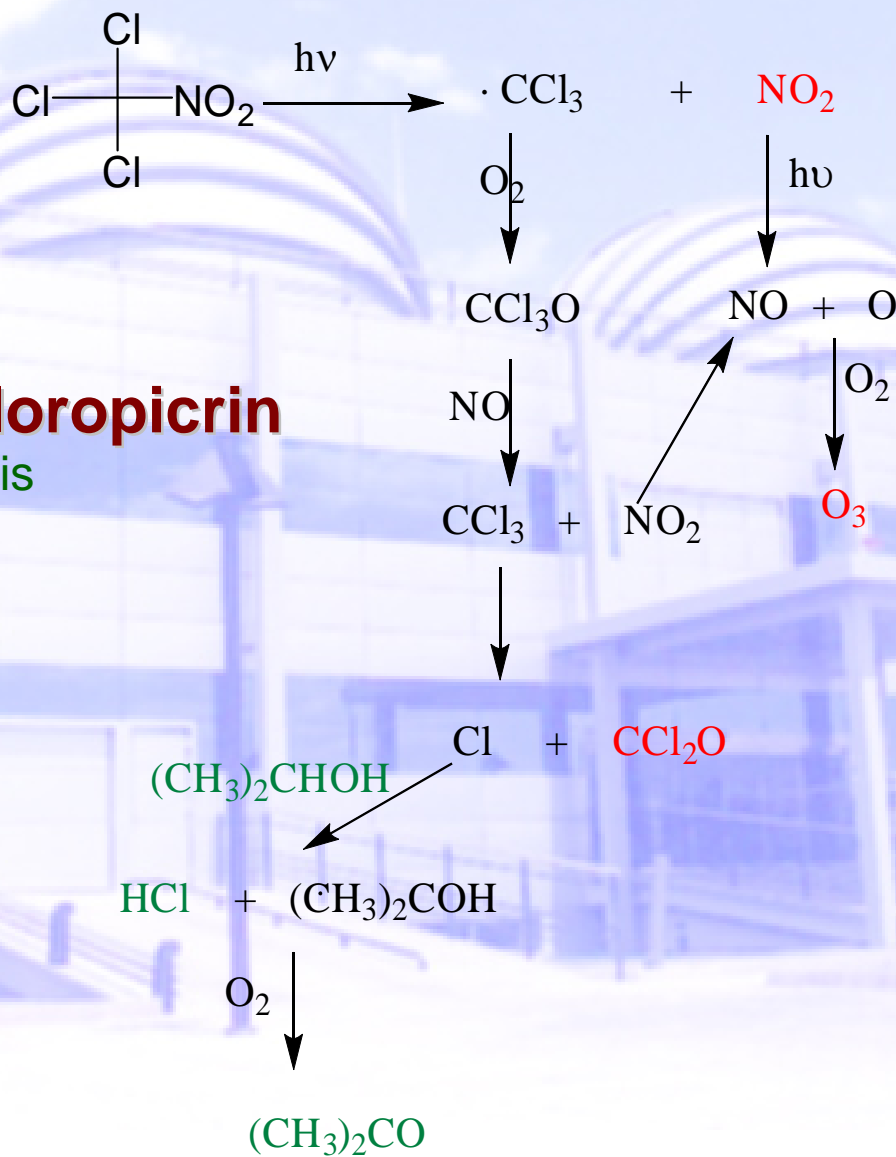
$t_{\text{photolysis}} \sim 8 \text{ h}$
 $t_{1/2 \text{ photolysis}} \sim 5.4 \text{ h}$



Plot of $\ln([\text{Chloropicrin}]_0/[\text{Chloropicrin}]_t)$ vs photolysis time for the photolysis exp with Isopropanol as scavenger

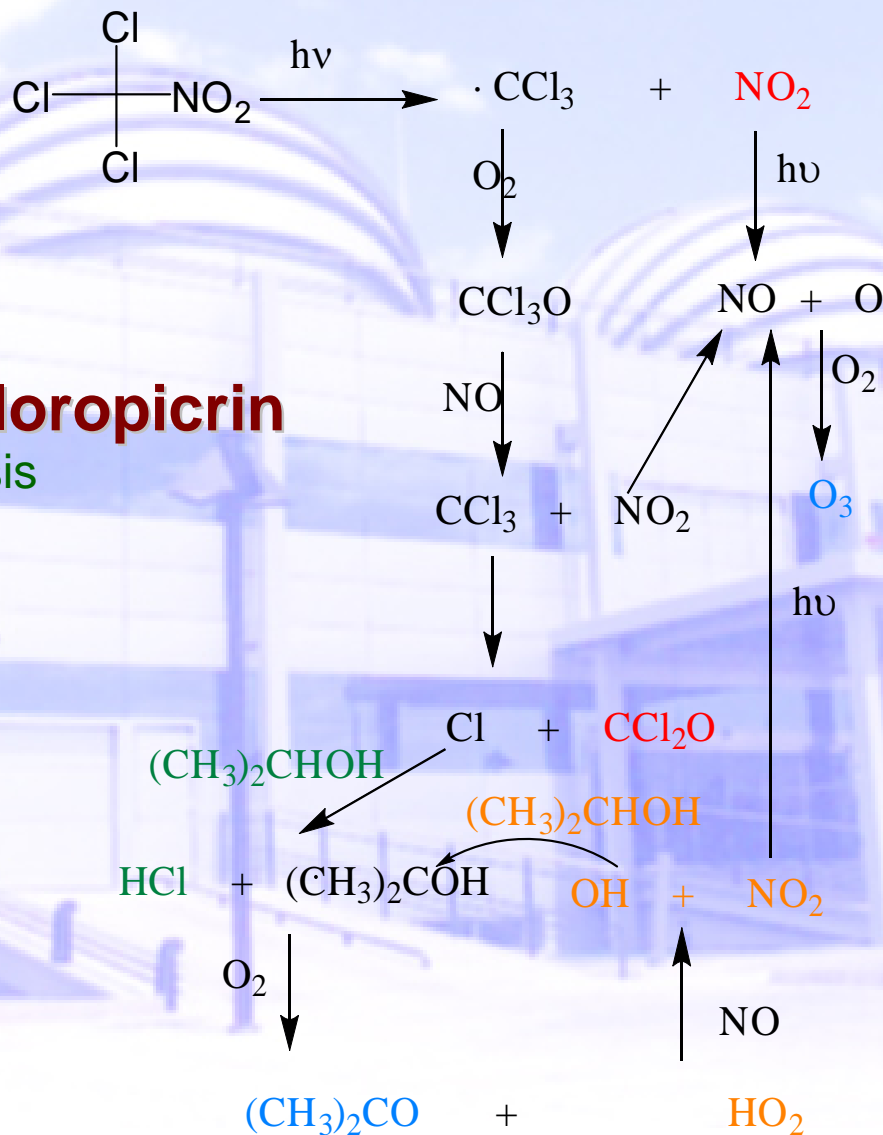
ATMOSPHERIC FATE OF PESTICIDES: STUDIES OF THE ATMOSPHERIC DEGRADATION OF PESTICIDES AT EUPHORE CHAMBERS

Examples: Chloropicrin
 Photolysis



ATMOSPHERIC FATE OF PESTICIDES: STUDIES OF THE ATMOSPHERIC DEGRADATION OF PESTICIDES AT EUPHORE CHAMBERS

Examples: Chloropicrin
 Photolysis



Examples: Chloropicrin

Comparison with other studies:

- $(t_{1/2}) \sim$ **20 days** (Moylanen et al, 1978)
- $(t_{1/2}) \sim$ **18 hours** $J = (6.3 \pm 0.2) \times 10^{-4} \text{ min}^{-1}$ (Carter 1997, experimental)
- $(t_{1/2})$ from **3.4 h to 7.6 hours** (Carter 1997, teoric, using actinic fluxes calculated by Peterson, 1976)
- $(t_{1/2}) \sim$ **5.4 hours** (our work).




Artificial
light

$$K_{O_3} \sim (4.8 \pm 2.3) \times 10^{-19} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$$

K_{OH} Calculation not possible

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**

Interesting links

<http://www.era-orleans.org/AFIP/portail.html>

AFIP project

<http://euphore.es>

EUPHORE Home Page

<http://www.ceam.es>

CEAM Web Page

ATMOSPHERIC FATE OF PESTICIDES: STUDIES OF THE ATMOSPHERIC DEGRADATION OF PESTICIDES AT EUPHORE CHAMBERS



Homepage info@afip.org

A F I P

Atmospheric Fate & Impact of Pesticides

PERSPECTIVE 2007-2013

Last update: 23th May 2007

summary

- What is new?
- The AFIP project
- What are pesticides ?
- Database
- Search
- Links
- Index

AFIP

mapsite • webmaster

Welcome at the AFIP website

The région Centre

