OVERVIEW OF THE USE OF THE OUTDOOR SIMULATION CHAMBER EUPHORE FOR STUDYING THE ATMOSPHERIC FATE OF ORGANOPHOSPHOROUS INSECTICIDES AND CHLOROACETANILIDE AND DINITROANILINE HERBICIDES.

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INTRODUCTION

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

Pesticides used for:

- Agriculture
- Gardening operations
- House uses

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

Introduction

Some references about studies of pesticides:

On aerosols

- Pflieger et al, 2011 Atmospheric Environment, 7127-7134
  And FEW more...

In soils

  And MUCH MORE...

In water

  And MUCH MORE....

In air

  And FEW more...

Pesticide Behaviour in Soils, Water and Air. 2-4 September 2013, York, UK
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

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, ECO ALPPT
- NO, API 200AU
- NO⁻, TAPI200UP
- O₃
- CO
- SO₂
- HONO
- HCHO

**AEROSOL INSTRUMENTATION**
- SMPS
- TEOM

**RADIOMETERS**
- ACTINOMETERS
- SPECTORADIOMETER

**OTHERS**
- BAROMETERS
- HYGROMETERS
- TEMPERATURE SENSORS
- AEROSOL GENERATOR
- DIESEL ENGINE
PROCEDURE TO PERFORM AN EXPERIMENT

Final results:
- photolysis rate
- $k_{OH}$
- $k_{O3}$
- identification of products

Analysis of the samples

Blank samples

Sampling with several analytical instruments and monitors

ATMOSPHERIC FATE OF SELECTED PESTICIDES

Examples of pesticides studied at EUPHORE chambers

Organophosphorous insecticides and degradation products
- Dichlorvos
- Diazinon
- Diazoxon
- Chlorpyrifos-methyl
- Chlorpyrifos
- Chlorpyrifos-oxon

Fungicides
- Chloropicrin
- Trifluralin
- Propachlor

Chloroacetanilide and dinitroaniline herbicides
- Hymexazol
- Ethalfluinal

Introduction of the target compound
- $SF_6$ introduction (for dilution rate)
- Introduction of chemicals

Sampling
- Wall loss (in the dark)

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### ATMOSPHERIC FATE OF SELECTED PESTICIDES

#### Main type of experiments

<table>
<thead>
<tr>
<th>Type of experiment</th>
<th>Main objective</th>
<th>Usual conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Photolysis</strong></td>
<td>Determination of Photolysis rate constant and degradation products</td>
<td>Experiments carried out in the presence of OH and/or Cl scavenger in order to prevent the reaction with those radicals.</td>
</tr>
<tr>
<td><strong>Reaction with OH radical</strong></td>
<td>Determination of the rate constant for the OH reaction with pesticides</td>
<td>Depending on the compound and the estimated value of the OH constant 1,3,5-trimethylbenzene, cyclohexane, n-butyl ether, methylene 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.</td>
</tr>
<tr>
<td><strong>Reaction with OH radical</strong></td>
<td>Determination of degradation products of the reaction of OH. Reaction mechanism</td>
<td>Gas and particle phase analysis. Experiments carried out in the presence or in the absence of NOx.</td>
</tr>
<tr>
<td><strong>Reaction with Ozone</strong></td>
<td>Determination of Ozone rate constant and degradation products</td>
<td>Dark conditions. Pseudo-first order conditions. OH radical scavenger used.</td>
</tr>
</tbody>
</table>
ATMOSPHERIC FATE OF SELECTED PESTICIDES

Kinetics

Photolysis (J)

\[
Pest + h\nu \rightarrow \text{Products} \quad J(\text{Pest})
\]

\[
Pest + \text{Wall} \rightarrow \text{Wall loss} \quad k_{\text{wall}}(\text{Pest})
\]

\[
Pest \rightarrow \text{Dilution} \quad k_{\text{dil}}
\]

\[
\ln(\frac{[\text{SF}_6]_o}{[\text{SF}_6]_t}) = k_{\text{dil}}t
\]

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

\[
\ln(\frac{[\text{Pest}]_o}{[\text{Pest}]_t}) = (J_{\text{meas}})t
\]

\[
J_{\text{meas}} = J(\text{Pest}) + k_{\text{dil}} + k_{\text{wall}}(\text{Pest})
\]

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**ATMOSPHERIC FATE OF SELECTED PESTICIDES**

**Kinetics**

**Photo-oxidation** ($k_{OH}$)

\[
\ln\left(\frac{[\text{CYCL}']_0}{[\text{CYCL}']_t}\right) = \ln\left(\frac{[\text{Ref}]}{[\text{Ref}]}\right)_t \cdot \frac{k_{OH}(\text{Pest})}{k_{OH}(\text{Ref})} - k_{dil} t
\]

\[
\tau = \frac{1}{k_{OH}(\text{Pest})[\text{OH}]}
\]

\[
[\text{OH}] = 2 \times 10^6 \text{ molecule cm}^{-3}
\]

\[
\ln\left(\frac{[\text{Pest}]_0}{[\text{Pest}]}_t\right) - (k_{dil} + k_{wall})t = k_{OH}(\text{Pest})/k_{OH}(\text{Ref})\ln\left(\frac{[\text{Ref}]}{[\text{Ref}]}\right)_t - k_{dil} t
\]
Chlorpyrifos

The proposed reaction pathway for the OH Reaction with chlorpyrifos.

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
ATMOSPHERIC FATE OF SELECTED PESTICIDES

Products and mechanisms

Chloroacetanilide and dinitroaniline herbicides

Propachlor. OH reaction

Ethalfluralin. Photolysis

Peroxy bicyclic

Ring opening

Oligomers
### Atmospheric Fate of Selected Pesticides

#### Organophosphate insecticides

<table>
<thead>
<tr>
<th>COMPOUND</th>
<th>J [s⁻¹]</th>
<th>$k_{OH}$ [cm³ molec⁻¹ s⁻¹]</th>
<th>Lifetime /Main degradation pathway</th>
<th>Main degradation products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorpyrifos (¹)</td>
<td>$1.4 \times 10^{-5}$</td>
<td>$(9.1 \pm 1.8) \times 10^{-11}$</td>
<td>2 hours / Reaction with OH</td>
<td>SO₂, 3,5,6-tricloro-2-pyridinol, SOA, chlorpyrifos oxon, CH₃CHO, PAN (in the presence of NOx)</td>
</tr>
<tr>
<td>Chlorpyrifos oxon (¹)</td>
<td>$&lt; 4.8 \times 10^{-5}$</td>
<td>$(1.6 \pm 0.8) \times 10^{-11}$</td>
<td>11 hours / Reaction with OH</td>
<td>SOA, PAN (in the presence of NOx)</td>
</tr>
<tr>
<td>Chlorpyrifos-methyl (²)</td>
<td>$&lt; 2 \times 10^{-5}$</td>
<td>$(4.1 \pm 0.4) \times 10^{-11}$</td>
<td>3.5 hours / Reaction with OH</td>
<td>SO₂, 3,5,6-tricloro-2-pyridinol, SOA*, chlorpyrifos-methyl oxon</td>
</tr>
<tr>
<td>Diazinon (³, ⁴)</td>
<td>$&lt; 1 \times 10^{-5}$</td>
<td>$(9.6 \pm 1.8) \times 10^{-11}$</td>
<td>1.8 hours / Reaction with OH</td>
<td>SO₂, 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*</td>
</tr>
<tr>
<td>Diazoxon (⁴)</td>
<td>$&lt; 4.8 \times 10^{-5}$</td>
<td>$(3.0 \pm 1.1) \times 10^{-11}$</td>
<td>5.9 hours / Reaction with OH</td>
<td>Hydroxydiazoxon, PAN (in the presence of NOx), SOA</td>
</tr>
<tr>
<td>Dichlorvos (⁵)</td>
<td>negligible</td>
<td>$(2.6 \pm 0.3) \times 10^{-11}$</td>
<td>11 hours / Reaction with OH</td>
<td>Phosgene, CO</td>
</tr>
</tbody>
</table>

(¹) Muñoz et al., 2013a, Submitted.  
(²) Muñoz et al., 2011a, EST.  
(³) Muñoz et al., 2011b, Chemosphere.  
(⁴) Muñoz et al., In Preparation.  
(⁵) Feigenbrugel et al., 2006, EST.  
* Poster: Borras et al. Particulate matter formation from photochemical degradation of pesticides

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### Chloroacetanilide and dinitroaniline herbicides

<table>
<thead>
<tr>
<th>COMPOUND</th>
<th>J [s(^{-1})]</th>
<th>(k_{\text{OH}}) [cm(^3) molec(^{-1}) s(^{-1})]</th>
<th>(k_{\text{O}_3}) [cm(^3) molec(^{-1}) s(^{-1})]</th>
<th>Lifetime / Main degradation pathway</th>
<th>Main degradation products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethalfuralin (6) **</td>
<td>(1.3±0.2)×10(^{-3})</td>
<td>(9.6±1.8)×10(^{-11})</td>
<td>(1.6±0.4)×10(^{-17})</td>
<td>12 minutes / Photolysis</td>
<td>Methacrolein, Acetaldehyde, SOA, nitroaniline and benzimidazol type compounds</td>
</tr>
<tr>
<td>Propachlor (7)</td>
<td>&lt;(2±0.5)×10(^{-5})</td>
<td>(1.5±0.3)×10(^{-11})</td>
<td>&lt;1.5±0.4)×10(^{-19})</td>
<td>20 hours / Reaction with OH</td>
<td>carbonyl group-containing oligomers with molecular weights in the region of 280-500 (SOA*)</td>
</tr>
<tr>
<td>Trifluralin (8)</td>
<td>(1.2±0.5)×10(^{-3})</td>
<td>(1.7±0.4)×10(^{-11})</td>
<td>-</td>
<td>15 minutes / Photolysis</td>
<td>2-ethyl-4-nitro-6-(trifluoromethyl)-1H-benzimidazole, Propanal, acetaldehyde, formaldehyde, SOA*</td>
</tr>
</tbody>
</table>

(6) Muñoz et al., 2013b, Submitted.
(7) Muñoz et al., 2012, Atmospheric Environment
(8) Le Person et al., 2007, Chemosphere.
* Poster: Borras et al. Particulate matter formation from photochemical degradation of pesticides
** Poster: Muñoz et al. Atmospheric degradation of ethalfuraline
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
ATMOSPHERIC FATE OF SELECTED PESTICIDES

Acknowledgements

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Thanks your for your attention