Atmospheric Heterogeneous Reactivity Of Pesticides:
Parameters Influencing the Degradation Kinetics

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Heterogeneous degradation
Heterogeneous degradation

Degradation by

\[ \text{O}_3 \cdot \text{OH} \quad \text{NO}_3 \cdot \quad \text{hv} \]

\( \text{O}_3 \) formed mainly by photolysis of \( \text{O}_2, \text{NOx}, \text{VOCs} \)

\( \approx 10^{12} \text{ molecule.cm}^{-3} \)

\( \approx 40 \text{ ppb} \)

\( \cdot \text{OH} \) formed mainly by photolysis of ozone

\( \approx 10^7 \text{ molecule.cm}^{-3} \) by day

Very reactive
What are ye studying?

What are the parameters influencing the **heterogeneous** degradation kinetics of pesticides by **ozone** and \( \cdot \text{OH radicals} \)?
What are ye studying?

Permethrin (i) \( K_{\text{part}} = 0.97 \)

Cyprodinil (f) \( K_{\text{part}} = 0.07 \)

Deltamethrin (i) \( K_{\text{part}} = 0.91 \)

Tetraconazole (f) \( K_{\text{part}} = 0.38 \)

Oxadiazon (h) \( K_{\text{part}} = 0.62 \)

Difenoconazole (f) \( K_{\text{part}} = 0.99 \)

Pendimethalin (h) \( K_{\text{part}} = 0.01 \)

Fipronil (i) \( K_{\text{part}} = 0.84 \)

K_{\text{part}} estimé par AEROWINTM Software V1.0 using the Junge-Pankow adsorption mode
Parameters under study

Humidity

Particle type

Hydrophilic silica R812
- Specific surface area: 255 m².g⁻¹
- 5 nm to 50 nm Agglomerates 5 μm to 25 μm
- Surface: mainly silanols

Hydrophobic silica Aerosil 255
- Specific surface area: 260 m².g⁻¹
- 5 nm to 50 nm Agglomerates 5 μm to 25 μm
- Surface: mainly siloxanes

0-80% RH
Experimental Method
Simulation of atmospheric conditions

Surface coverage: 3%

Liquid/Solid adsorption

RH: 0 – 80%

C_t/C_0

Kinetic constants

Half life

Time

Analysis: GC-MS/MS

O_3: 400 ppb

• OH: 10^7 molecule.cm^{-3}
Results
8 pesticides under study

Permethrin

Cyprodinil

Deltamethrin

Pendimethalin

Tetraconazole

Oxadiazon

Difenoconazole

Fipronil
Ozone degradation
Degradation by ozone

Pendimethalin - O₃
Hydrophilic silica

Hydrophilic silica: reactivity ↘
when humidity ↗
Degradation by ozone

Pendimethalin - O$_3$

Hydrophobic silica

Hydrophobic silica: reactivity ↓ when humidity ↑
Degradation by ozone

Pendimethalin - O$_3$

Hydrophobic silica

Reactivity faster on hydrophilic silica under 80 % RH
Degradation by ozone

Reactivity:

Low humidity > high humidity

hydrophilic silica > hydrophobic silica

Except cyprodinil
·OH radical degradation
\[ \text{⋅OH radical production} \]

**Production:**

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{H}_3\text{C} \\
\quad & \quad \\
\text{CH}_3 & \quad \text{CH}_3
\end{align*}
\]

2,3-dimethyl-2-butene

\[ + \text{O}_3 \rightarrow \text{⋅OH} + \text{products} \]

**Analysis:**

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\quad & \quad \\
\text{m-xylene} & \quad \text{m-xylene}
\end{align*}
\]

\[ + \text{⋅OH} \rightarrow \text{products} \]

\[ \text{⋅OH} : 10^7 \text{ molecule.cm}^{-3} \]

**PTR-MS**
Example of pendimethalin

Degradation by $\cdot$OH

Relative humidity influences the kinetics

$K_{\text{OH}}$ (cm$^3$ molecule$^{-1}$ S$^{-1}$)

Relative humidity (%)

Hydrophobic silica
Hydrophilic silica

X3
Example of pendimethalin

Degradation by $\cdot$OH

Particle type influences the kinetics
Other pesticides

Degradation by •OH

Deltamethrin

Permethrin

Relative humidity and particle type influences the degradation kinetics.
### Atmospheric implications

<table>
<thead>
<tr>
<th>Pesticide</th>
<th>Oxidant</th>
<th>$t_{1/2 \text{part}}$ (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyprodinil</td>
<td>Ozone</td>
<td>0.4 - 91</td>
</tr>
<tr>
<td></td>
<td>·OH</td>
<td>/</td>
</tr>
<tr>
<td>Pendimethalin</td>
<td>Ozone</td>
<td>0.2 - 17</td>
</tr>
<tr>
<td></td>
<td>·OH</td>
<td>3 - 40</td>
</tr>
<tr>
<td>Deltamethrin</td>
<td>Ozone</td>
<td>4 - 35</td>
</tr>
<tr>
<td></td>
<td>·OH</td>
<td>5 - 18</td>
</tr>
<tr>
<td>Permethrin</td>
<td>Ozone</td>
<td>5 - 20</td>
</tr>
<tr>
<td></td>
<td>·OH</td>
<td>4 - 57</td>
</tr>
</tbody>
</table>

**Persistent Organic Pollutant:** $t_{1/2 \text{total}} \geq 2$ days

Stockholm convention, 2001
Conclusion

**Ozone and ·OH radicals degradation**

Degradation kinetics are influenced by:

- **Relative humidity**  
  Reactivity decreases when RH increases.

- **Particle type**  
  Hydrophilic > Hydrophobic.

- **Pesticide nature**

Realistic kinetic constants can hardly be estimated at 0% RH.

**Follow up:**

- Heterogeneous degradation by NO$_3^-$.
- Heterogeneous degradation on Arizona dust.
• Project COPP’R “Modelling of atmospheric contamination by plant protection products at the regional scale”

• Ph.D. grant