Atmospheric Heterogeneous Reactivity Of Pesticides:

Parameters Influencing the Degradation Kinetics

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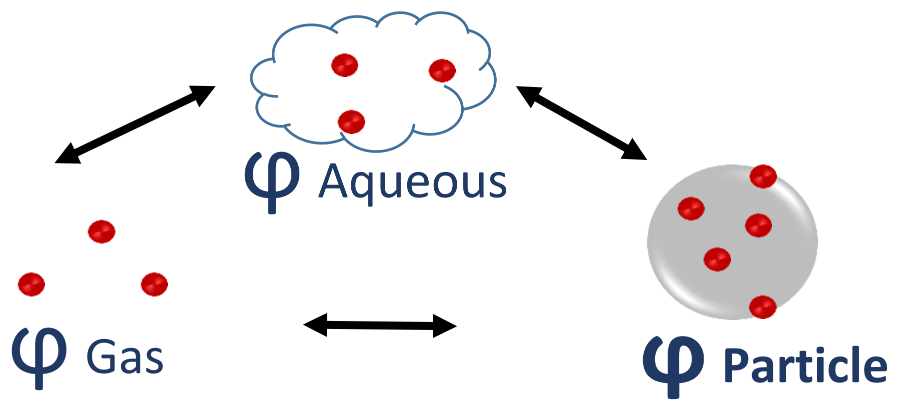
cnrs
ADEME Agence de l'Environnement et de la Maîtrise de l'Energie

Heterogeneous degradation

Heterogeneous degradation



Degradation by

O_3 **·OH** NO_3· hv

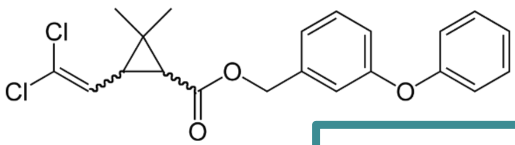
O_3 formed mainly by photolysis of O_2, NOx, VOCs

≈10^{12} molecule.cm^{-3}
≈ 40 ppb

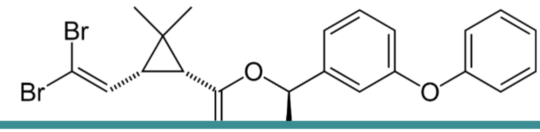
·OH formed mainly by photolysis of ozone

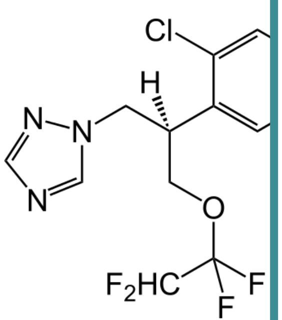
≈ 10^{7} molecule.cm^{-3} by day
Very reactive

What are ye studying?



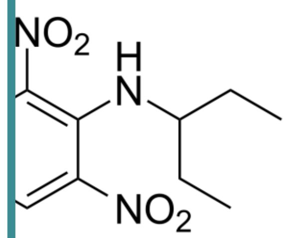
Permethrin
K_{part}=0.97



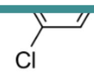


Tetraconazol
K_{part}=0.38

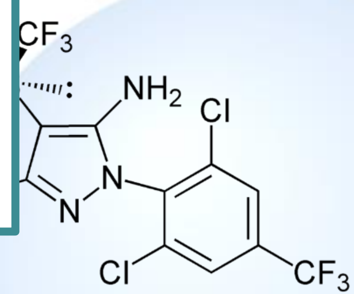
What are the parameters influencing the **heterogeneous** degradation kinetics of pesticides by **ozone** and·**OH radicals** ?



dimethalin (h)
K_{part}=0.01



Difenoconazole (f)
K_{part}=0.99



Fipronil (i)
K_{part}=0.84

K_{part} estimé par AEROWINTM Software V1.0 using the Junge-Pankow adsorption mode

What are ye studying?

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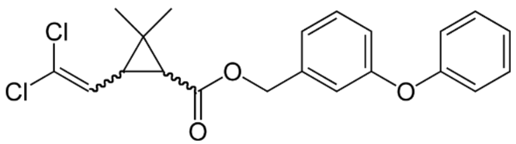
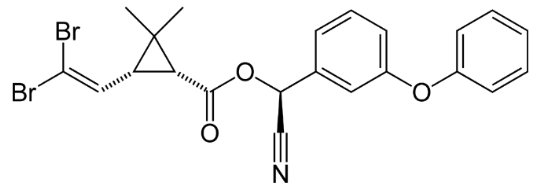
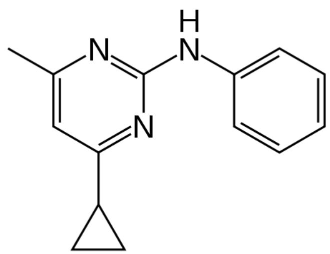


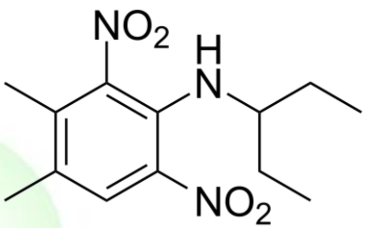
Permethrin (i)
K_{part}=0.97



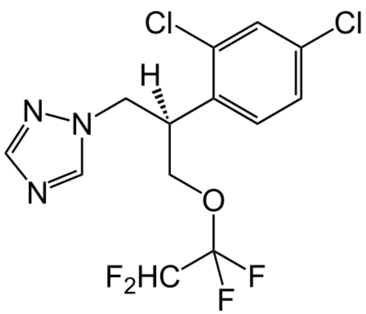
Deltamethrin (i)
K_{part}=0.91



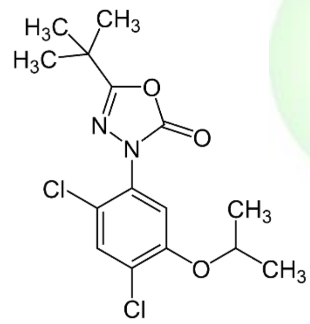
Cyprodinil (f)
K_{part}=0.07



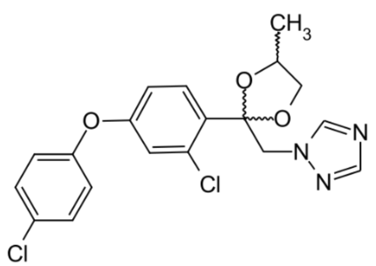
Pendimethalin (h)
K_{part}=0.01



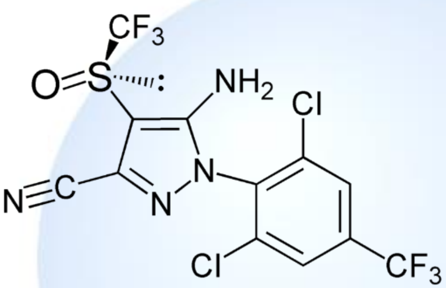
Tetraconazole (f)
K_{part}=0.38



Oxadiazon (h)
K_{part}=0.62



Difenoconazole (f)
K_{part}=0.99

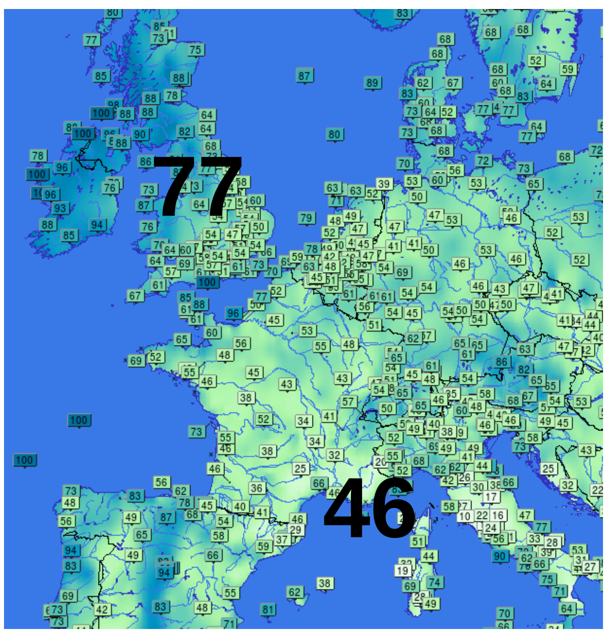


Fipronil (i)
K_{part}=0.84

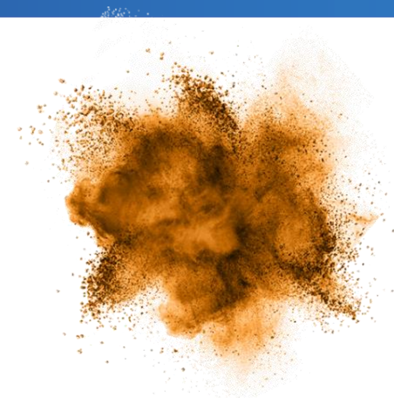
K_{part} estimé par AEROWINTM Software V1.0 using the Junge-Pankow adsorption mode

Parameters under study

Humidity

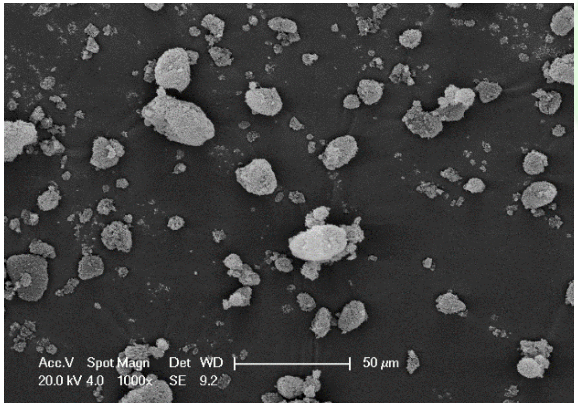


0-80% RH



Particle type

Hydrophilic silica R812

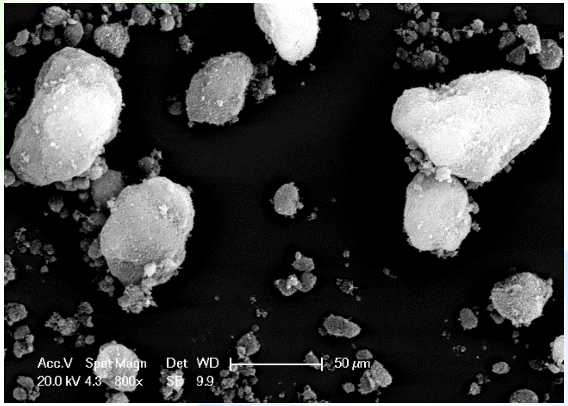


X 1000
Specific surface area: 255 $m^2.g^{-1}$

5 nm to 50 nm
Agglomerates 5 µm to 25 µm

Surface : mainly silanols

Hydrophobic silica Aerosil 255



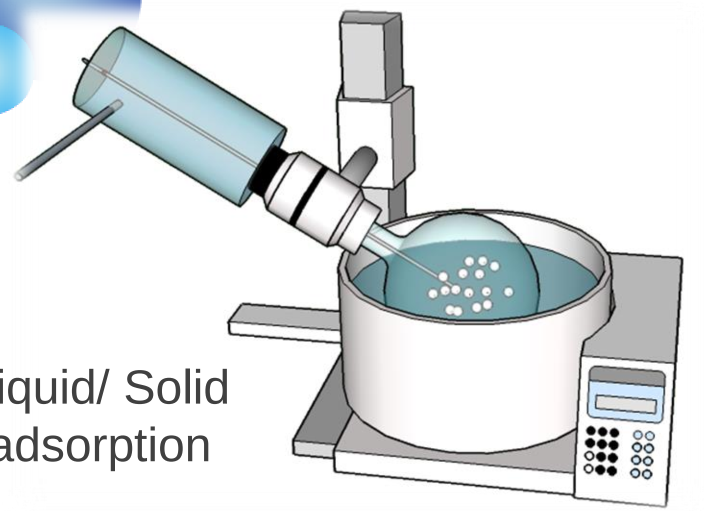
X 800
Specific surface area : 260 $m^2.g^{-1}$

5 nm to 50 nm
Agglomerates 5 µm to 25 µm

Surface :mainly siloxanes

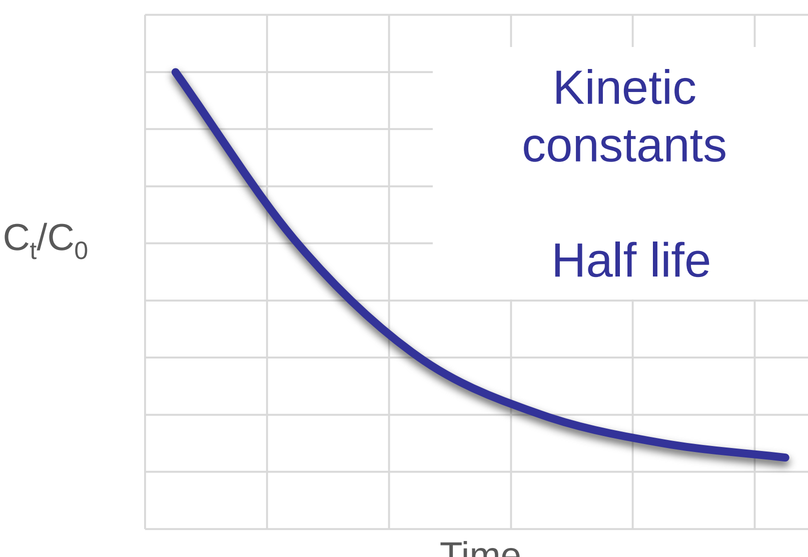
Experimental Method

Simulation of atmospheric conditions



Liquid/ Solid adsorption

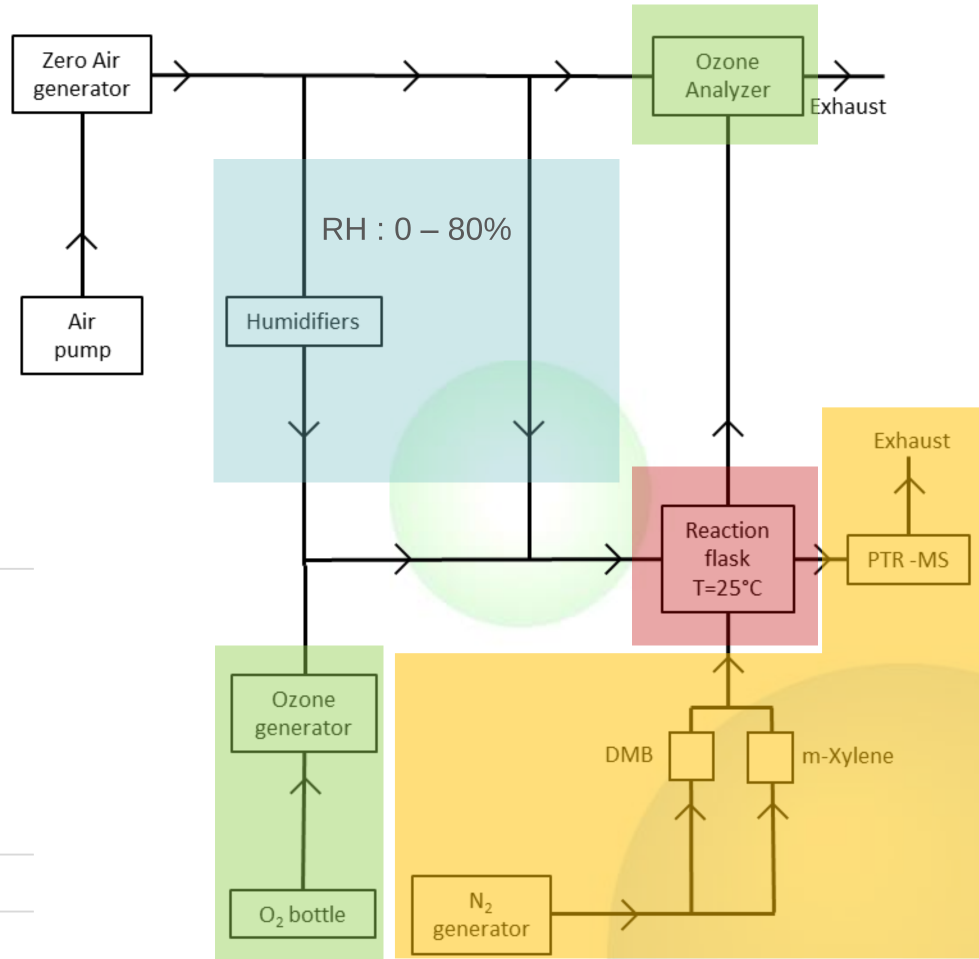
Surface coverage: 3 %



Kinetic constants

Half life

Analysis : GC-MS/MS



O_3 : 400 ppb

$\cdot OH$: 10^7 molecule.cm^{-3}

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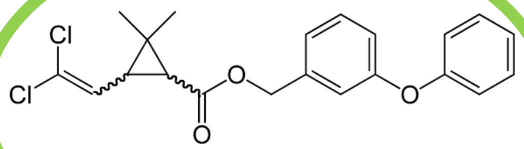
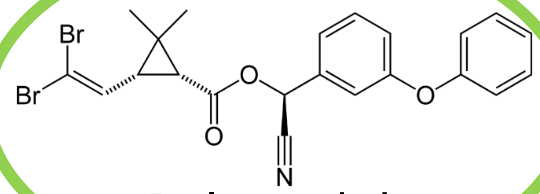
Results

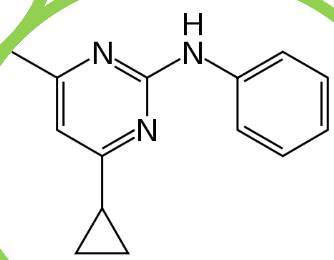
8 pesticides under study



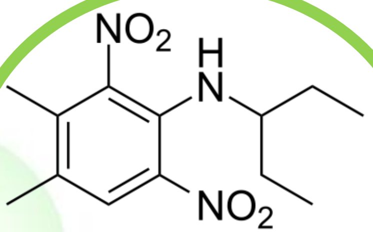
Permethrin



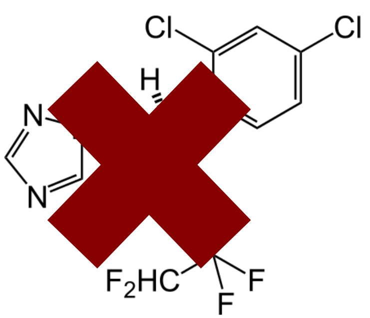
Deltamethrin



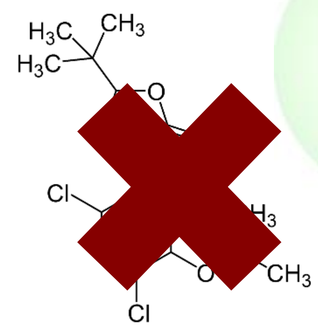
Cyprodinil



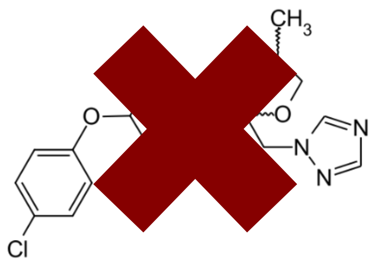
Pendimethalin



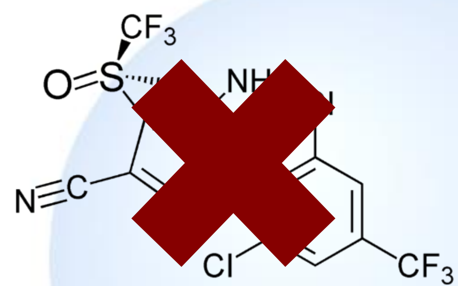
Tetraconazole



Oxadiazon



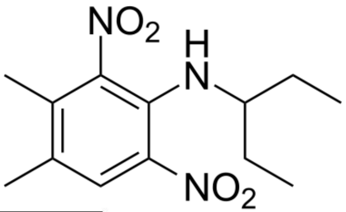
Difénoconazole



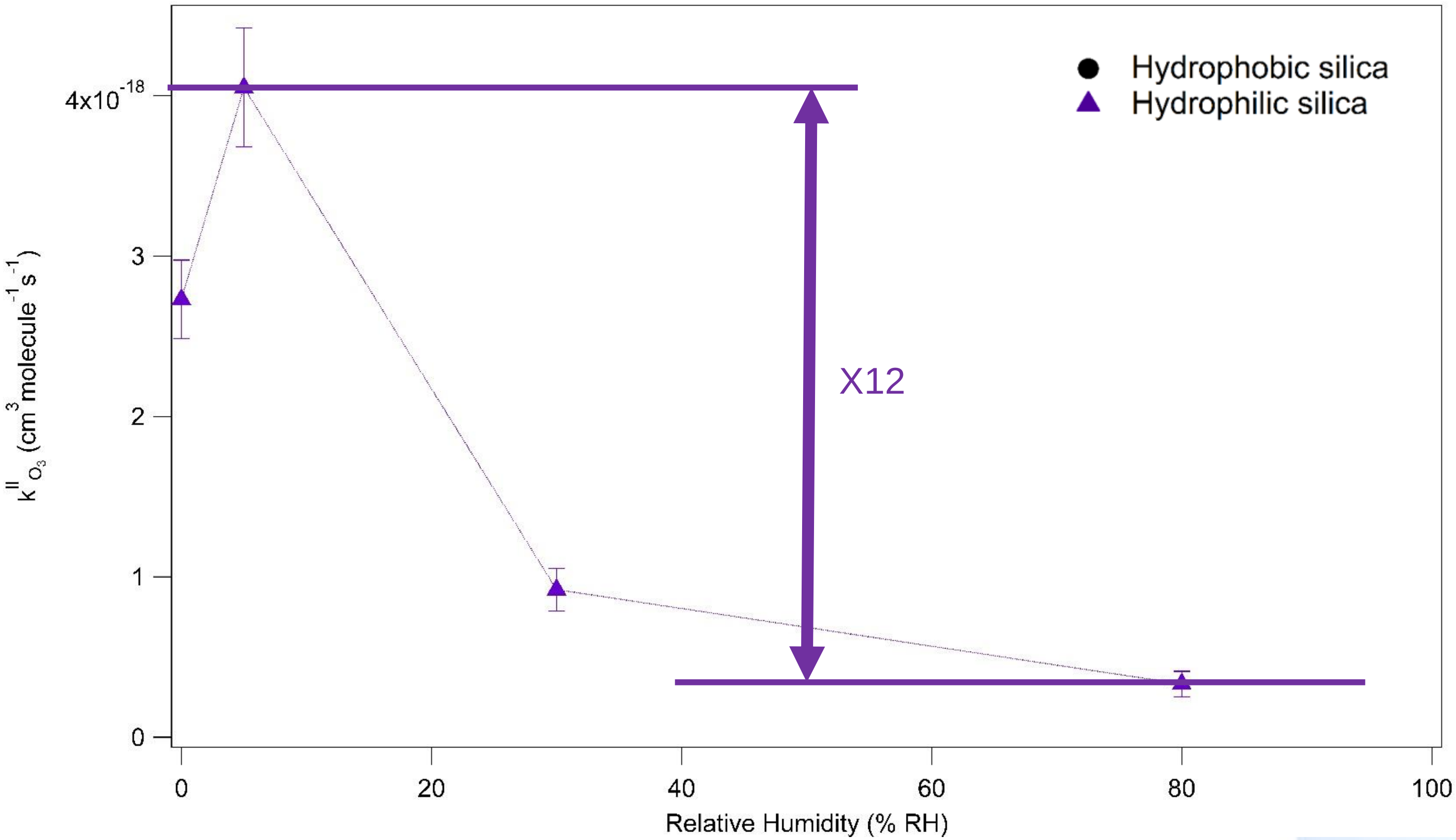
Fipronil

Ozone degradation

Degradation by ozone



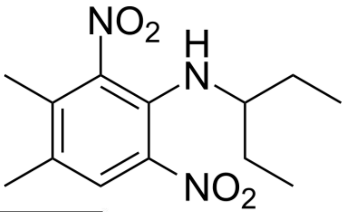
Pendimethalin - O_3
Hydrophilic silica

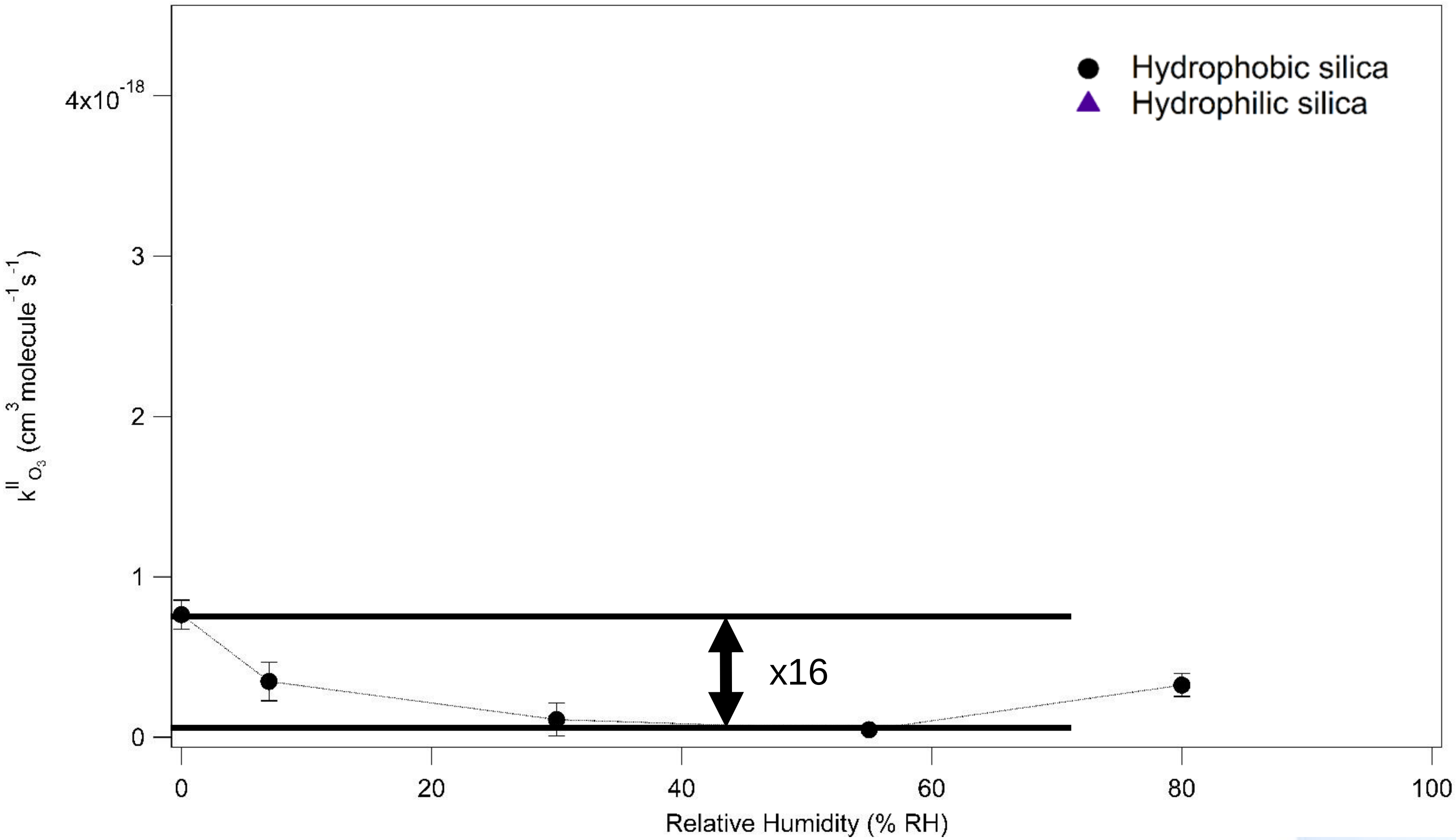


Hydrophilic silica: reactivity ↘
when humidity ↗

Degradation by ozone

Pendimethalin - O_3
Hydrophobic silica

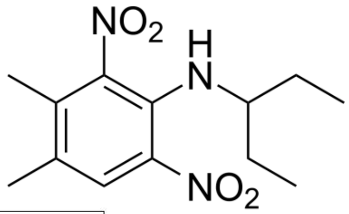


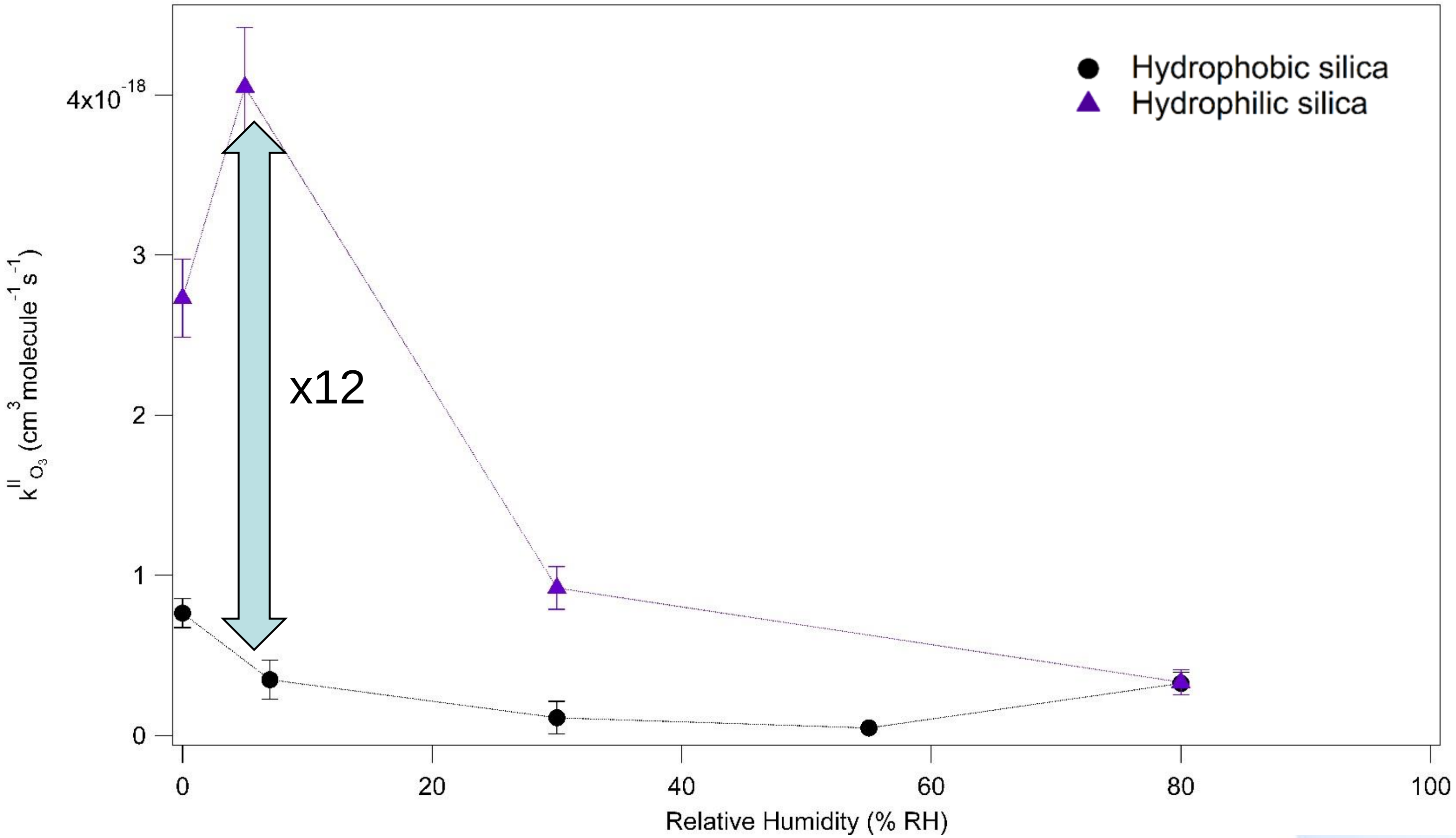


Hydrophobic silica: reactivity ↘
when humidity ↗

Degradation by ozone

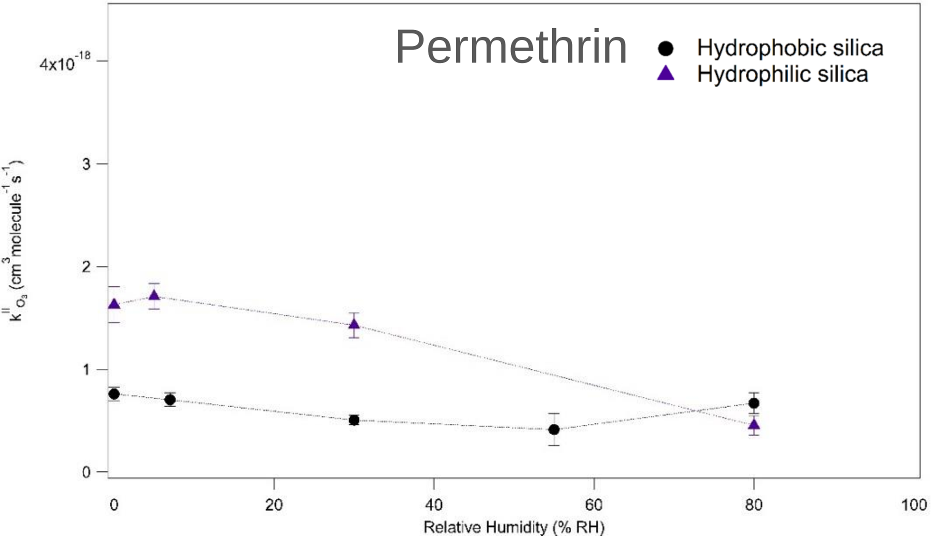
Pendimethalin - O_3
Hydrophobic silica

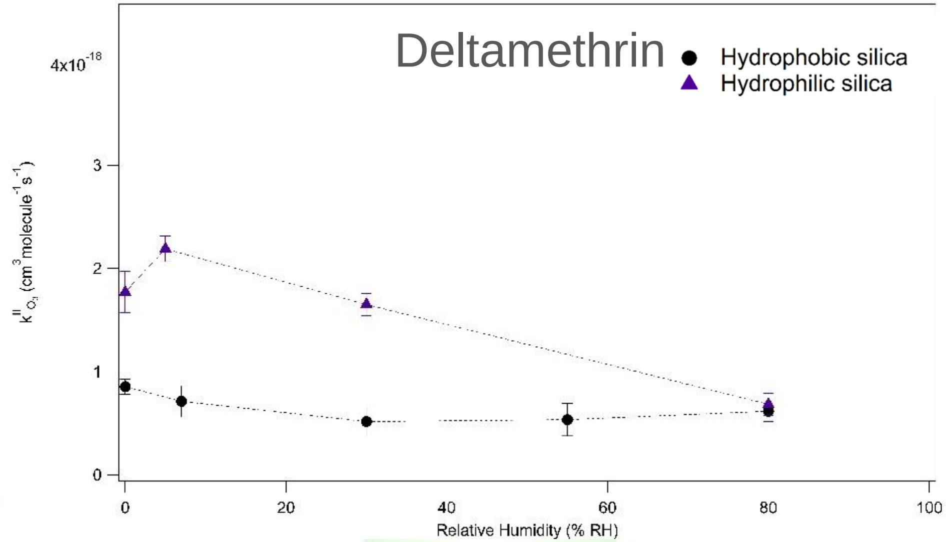


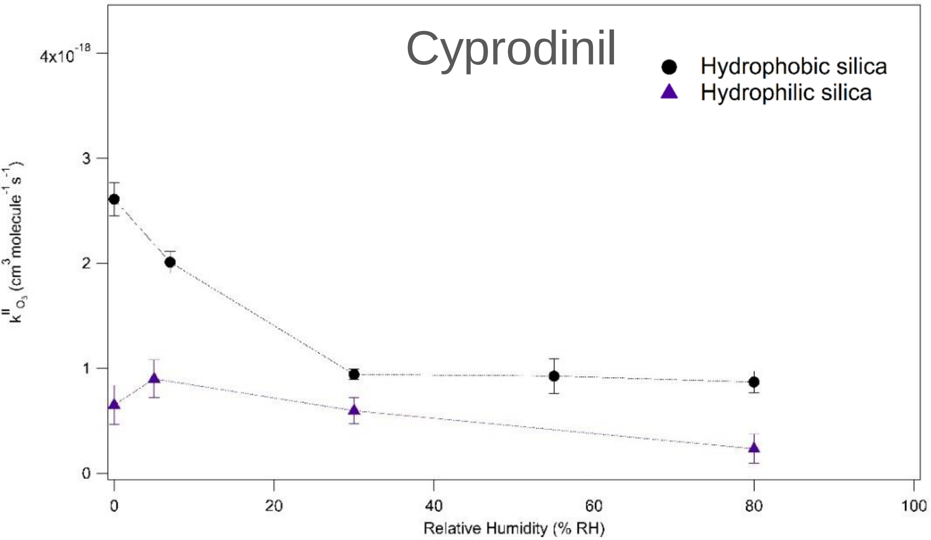


Reactivity faster on hydrophilic silica under 80 % RH

Degradation by ozone







Reactivity :

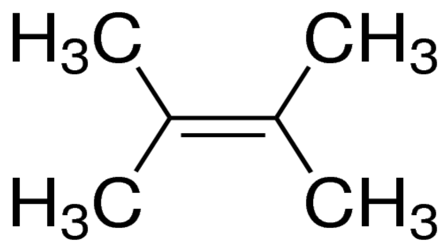
Low humidity > high humidity

hydrophilic silica > hydrophobic silica
Except cyprodinil

•OH radical degradation

· OH radical production

Production:

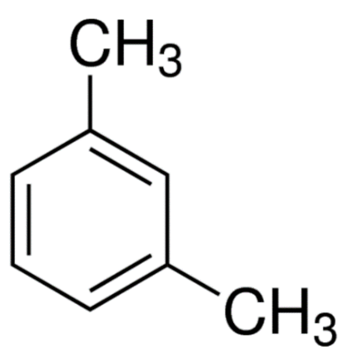


2,3-dimethyl-2-butene

$+ O_3 \rightarrow \cdot OH + \text{products}$

$\cdot OH : 10^7$ molecule.cm^{-3}

Analysis:



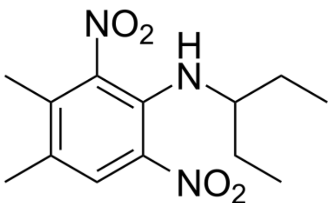
m-xylene

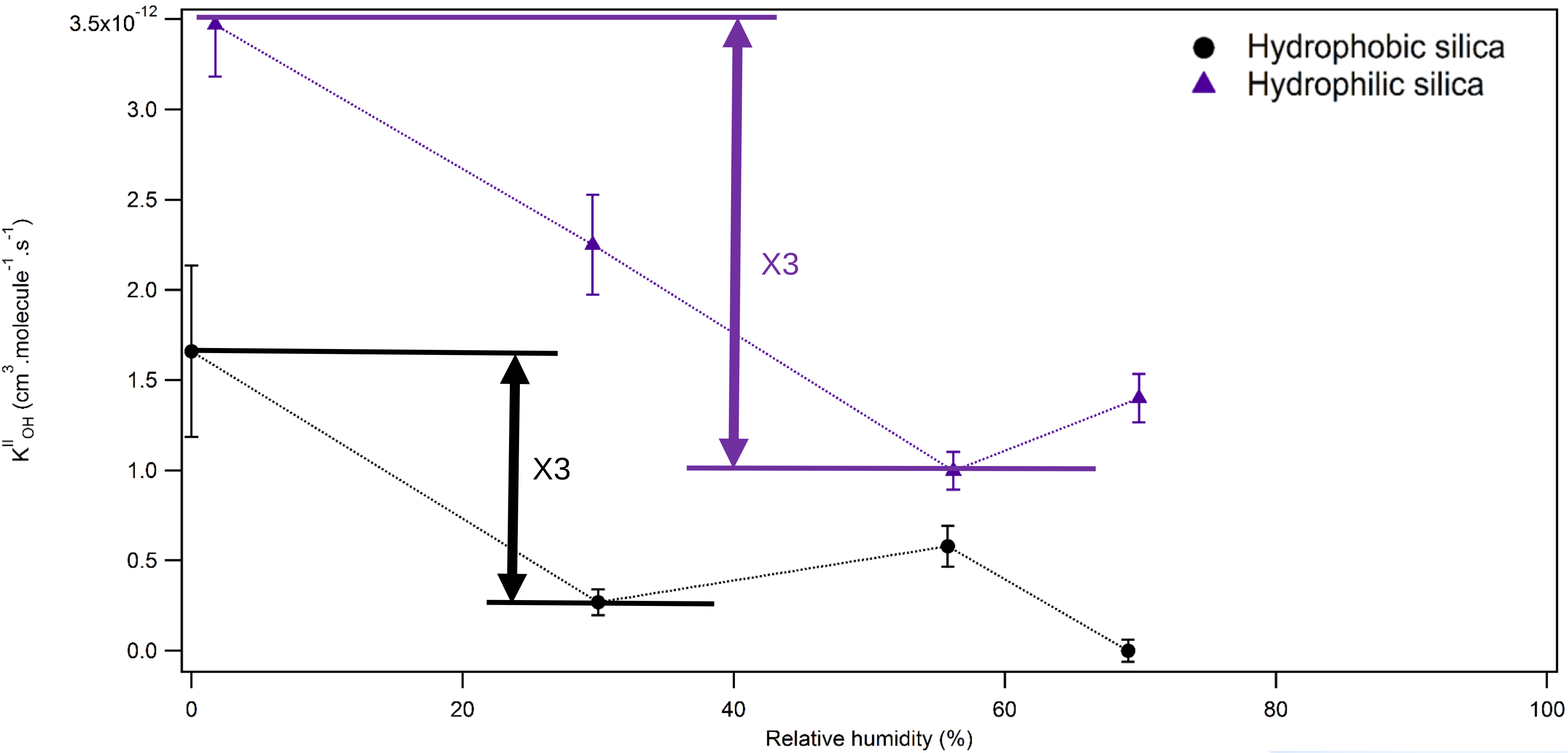
$+ \cdot OH \rightarrow \text{products}$

PTR-MS

Example of pendimethalin

Degradation by ·OH

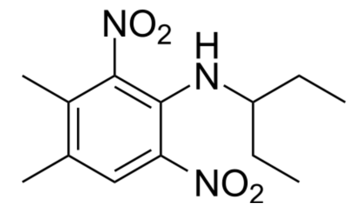


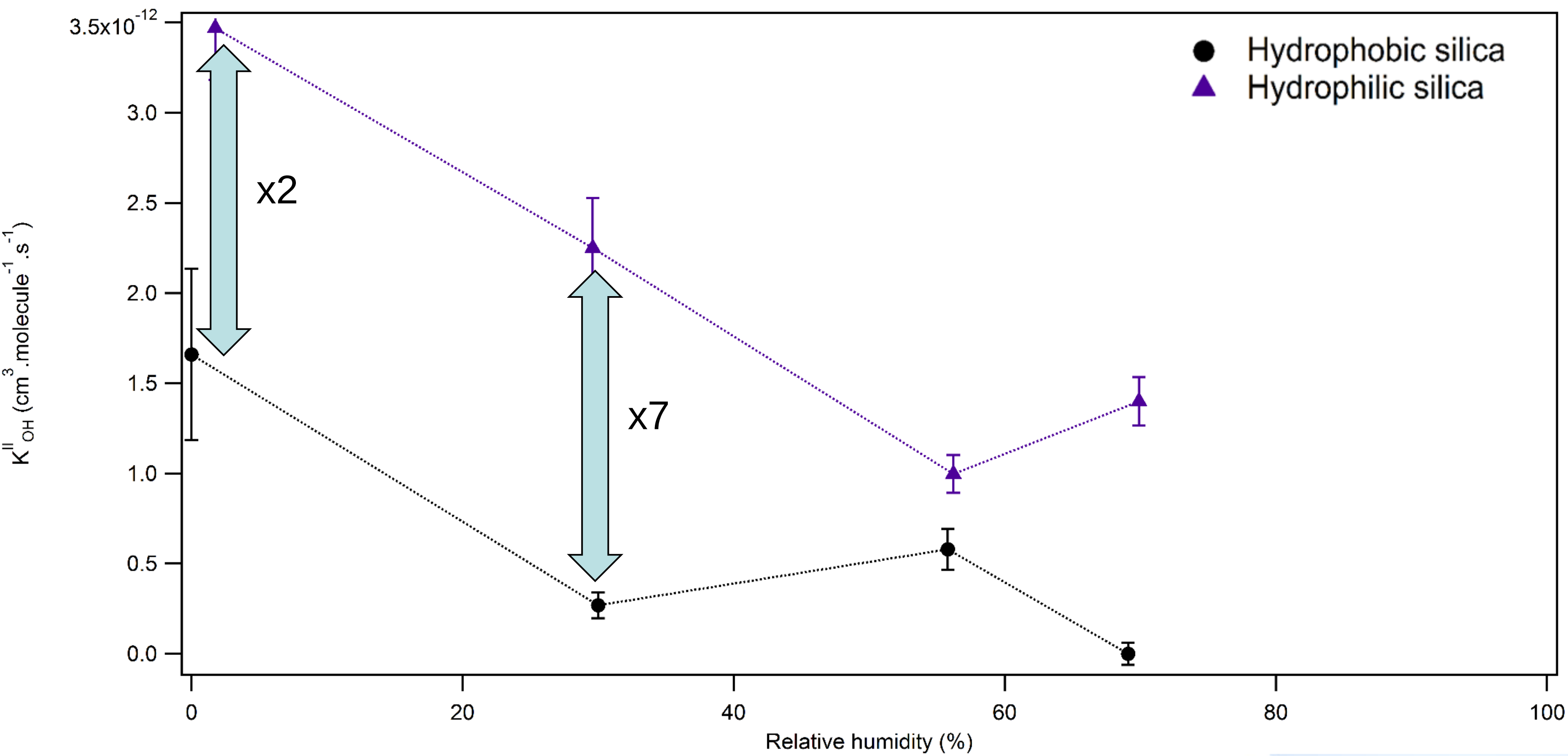


Relative humidity influences the kinetics

Example of pendimethalin

Degradation by ·OH



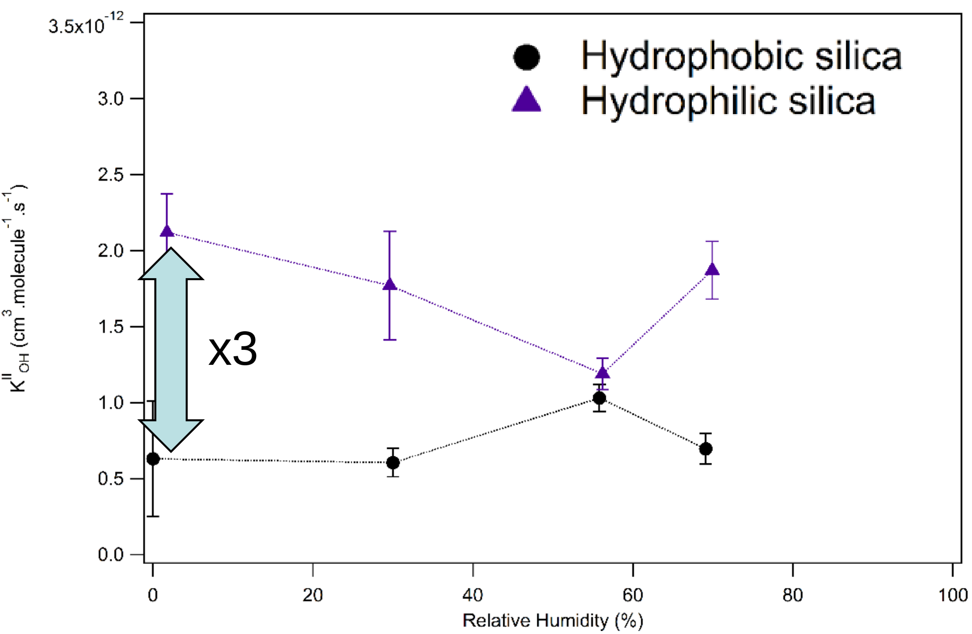


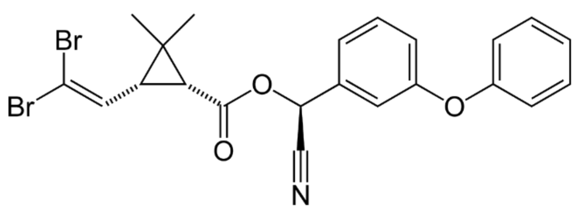
Particle type influences the kinetics

Other pesticides

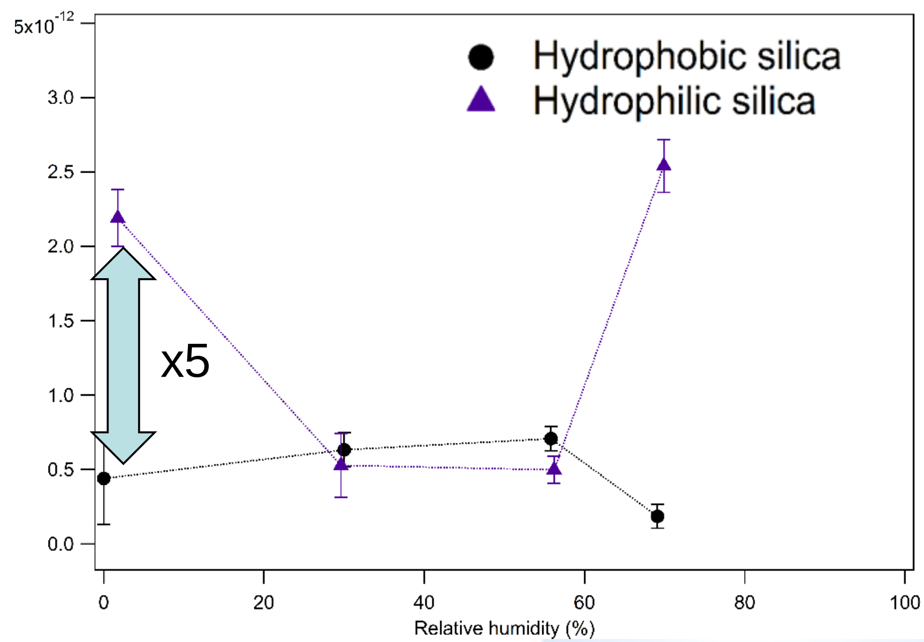
Degradation by ·OH

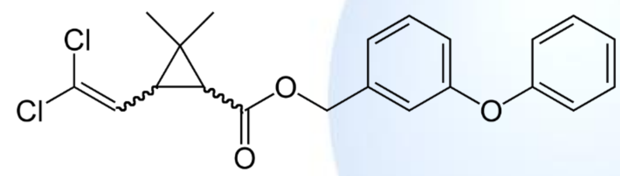
Deltamethrin





Permethrin





Relative humidity and particle type influences the degradation kinetics

Atmospheric implications

Pesticide	Oxidant	$t_{1/2part}$ (days)
Cyprodinil	Ozone	0.4 - 91
	·OH	/
Pendimethalin	Ozone	0.2 - 17
	·OH	**3 - 40**
Deltamethrin	Ozone	4 - 35
	·OH	**5 - 18**
Permethrin	Ozone	5 - 20
	·OH	**4 - 57**

Persitant Organic Pollutant: $t_{1/2total} \geq 2$ days

Stockholm convention, 2001

Conclusion

Ozone and ·OH radicals degradation

degradation kinetics are influenced by *:*

- ✓ **Relative humidity** reactivity ↘ when RH ↗
- ✓ **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

Acknowledgement / Funding

- Project COPP'R "*Modelling of atmospheric contamination by plant protection products at the regional scale*"

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- Ph.D. grant

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Thank you for your attention