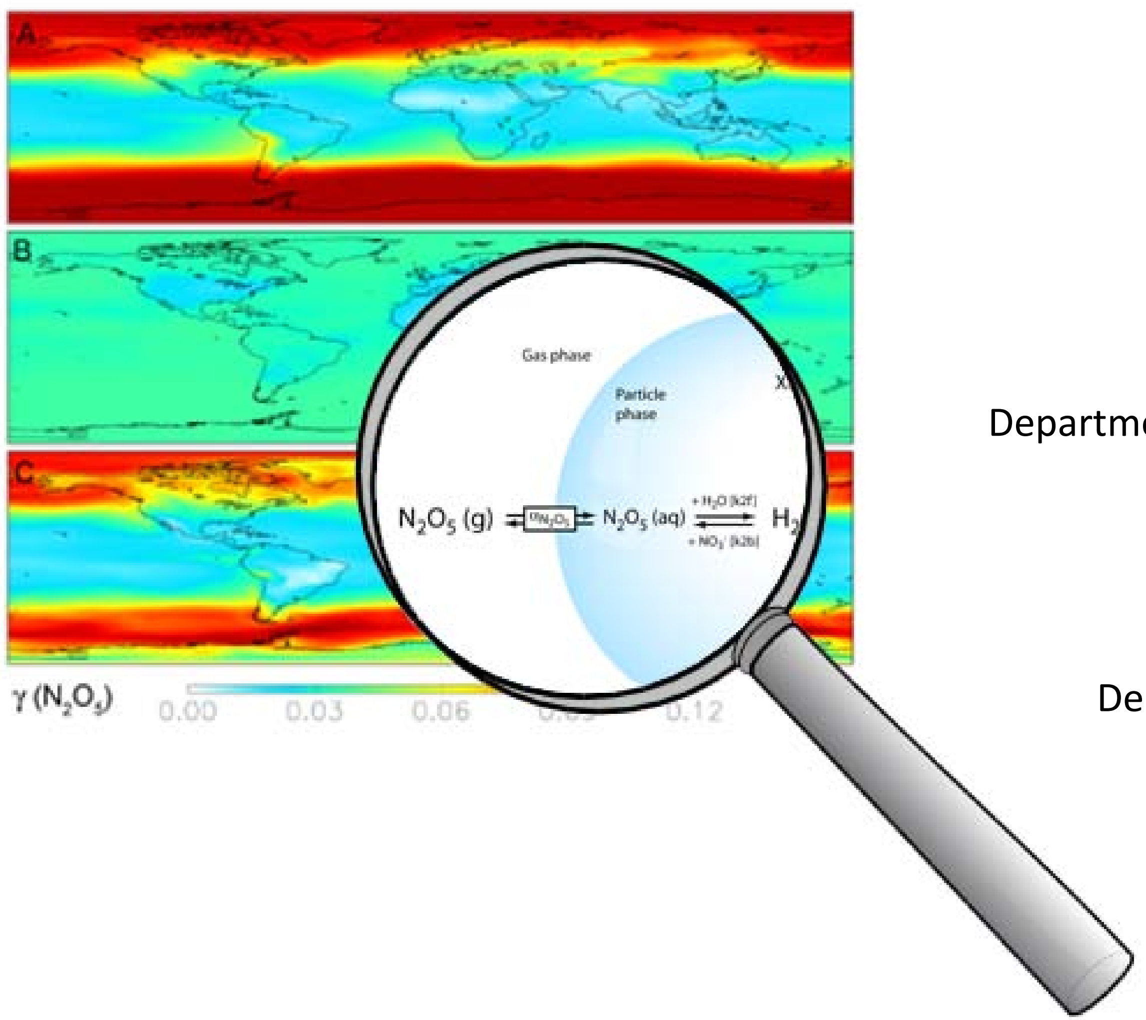
From the molecular level to the global scale:

Bridging disparate time and length scales in atmospheric chemistry



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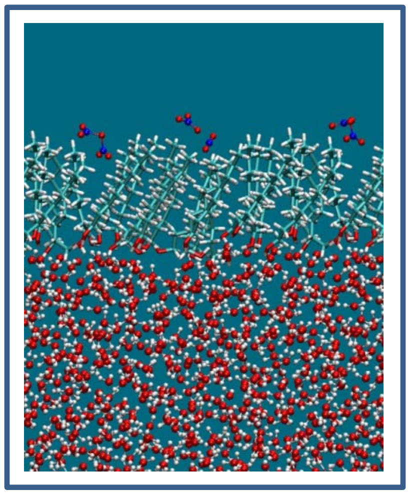
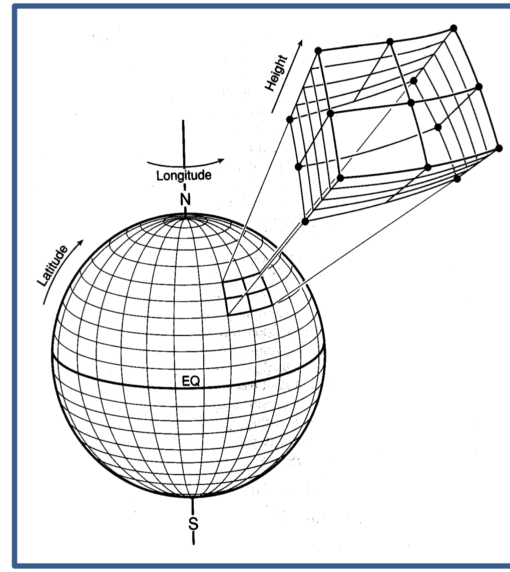
Disparate Time and Length Scales

Time [t < 1E-6 seconds] [t > 1 day]

Length [l < 1 nm] [l > 100 km]





Observation:

e.g., Strong dependence of surface reaction rate on surfactant coverage.

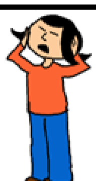
Science question:

e.g., Surface reactions impact oxidant loadings and lifetime of GHGs

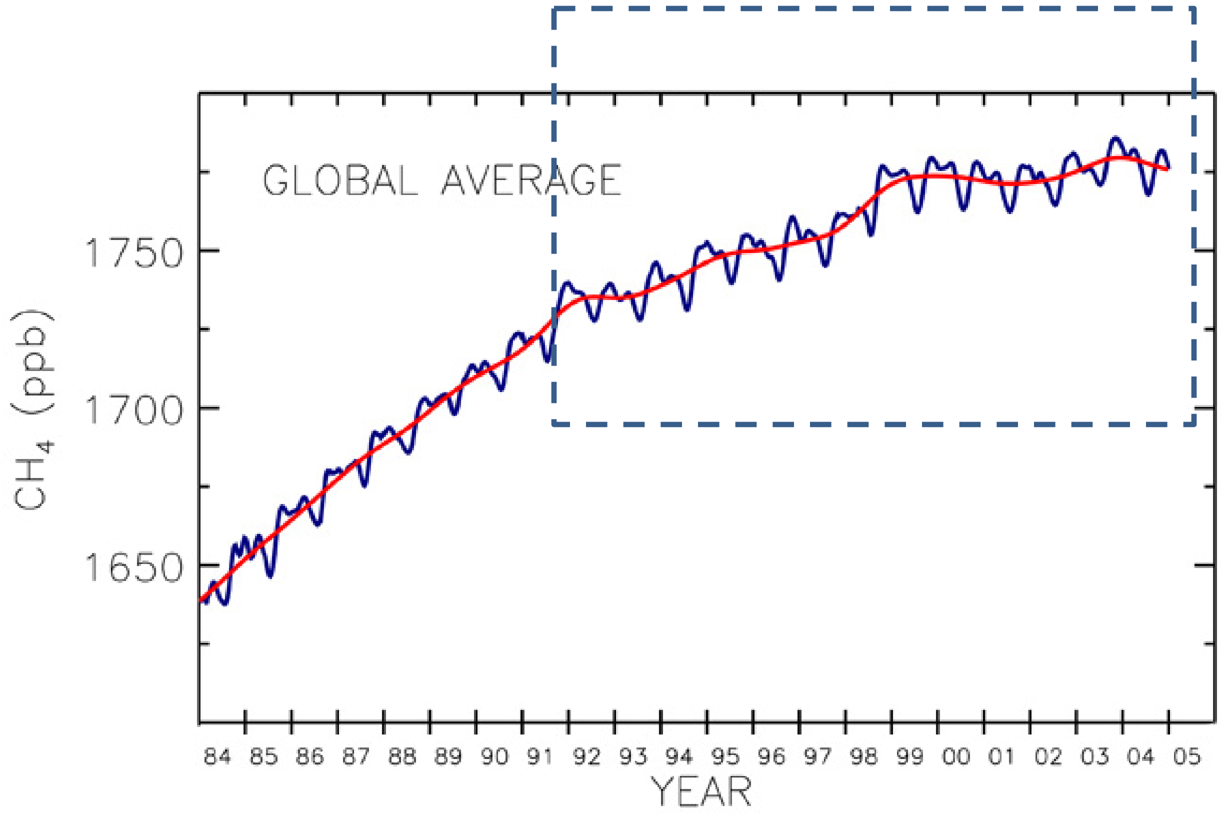
Reference: MD Simulation courtesy F. Paesani (UCSD)

Communication Breakdown

Legend

 = Climate Modeler  = Laboratory Chemist

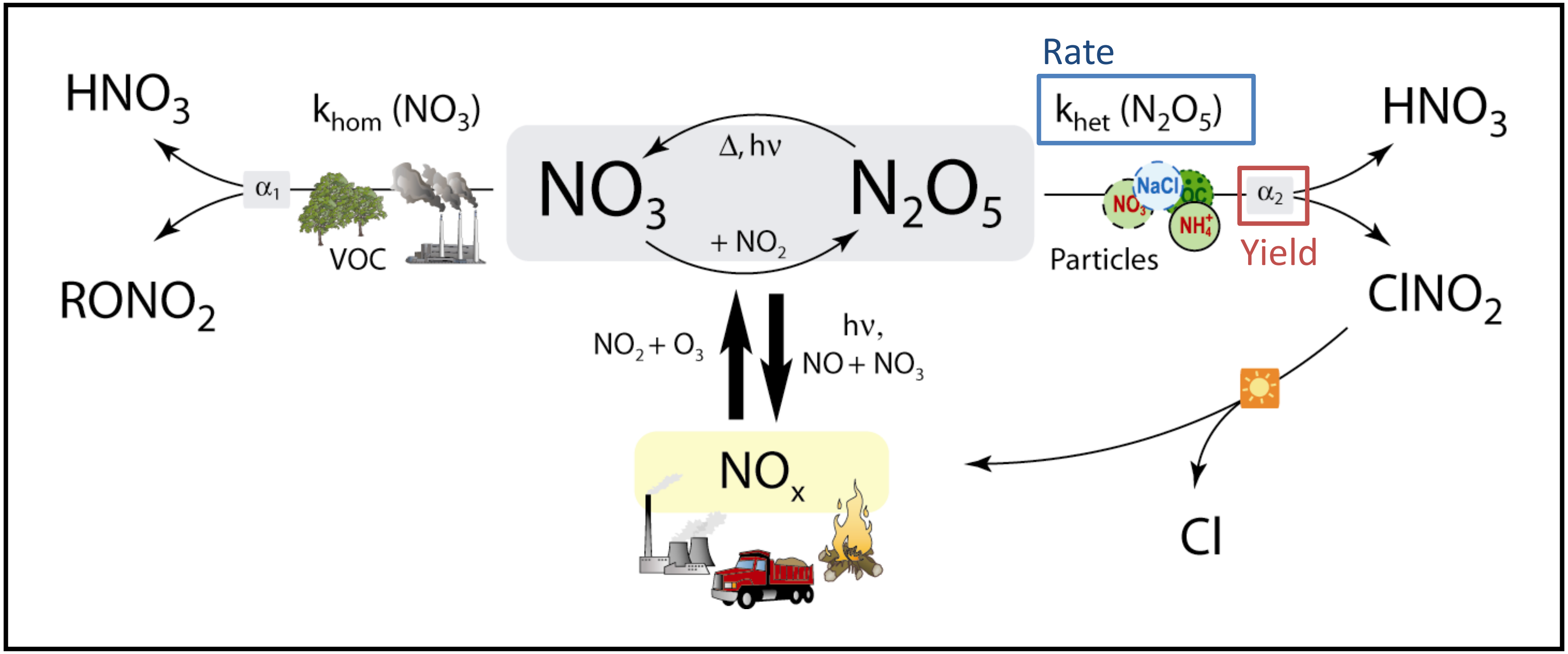
An Example: Halogen Activation Mechanisms



$$\frac{d[CH_4]}{dt} = \sum Sources - k[CH_4][OH] - k[CH_4][Cl] - k_{dep}[CH_4]$$

Reference: IPCC Report 2007 http://www.ipcc.ch/

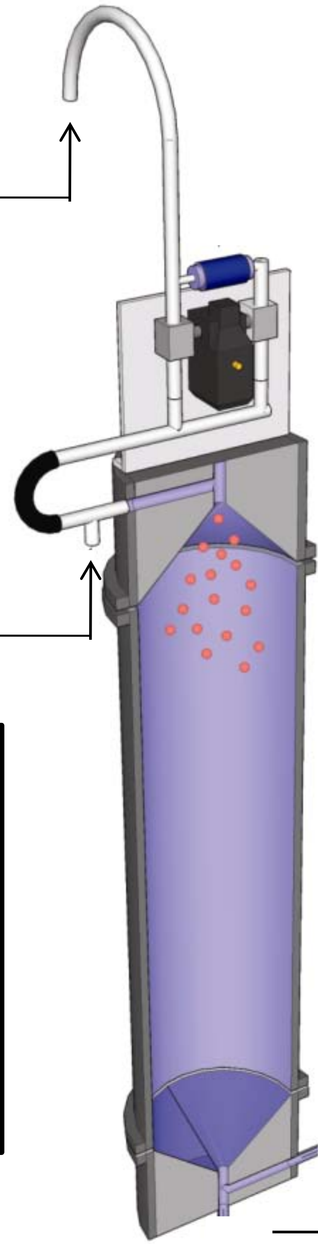
An Example: Halogen Activation Mechanisms



Science Questions:

1. Are heterogeneous reactions involving N_2O_5 a significant source of chlorine radicals?
2. What level of molecular complexity is required to accurately model the reaction mechanism?

Experiment Design



Surrogate **or** Ambient Aerosol Particles

Reactive Trace Gas

Trace Gas Detection [CI-ToFMS]

Single Particle Chemical Composition [ATOFMS]

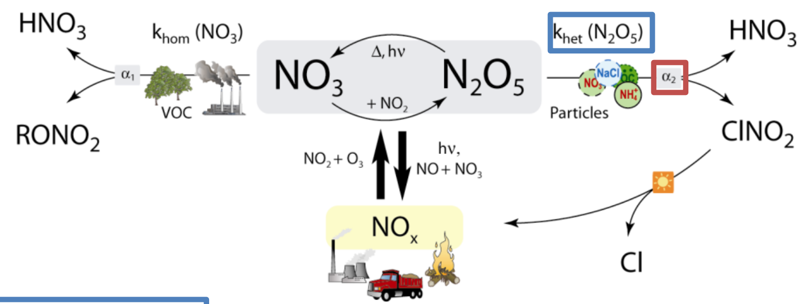
Observable:

Reaction Rate, $\gamma(N_2O_5)$
Product Yield, $Y(ClNO_2)$

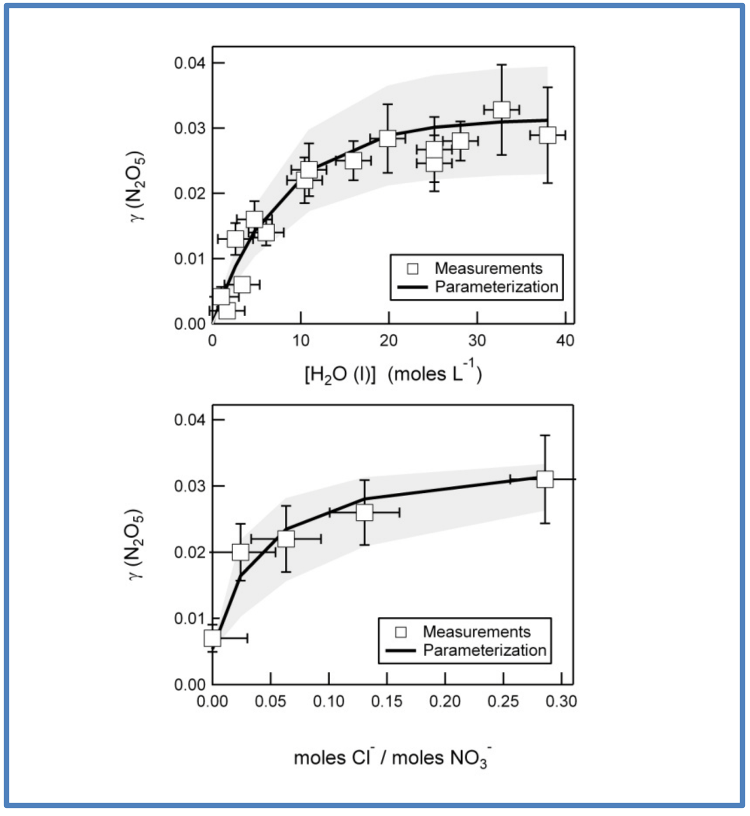
From **BOTH** gas and aerosol measurements

Reference: Bertram et al., *Atmos. Meas. Tech.*, **2009a**

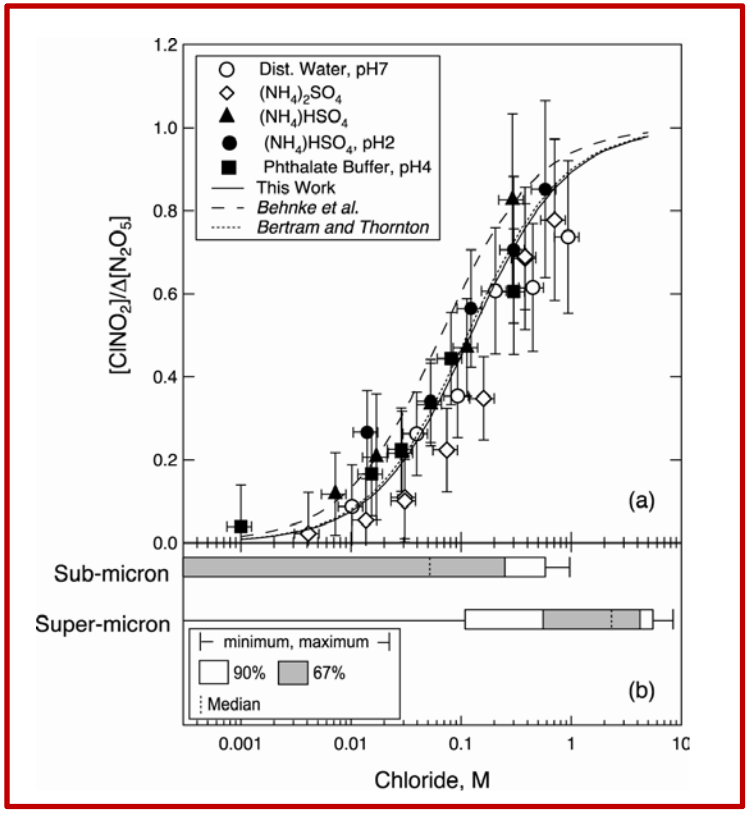
Molecular Level Findings



Reaction rate (γ)



Yield of $ClNO_2$



Reference: Bertram and Thornton, ACPD (2009), Roberts et al., GRL (2010)

Toward a General Parameterization of $\gamma(N_2O_5)$

Goal:

MODEL INPUT
particle chemical composition
relative humidity

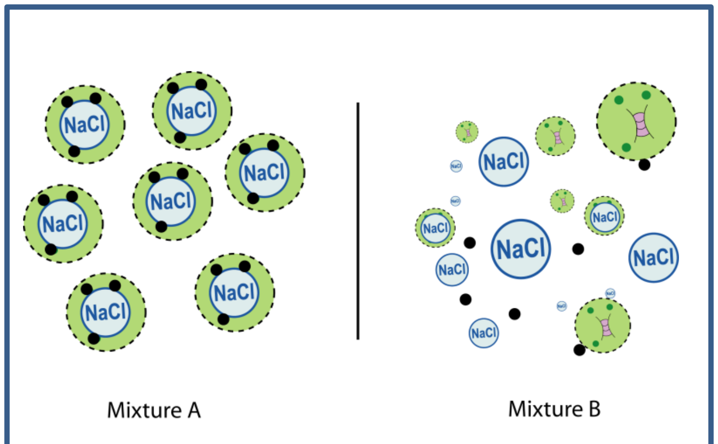
→

Empirical
γ (N_2O_5)
parameterization

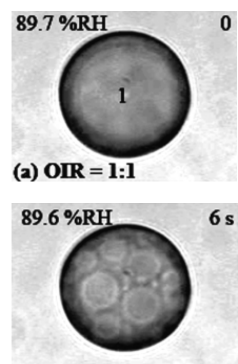
→

MODEL OUTPUT
P(Cl), $\tau(NO_x)$, $\tau(CH_4)$

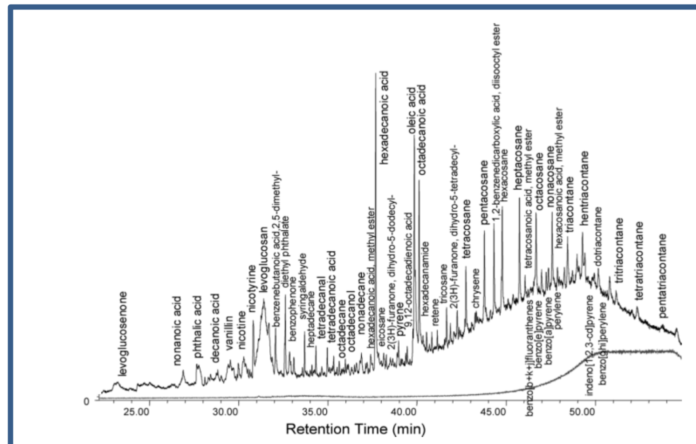
Confounding Factors



Mixing State



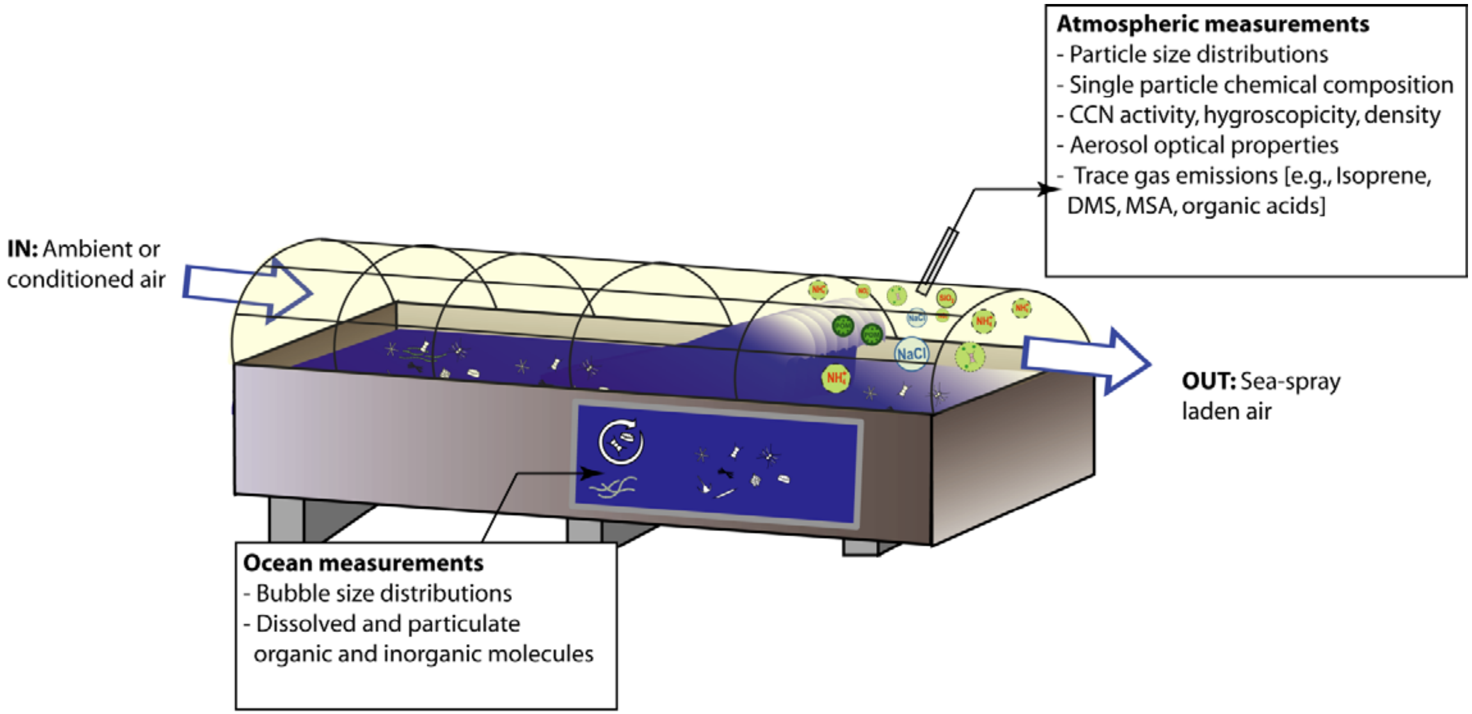
Morphology

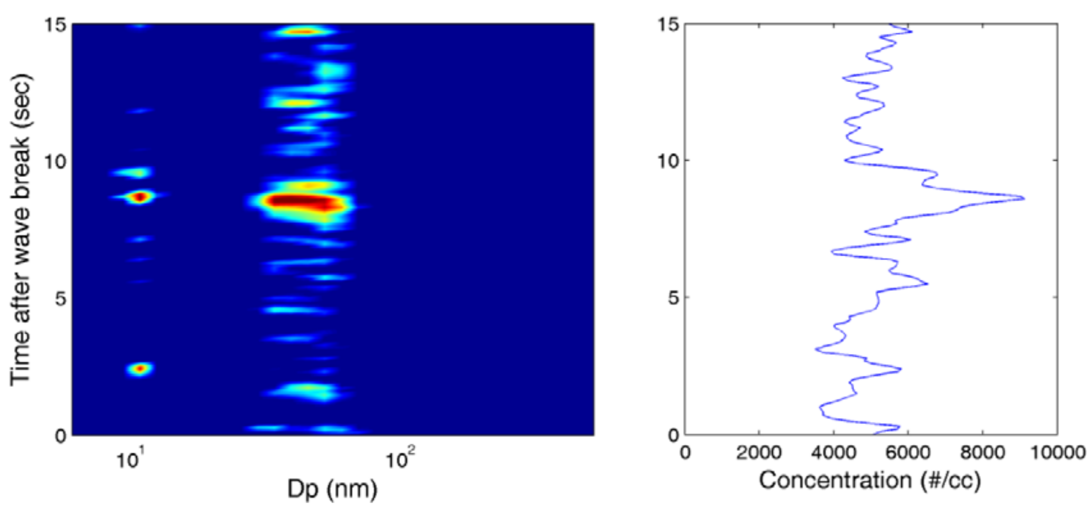


Complex organic component

References: Ciobanu et al., *JPC A* **2009** Williams et al., *Aerosol Sci. and Tech*. **2006**

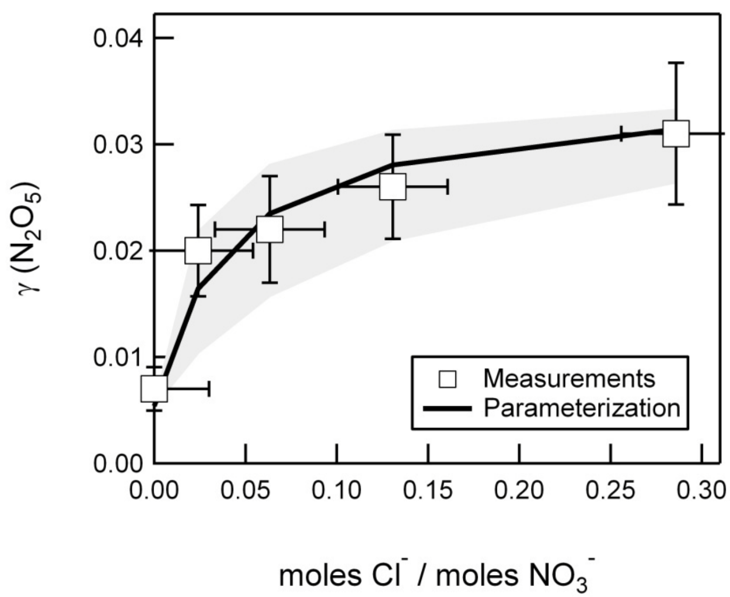
Macroscopic Laboratory Experiment





Reference: A collaborative project with the SIO hydraulics lab [Grant Deane, Lynn Russell, Kim Prather]

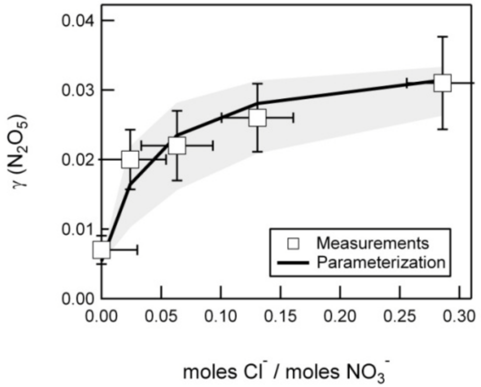
In Situ Observations of Kinetics



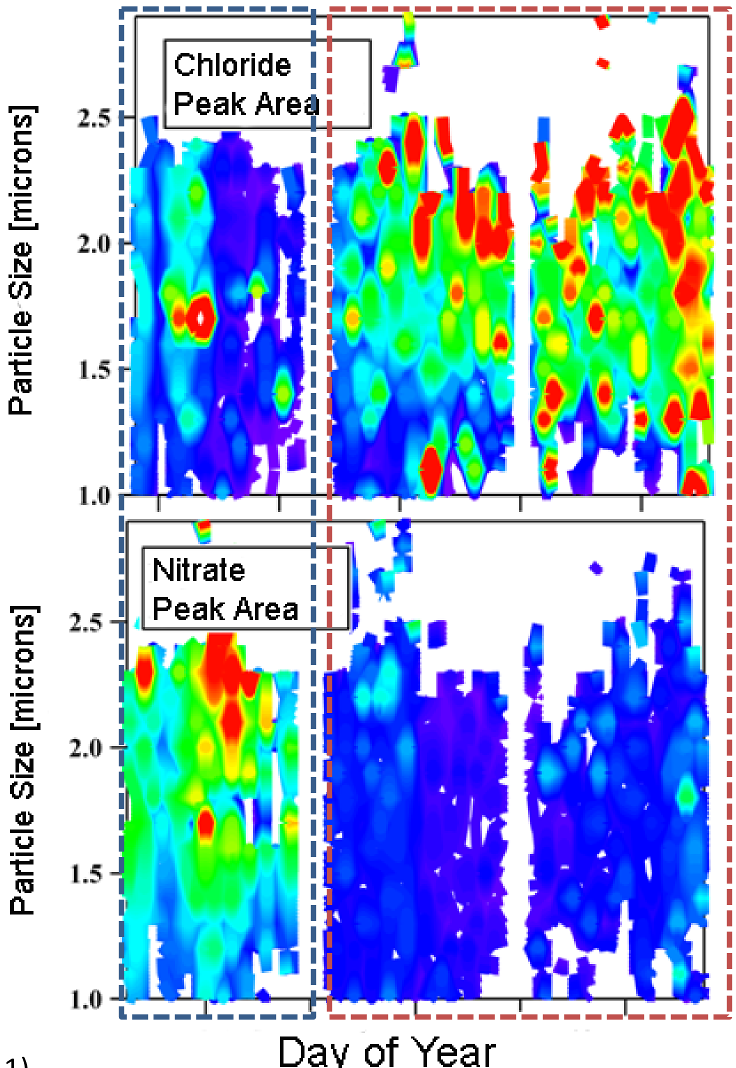
Reference: Bertram and Thornton, ACPD (2009)

In Situ Observations of Rates

Laboratory Prediction



Ambient Particle Composition

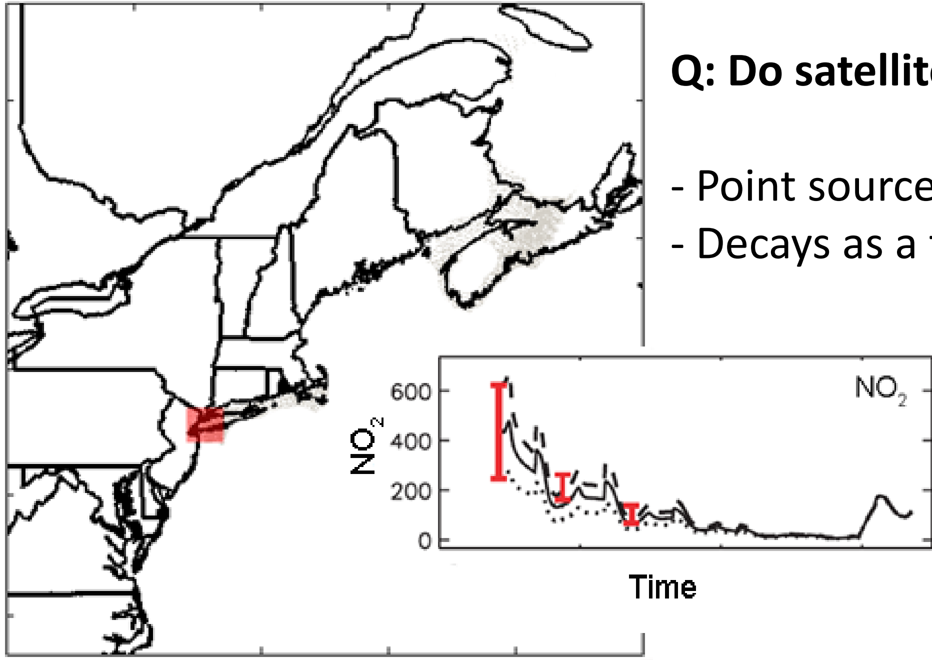


Region 1
$NO_3/Cl < 0.05$
$\gamma(N_2O_5) = 0.01$
$Y(ClNO_2) = 0.5$

Region 2
$NO_3/Cl > 0.5$
$\gamma(N_2O_5) = 0.035$
$Y(ClNO_2) = 1$

Reference: Ryder et al, in preparation (2011)

Remote Perspective



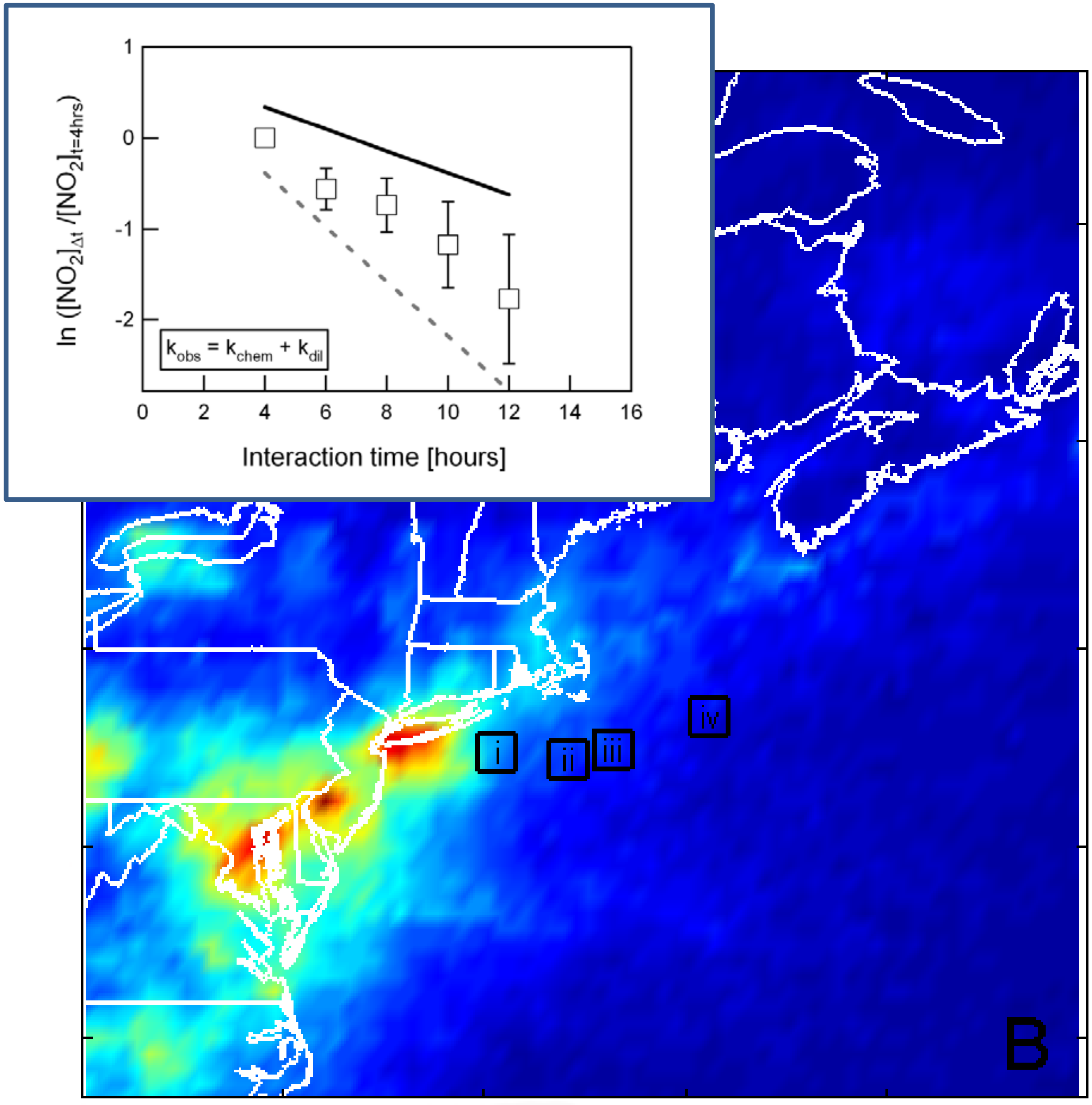
Q: Do satellite observations provide large scale constraints?

- Point source of NO_2
- Decays as a function of chemistry and mixing

Method: Use NO_2 observations from GOME-2 (9:30AM overpass)

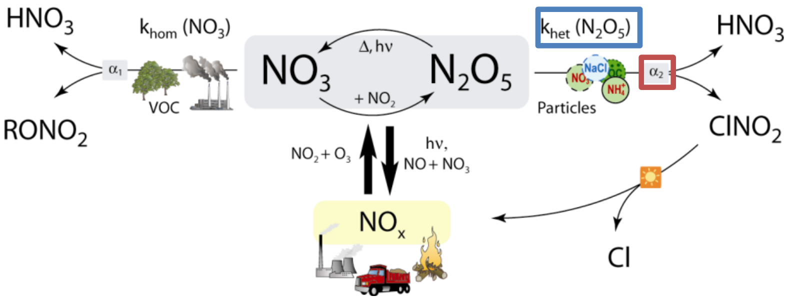
Point	Δt	Over NYC
i	4 hours	5:30 AM
ii	6 hours	3:30 AM
iii	8 hours	1:30 AM
iv	12 hours	9:30 PM

Remote Perspective



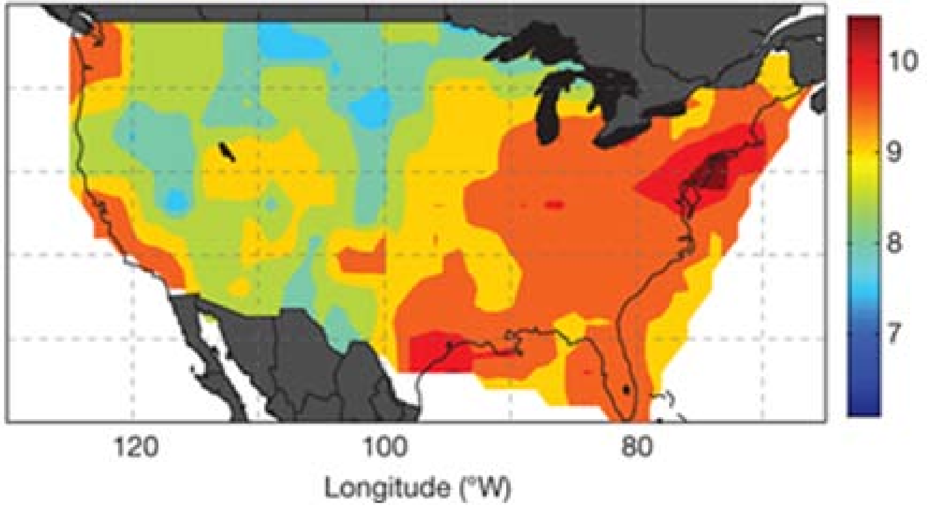
Model Integration

I. Laboratory: Rates and Yields



II. Model: Test empirical parameterizations

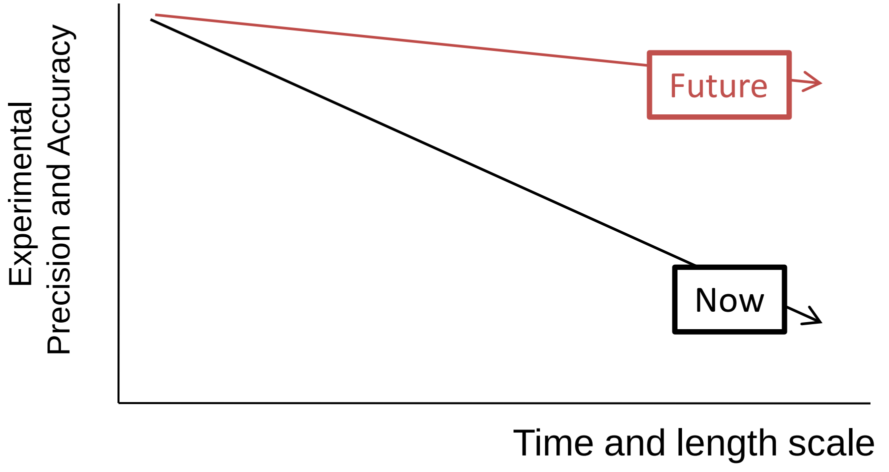
Modeled Cl production rates

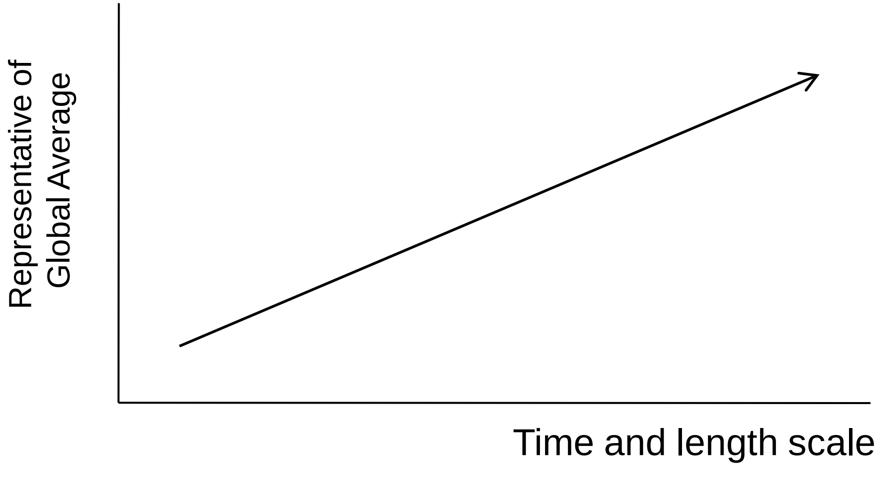


III. Challenge Model with observations on multiple scales

Reference: Thornton et al, Nature (2010)

Conclusions and Acknowledgements





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