Parameterization of N_2O_5 uptake and $ClNO_2$ yields

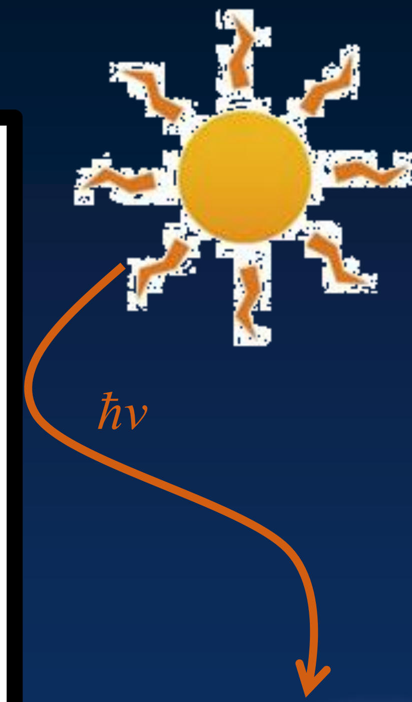
Jessica D. Haskins, Lyatt Jaeglé, Joel Thornton,
Cassandra Gaston, Viral Shah, Felipe Lopez-Hilfiker,
Ben Lee, & WINTER Science Team

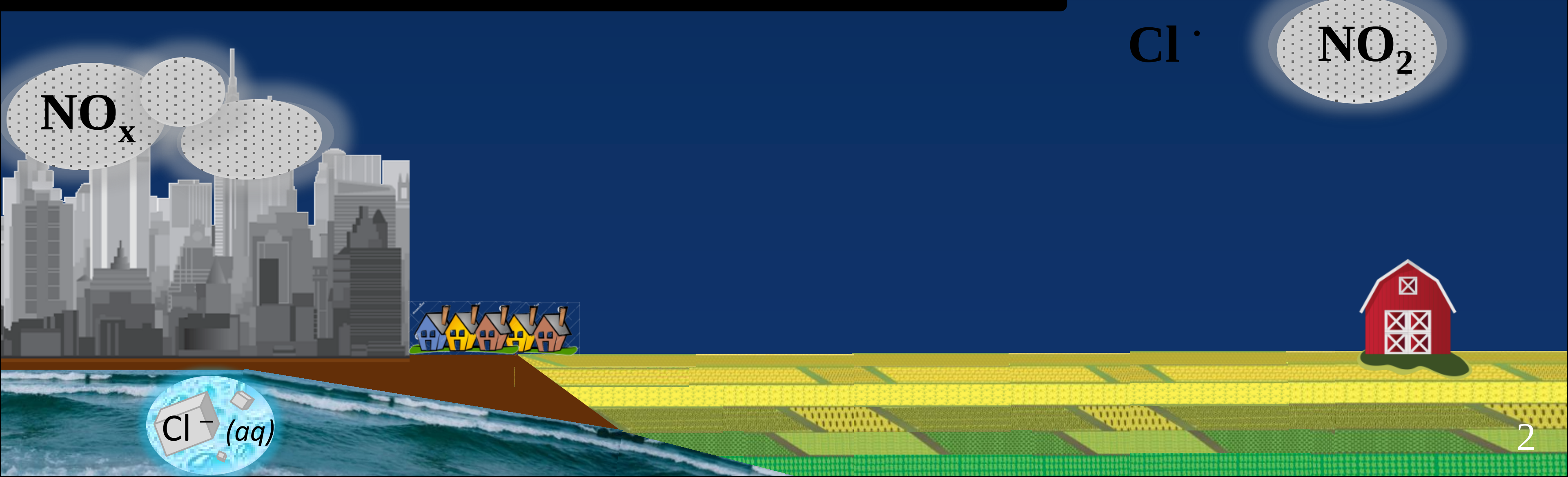
(1) $ClNO_2$ transports NO_x downwind affecting:

- Oxidative capacity
- Ozone production

(2) $Cl^{\cdot}$ acts as a morning radical source affecting:

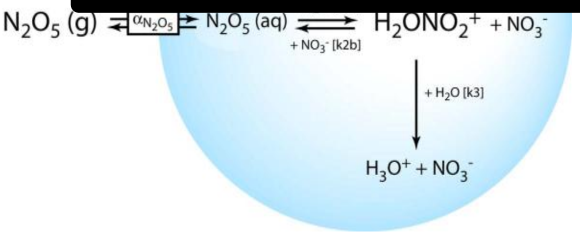
- Reactivity of organics
- PM concentration, composition





Goal: Use WINTER measurements to constrain and find the best parameterization to represent $\gamma(N_2O_5)$ and $\Phi(ClNO_2)$ in GEOS-Chem.

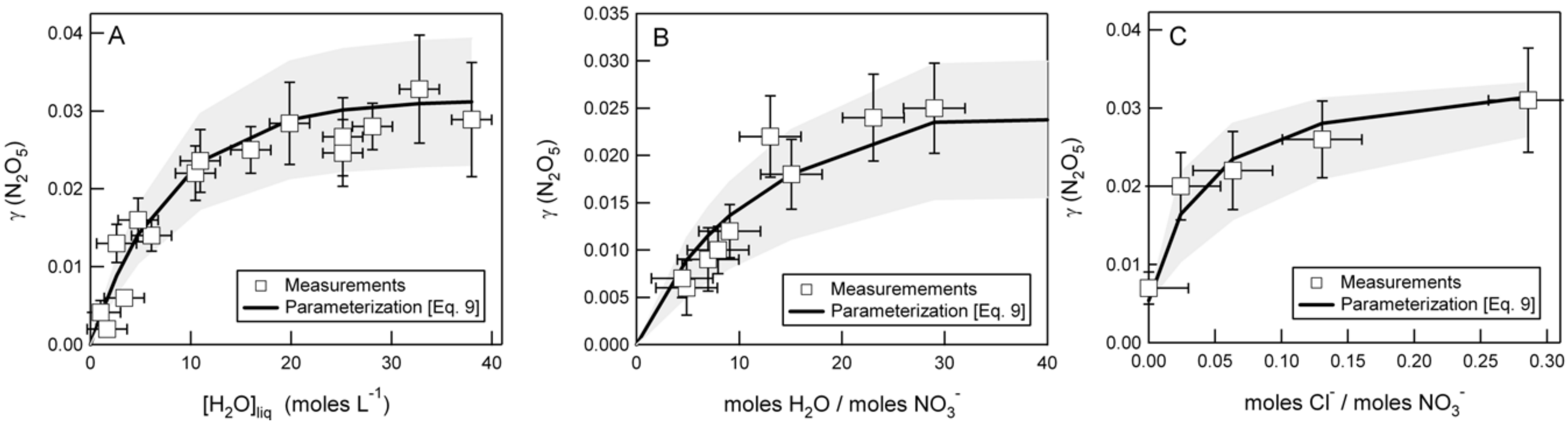
aq)



$$H_2ONO_2^+ (aq) + H_2O (l) \xrightarrow{k_3} H_3O^+ (aq) + HNO_3 (aq)$$

$$H_2ONO_2^+ (aq) + X^- \xrightarrow{k_4} XNO_2 + H_2O (l)$$

$$N_2O_5 (g) + Cl^- \xrightarrow{\gamma_{N_2O_5}} (2-\Phi)\ HNO_3 (g) + \Phi\ ClNO_2 (g)$$



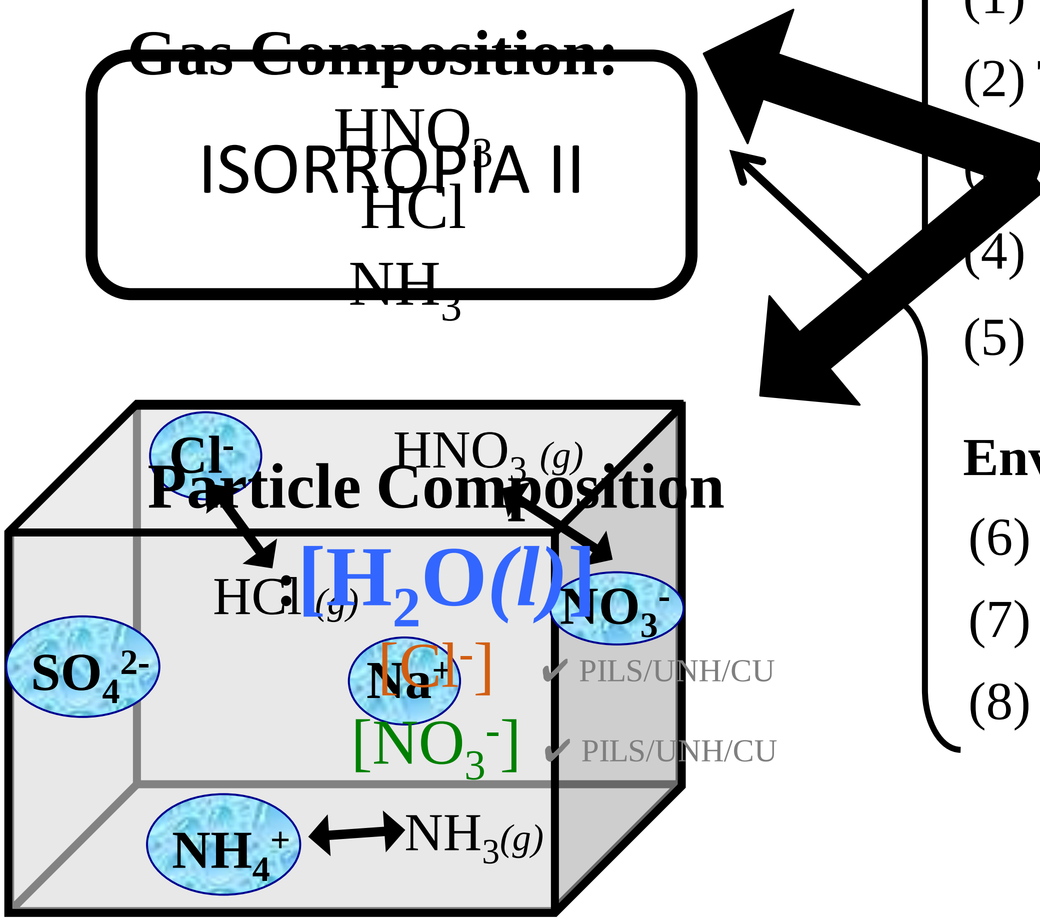
Bertram-Thornton Parameterization

$$\gamma(N_2O_5) = A\, k`_{2f} \left[1 - \left(\frac{k_3}{k_{2b}} \frac{[H_2O\,(l)]}{[NO_3^-]} + \frac{k_4}{k_{2b}} \frac{[Cl^-]}{[NO_3^-]} + 1 \right)^{-1} \right]$$

Need $[H_2O(l)]$, $[Cl^-]$, $[NO_3^-]$ to represent $\gamma(N_2O_5)$ and $\Phi(ClNO_2)$ with parameterization, but didn't measure $[H_2O(l)]$ in WINTER.

$$\Phi(ClNO_2) = \left(1 + \frac{k_3}{k_4} \frac{[H_2O\,(l)]}{[Cl^-]} \right)^{-1}$$

Methods: Model Description



Bulk Composition: **WINTER?**

(1) Total Chlorine ✔ CIMS1+PILs/UNH/CU

(2) Total Nitrate ✔ CIMS1+PILs/UNH/CU

(3) Total Ammonia ~GC+PILs/UNH/CU

(4) Sulfate ✔ PILS/UNH/CU

(5) Sodium ✔ PILS/UNH

Environment Variables:

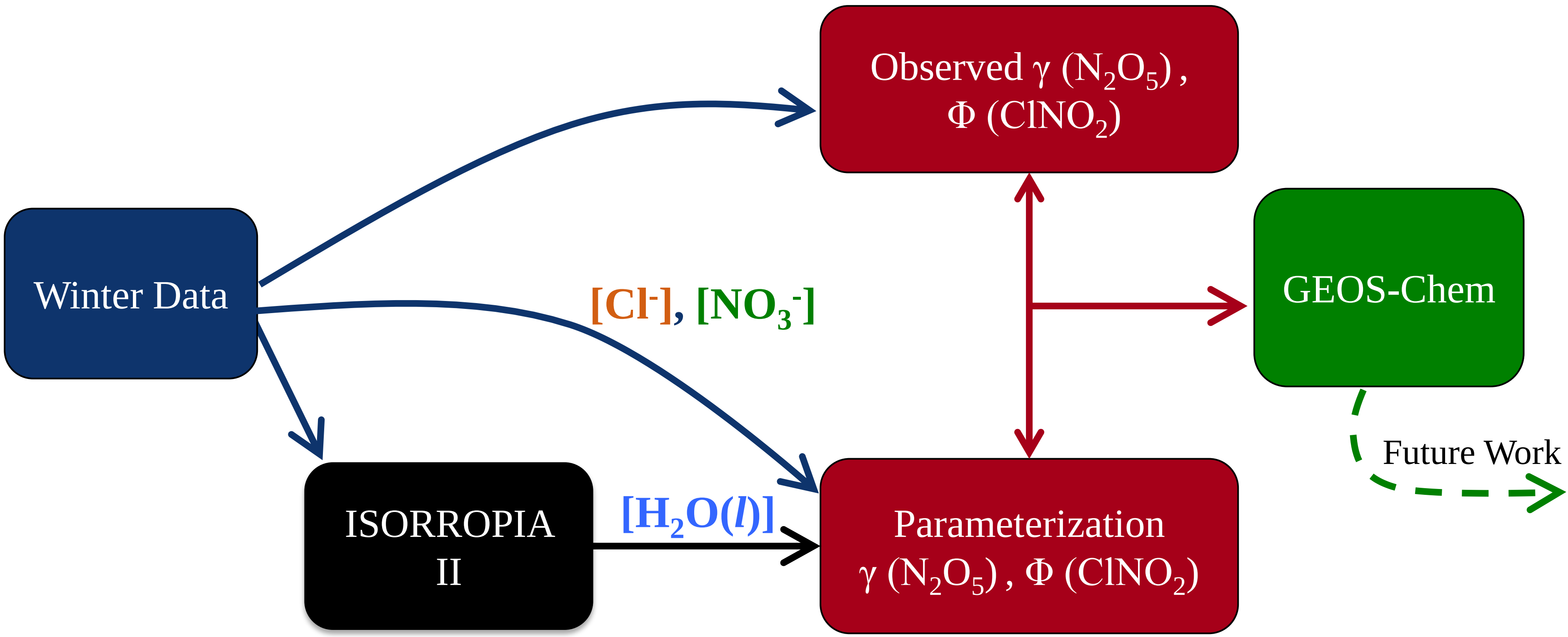
(6) Temperature ✔ RAF

(7) Relative Humidity ✔ RAF

(8) Pressure ✔ RAF

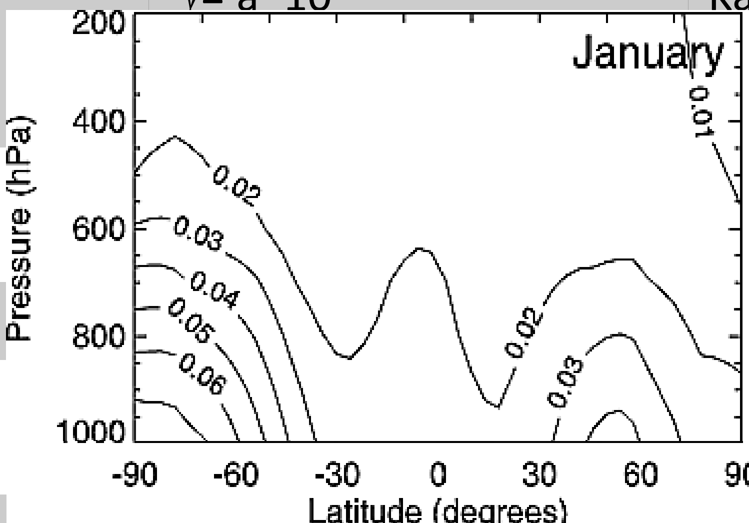
(Fountoukis & Nenes, 2007)

Methods: Data Flow



GEOS-Chem: $\gamma(N_2O_5)$ & $\Phi(ClNO_2)$

Aerosol Type	Reaction Probability	Reference
Sulfate	$\gamma = a*10^b$	Kane, et. al, 2001, liquist et. al, 2003,
Organic Carbon		ornton et. al, 2003
Black Carbon		nder et., 2003
Sea Salt		nder et., 2003
Dust	γ=0.01	Bauer, et., 2004



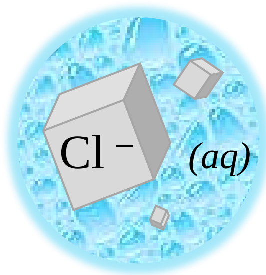
-Lyatt Jaeglé implemented simple $ClNO_2$ chemistry with:

$\Phi(ClNO_2)$ =1 on seasalt

$\Phi(ClNO_2)$ =0.02 on all other aerosols

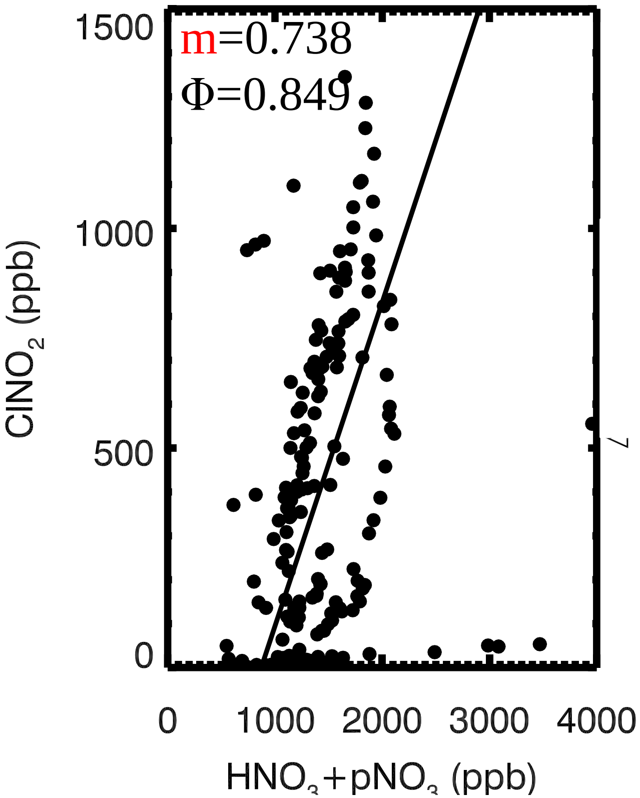
Inferences: $\Phi(ClNO_2)$

$N_2O_5(g)$ +



$\xrightarrow{\gamma_{N_2O_5}}$ $(2-\Phi)\ HNO_3(g) + \Phi\ ClNO_2(g)$

RF03



$$m = \Delta y / \Delta x$$

$$m = \frac{\Delta ClNO_2}{\Delta T(NO_3)} = \frac{\Phi}{2-\Phi} \rightarrow \boxed{\Phi = \frac{2m}{m+1}}$$

(1) Assumes no loss of $ClNO_2$ or $T(NO_3)$

(2) x-intercept is residual HNO_3 at sunset since all $ClNO_2 \rightarrow 0$ by sunset.

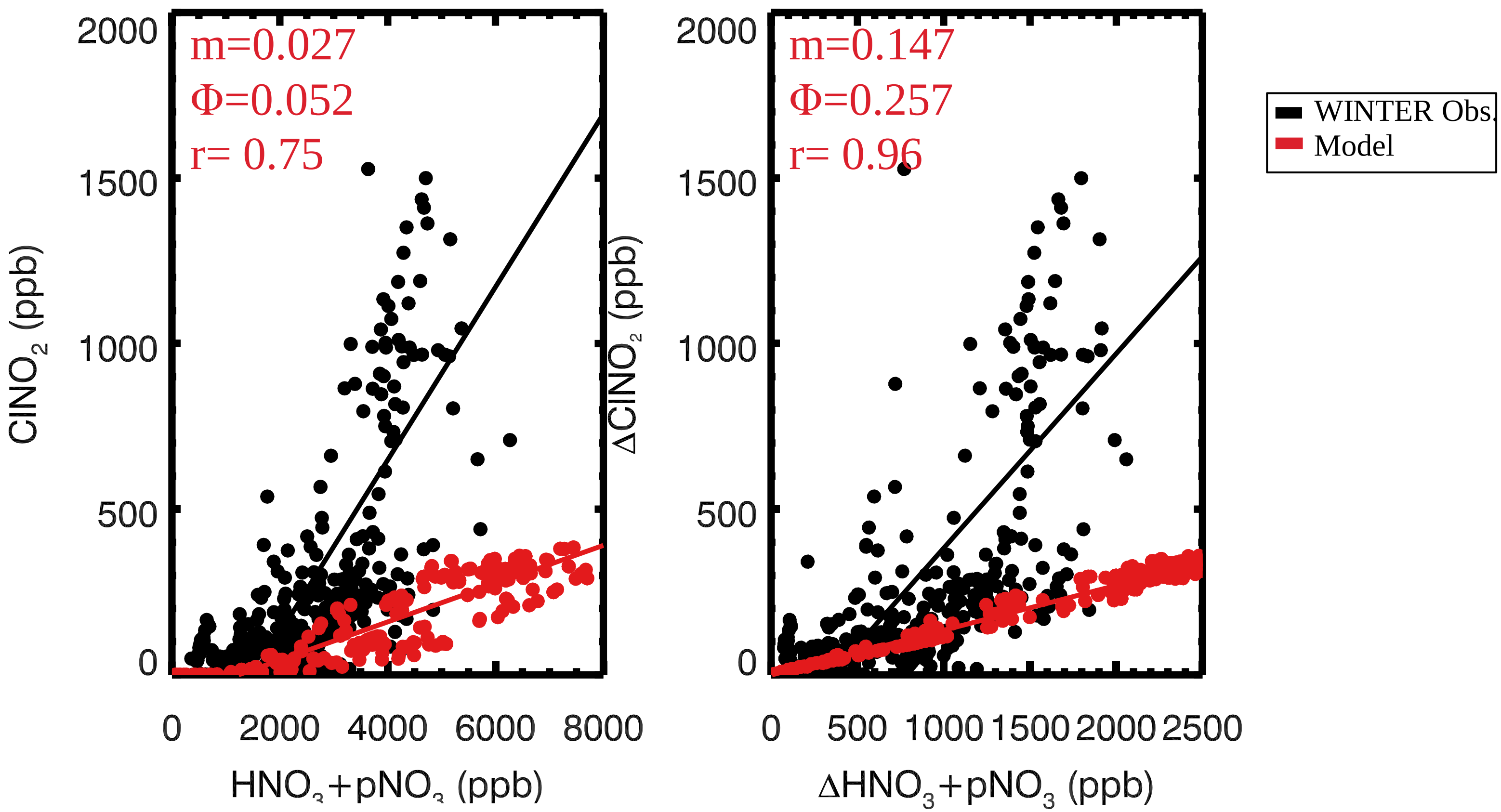
Inferences: $\Phi(ClNO_2)$

$$\text{Total}(NO_3)_{\text{adjusted}} = \text{Total}(NO_3)_{\text{original}} - \left[\frac{-b}{m}\right] \times \frac{\text{Inferred } \Phi_{GC}}{\text{Known } \Phi_{GC}}$$

$y = mx + b$

$x(0) = -b/m$

RF03- Aged Outflow



ISORROPIA II Inputs

Total Sulfate
PILS/CU/UNH

Total Sodium
PILS/PILS/UNH

Total Nitrate
PILS/CU/UNH +CIMS1

Total Ammonia
PILS/CU/UNH+ GEOS-Chem

Total Chlorine
PILS/CU/UNH + CIMS1

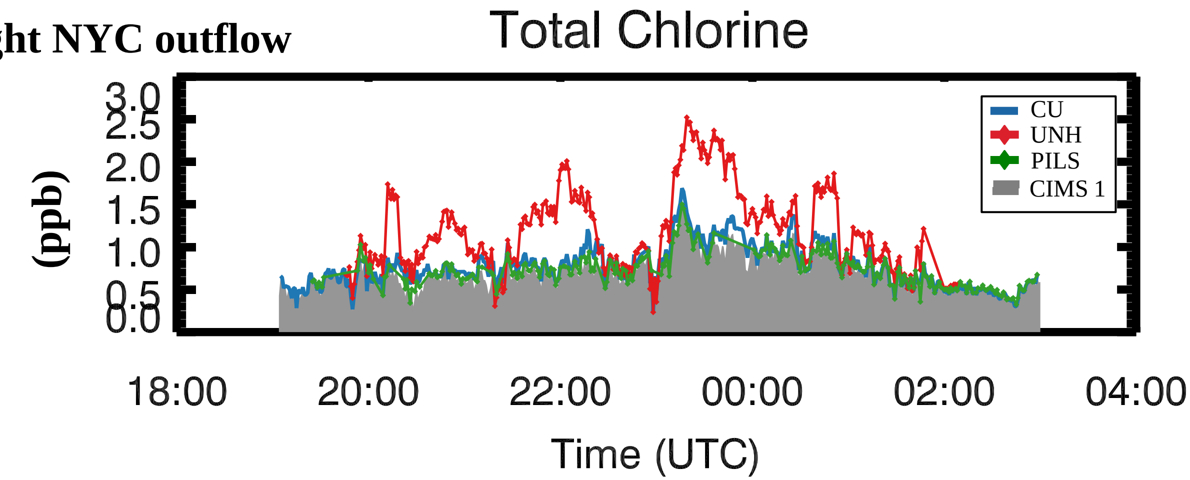
↓

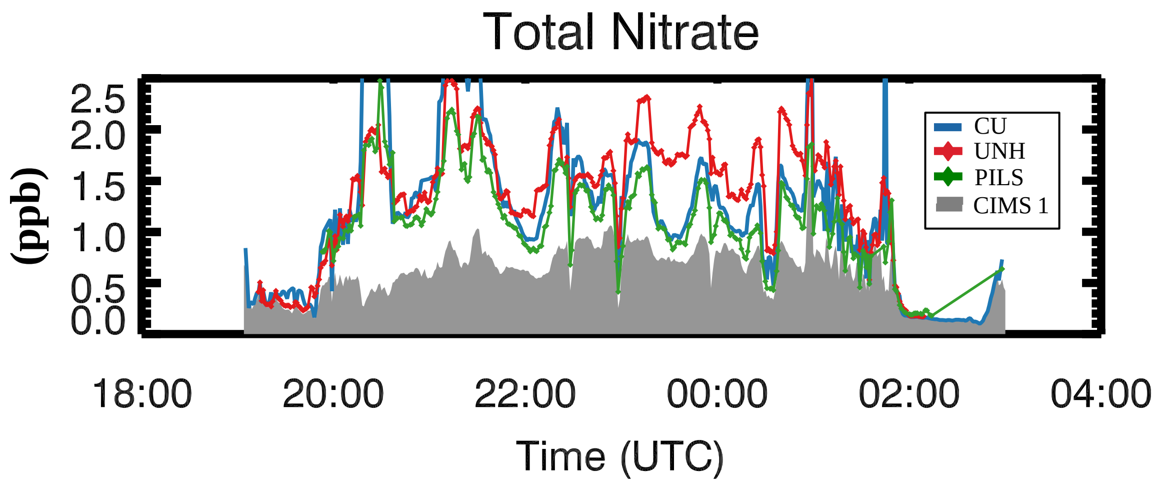
ISORROPIA II

- 3*x* ISORROPIA II runs with different particle data from PILS, CU, UNH, results from 2 flights contrasted.
- Interpolated between *NaNs* for a continuous data set, 60s merges

ISORROPIA II Inputs

RF03- Night NYC outflow

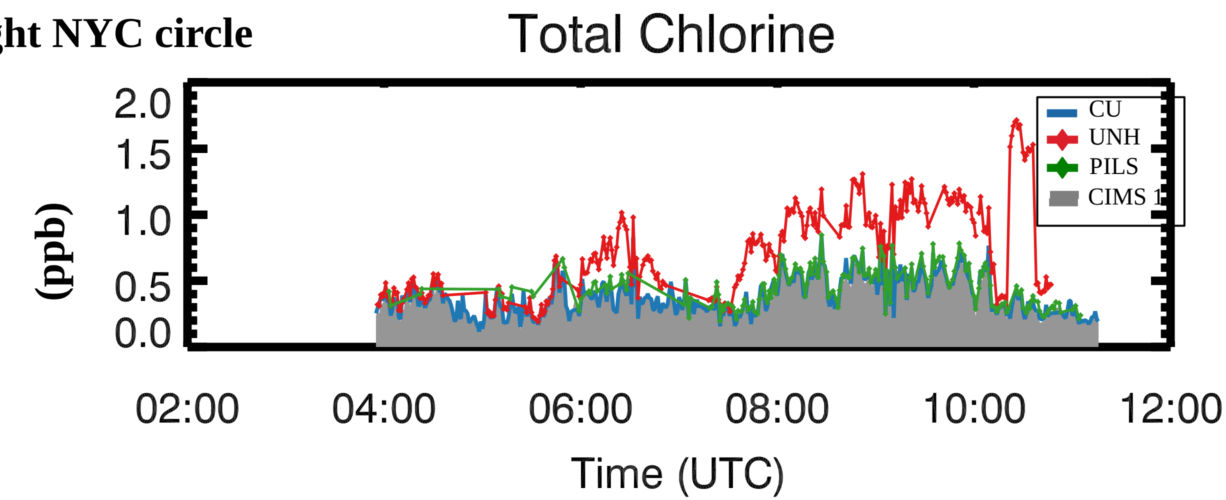


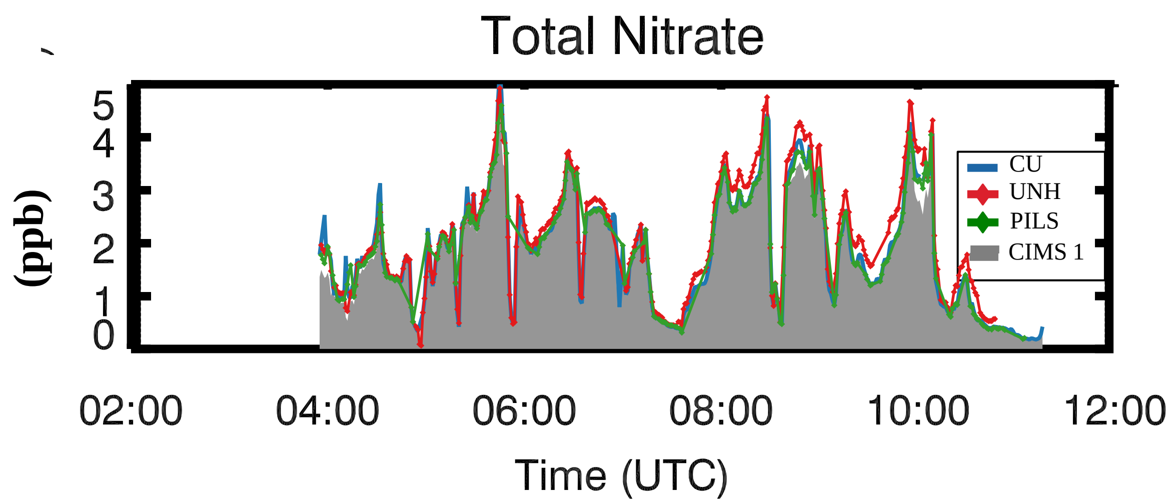


- Differences in Cl- measurements techniques, instruments → What is the most appropriate ISOROPIA input for bulk chlorine?

ISORROPIA II Inputs

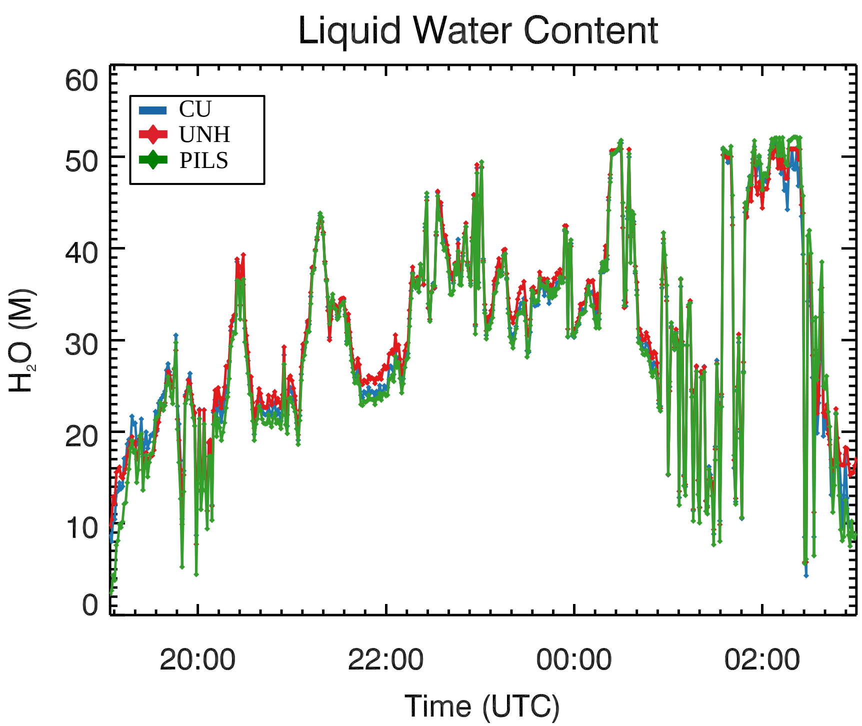
RF06- Night NYC circle



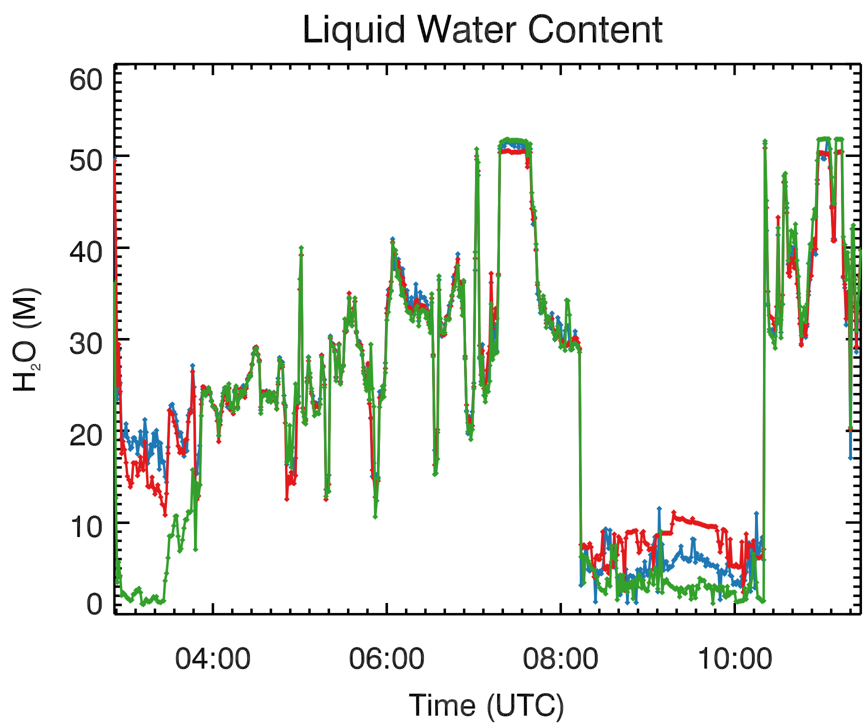


ISORROPIA II Output:

RF03- Aged Outflow



RF06- Nighttime NYC Circle

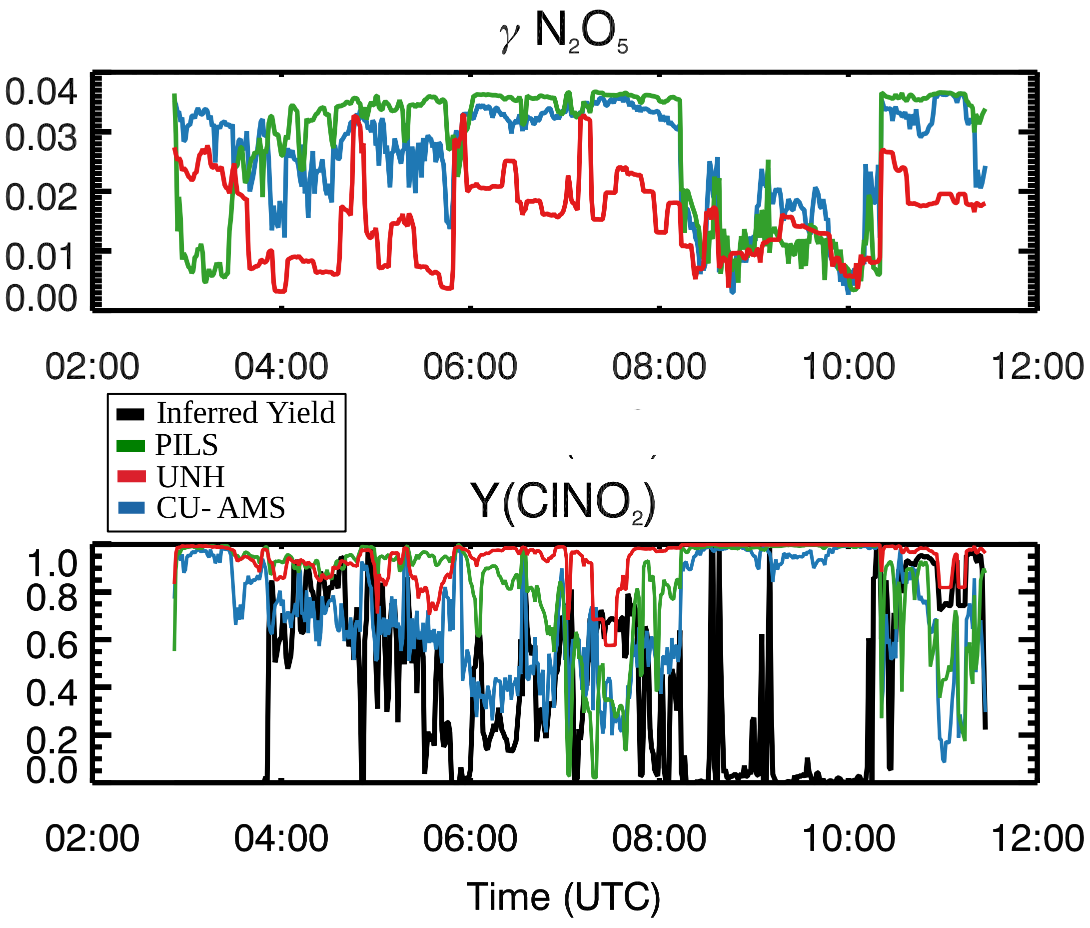


- ISOROPIA isn't that sensitive to the different inputs when it comes to predicting particle liquid water content.
- Caveat: Biggest differences show up when particle is more dry.

Results

$$\Phi\,(ClNO_2) = \left(1 + \frac{k_3}{k_4}\frac{[H_2O\,(l)]}{[Cl^-]}\right)^{-1}$$

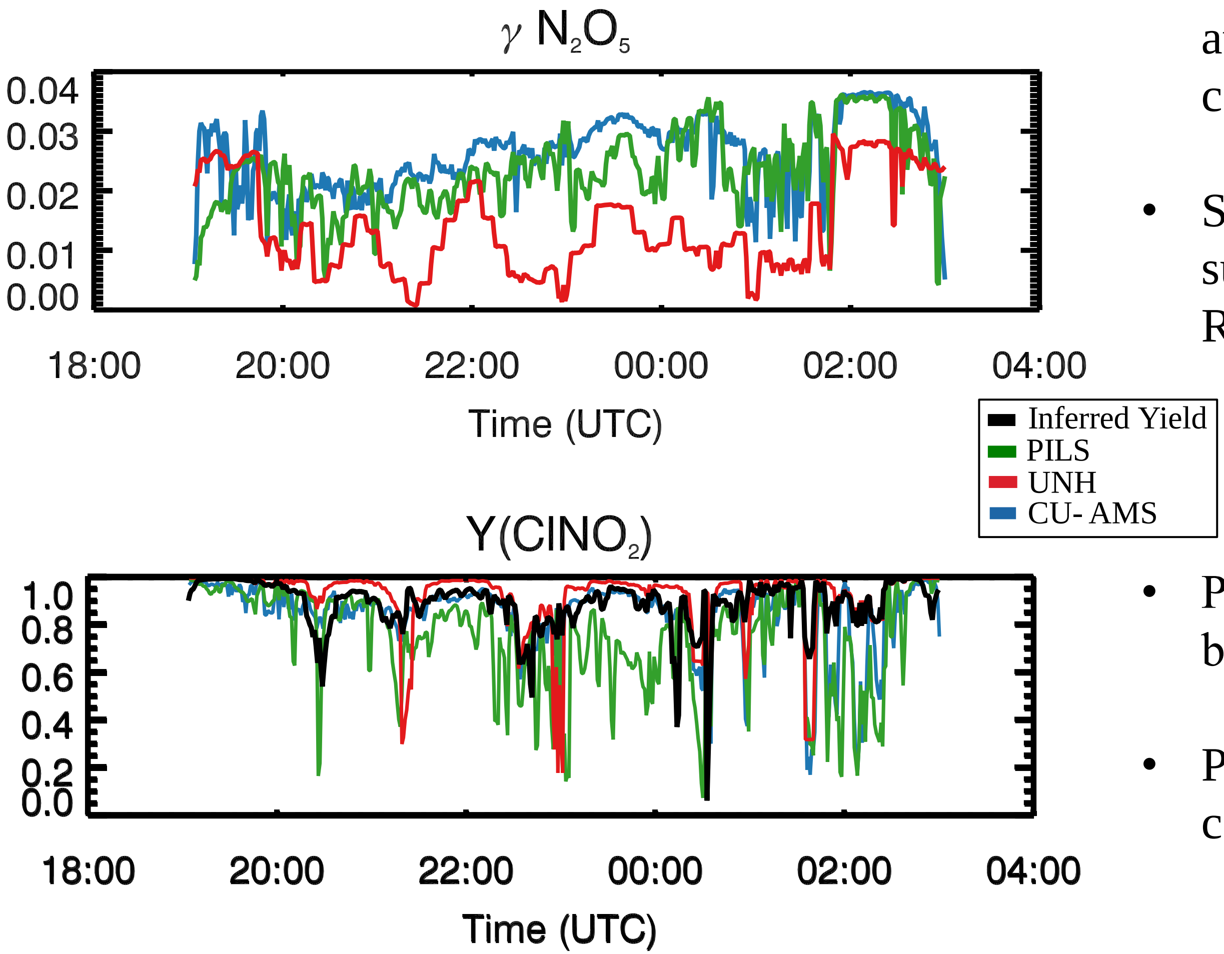
RF06- Night NYC Outflow



- It *matters* which data set for Cl^- is used in the parameterization!
- Coming soon: WINTER obs. $\gamma(N_2O_5)$
- Using larger Cl, UNH gives distinctly higher yield, lower gamma.

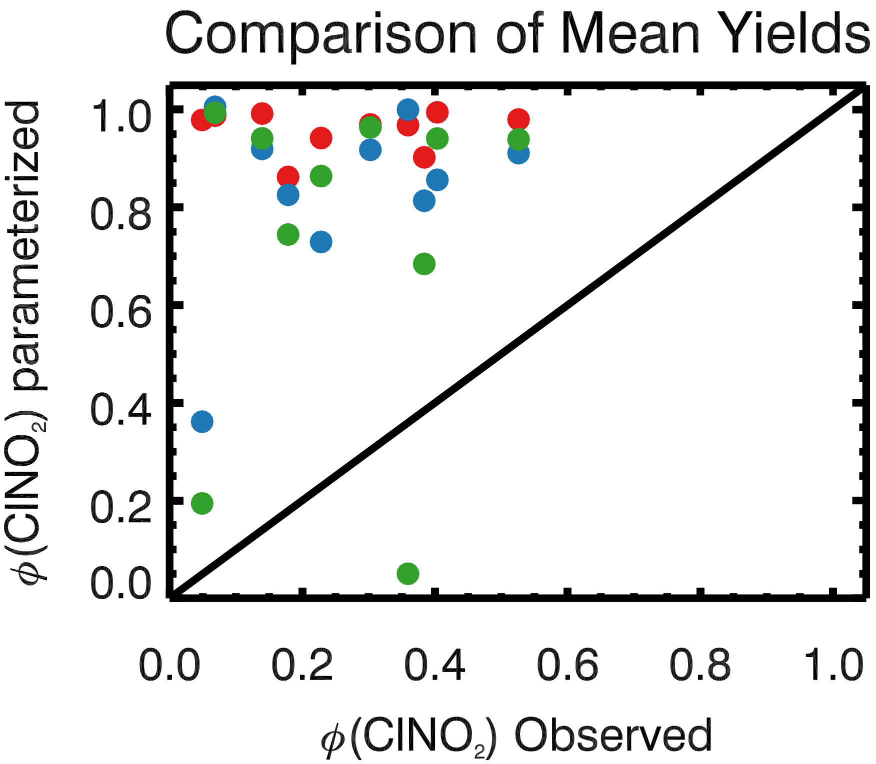
Results

RF03- Aged outflow



- Parameterized gamma ~0.035 at max, down to 0.01 in some cases
- Some particle nitrate case, suppress gamma compared to RF06.
- Parameterization isn't all bad…
- Predicts yields >0.8 in most cases

All flights comparison: Mean Yields

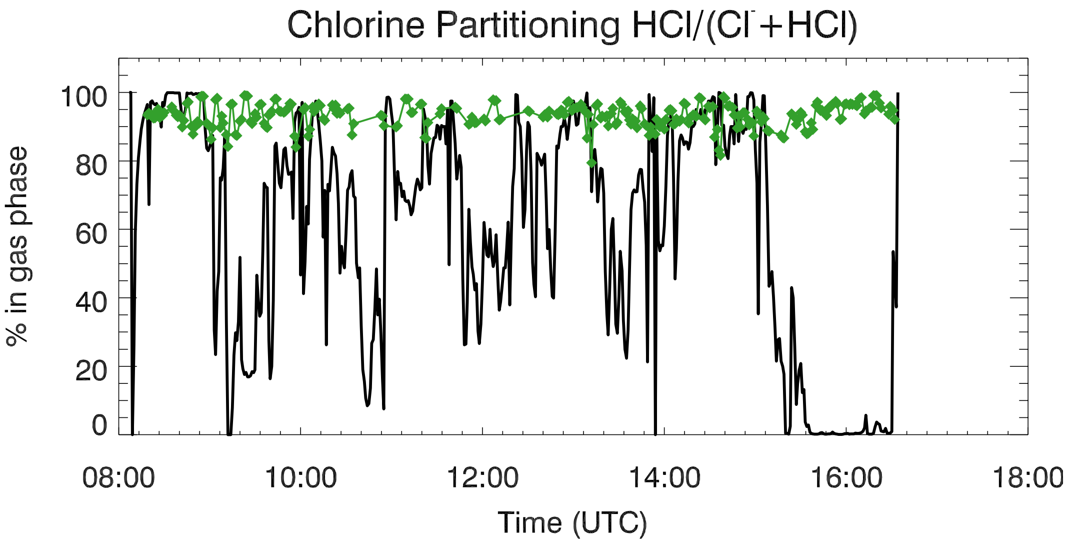


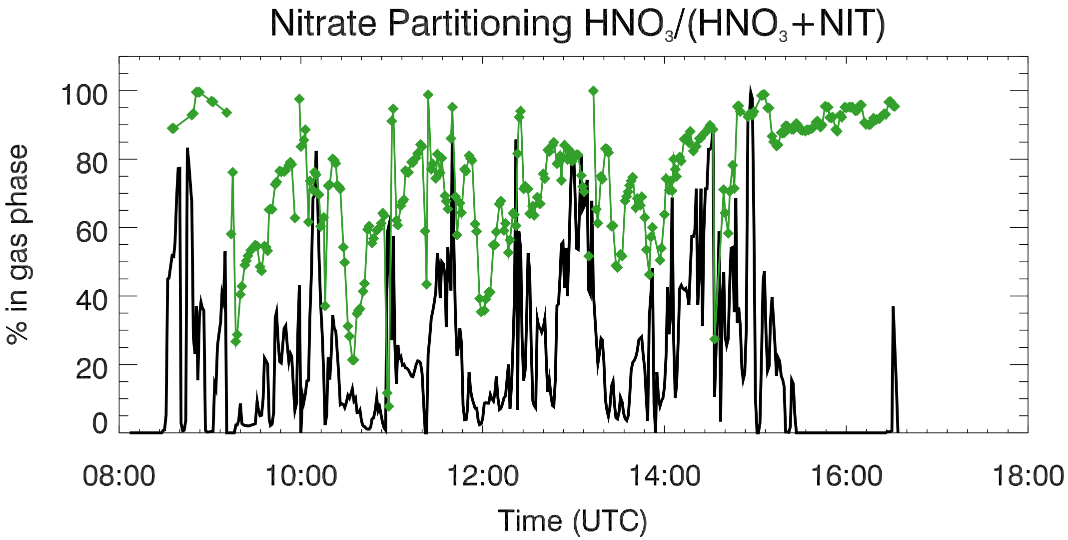
- Generally, parameterized yield higher than observed yields
- UNH, with larger Cl- always gives higher yield, rarely below 0.85
- Plume by plume analysis, more useful to see when parameterization good, when worse.

Going Forward…

- Compare parameterized $\gamma_{N_2O_5}$ to WINTER observational $\gamma_{N_2O_5}$
- Look into running with inferred NH_3 from iterative ISORROPIA calculations *(created by Viral Shah)*
- Better ways to calculate observational $\gamma_{N_2O_5}$ and Φ $ClNO_2$?
- Parameterizations with organics & temperature dependency
- Update GEOS-Chem & implement $ClNO_2$ chemistry to further investigate nighttime processing effects

Reality Check: ISOROPIA partitioning





RF08- Night NYC hourglass

WINTER: (CIMS 1 + PILS)

ISOROPIA output

- ISOROPIA predicts more partitioning into the particle phase than is seen.
- Disagreement generally **worse for chlorine** partitioning than nitrate partitioning across all flights
- Need to know NH_3… & which Cl^- measurement actually represents the bulk.