# Measurement and Model Evaluation of $N_2O_5$ Heterogeneous Chemistry in the Upper Troposphere and Lower Stratosphere

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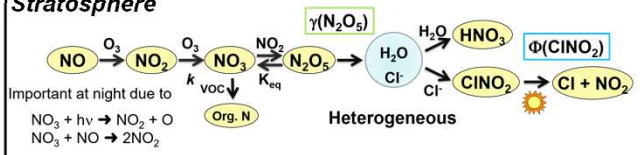
## SUMMARY

Dinitrogen Pentoxide ($N_2O_5$) is a key $NO_x$ reservoir with impacts on $O_3$ production, $NO_y$ partitioning, and halogen activation. The atmospheric fate of $N_2O_5$ is in part controlled by heterogeneous uptake to aerosol particles. Observational constraints on $N_2O_5$ heterogeneous chemistry in the upper troposphere/ lower stratosphere (UT/LS) are extremely sparse.

We present measurements of $N_2O_5$ mixing ratios in the UT/LS from the NASA ATom campaign and use them to inform an observationally constrained chemical box model to determine the heterogeneous uptake coefficient of $N_2O_5$ ($\gamma(N_2O_5)$).

Median $\gamma(N_2O_5)$ was 0.023 with an 25th-75th percentile range of 0.008 – 0.057. $\gamma(N_2O_5)$ was highly correlated with aerosol sulfate mass fraction ($R^2$ = 0.74) providing a potential simple method to parameterize $\gamma(N_2O_5)$ in the UT/LS.

## I. *$N_2O_5$ chemistry in the Upper Troposphere/Lower Stratosphere*

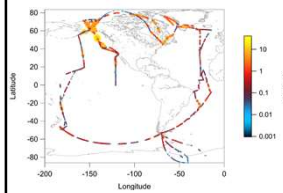



| | Lower Atmosphere | Upper Atmosphere |
|---|---|---|
| Thermal lifetime of $N_2O_5$ | < 1 hour | Days to years |
| Role of $NO_3$ | Strong oxidant | Suppressed in $N_2O_5$ equilibrium |
| Het. $N_2O_5$ uptake | Major $NO_x$ Loss → Regional $O_3$ | $NO_y$ partitioning → UT/LS $O_3$ |
| Role of $ClNO_2$ | Regional halogen source | Unexplored |

**$N_2O_5$ Heterogeneous Uptake Coefficient: $\gamma(N_2O_5)$**

**$ClNO_2$ yield: $\Phi(ClNO_2)$**

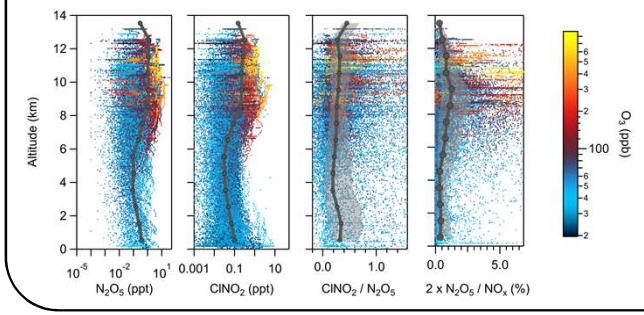
## II. *The Atmospheric Tomography Mission (ATom)*




$N_2O_5$ and $ClNO_2$ mixing ratios by I⁻ chemical ionization time-of-flight mass spectrometry on the ATom 3 and 4 campaigns

Global sampling at altitudes from 0 to 14 km during the ATom 3 and 4 campaigns on the NASA DC-8 aircraft

| Molecule | Mean (ppt) | Median (ppt) | 1σ (ppt) | Interquartile Range (ppt) | LOD (ppt, 1 σ, 1 Hz) |
|---|---|---|---|---|---|
| $N_2O_5$ | 0.88 | 0.13 | 1.93 | 0.01 – 0.73 | 0.1 |
| $ClNO_2$ | 0.17 | 0.05 | 0.42 | 0.01 – 0.14 | 0.1 |




## III. Iterative chemical box model for $N_2O_5$ uptake

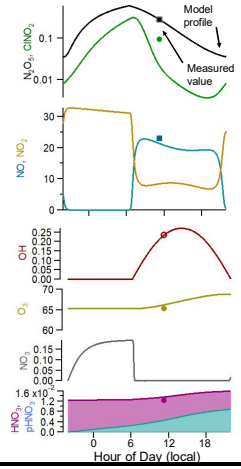
Diel cycle model for $N_2O_5$, iterated to fit each of the following:

1. Iterate $NO_x$ to match $NO_{obs}$ at fixed $O_3$; Calc. $NO_2$ from model
2. $k_{het}(N_2O_5)$; Calc. $\gamma(N_2O_5)$ from aerosol surface area
3. Calc. $\Phi$ ($ClNO_2$) to fit $ClNO_2$ using determined $\gamma(N_2O_5)$

Observationally constrained by measured T, P, $H_2O$, aerosol surface area, photolysis rates, $O_3$, etc.

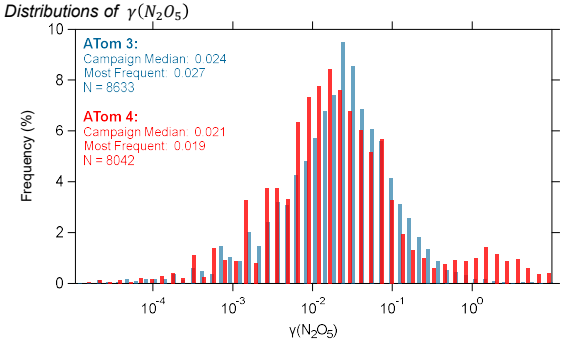
Assumes a closed box over the diel cycle (no transport in/out of the box)

Only consider data at altitudes >6 km to avoid interferences in $N_2O_5$ signal from an isobaric molecule.

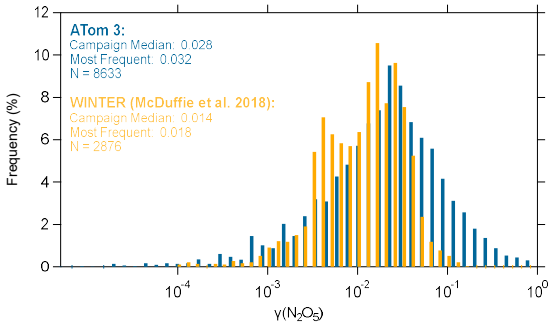



## IV. Results

*a.) Distributions of $\gamma(N_2O_5)$*

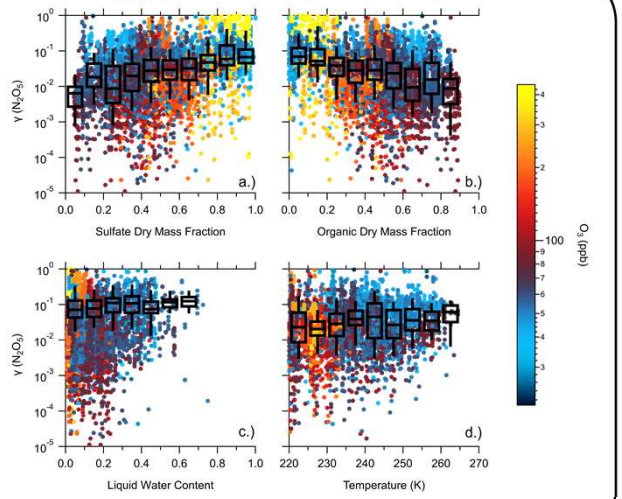



Distribution of $\gamma(N_2O_5)$ from the ATom 3 (fall 2017) and ATom 4 (spring 2018) campaigns.




Distribution of $\gamma(N_2O_5)$ from the ATom 3 (fall 2017) and the Wintertime INvestigation of Transport, Emissions, and Reactivity (WINTER) campaign sampling in the nocturnal residual boundary layer in 2015[1].

*b.) Correlation of $\gamma(N_2O_5)$ with aerosol composition and temperature*



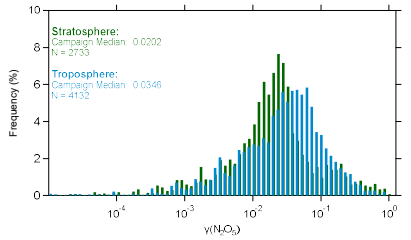

Correlations of $\gamma(N_2O_5)$ with aerosol sulfate (a), organic (b), and liquid water (c) mass fractions, and with temperature (d) for ATom 3. $\gamma(N_2O_5)$ is highly correlated with the aerosol sulfate mass fraction ($R^2$ = 0 .74), while organic mass fraction is strongly anticorrelated with $\gamma(N_2O_5)$. An increase in $\gamma(N_2O_5)$ with sulfate mass fraction is consistent with prior lab studies for stratospheric sulfuric acid aerosols[2,3].

*c.) Separating tropospheric and stratospheric trends*

$\gamma(N_2O_5)$ was found to be higher in tropospheric air masses.

The mechanism for this difference is unclear and is being actively investigated.

Future sampling deeper into the stratosphere at a wide latitude range will be critical to evaluate stratospheric $N_2O_5$ het chem.




## V. Conclusions and Next Steps

- Provided the first determination of $\gamma(N_2O_5)$ in the UT/LS constrained by airborne observations from the ATom 3 and 4 campaigns.
- $\gamma(N_2O_5)$ appears well correlated with aerosol sulfate mass fraction
- NOAA CSL has developed a new CIMS instrument which completed first test deployment on the NASA WB-57 aircraft in February 2022. This instrument will enable measurement of $N_2O_5$ and $ClNO_2$ up to 19km.

## References and Acknowledgments:

*1.) McDuffie et al. J. Geophys. Res. Atmos., 2018; 2.) Robinson et al. J. Geophys. Res. Atmos., 1997; 3.)Hallquist et al. J. Phys. Chem. A. 2000. Thanks to the full ATom flight and science teams for enabling this research*