The first in-situ observations of stratospheric N_2O_5 constrain heterogeneous chemistry on stratospheric aerosol

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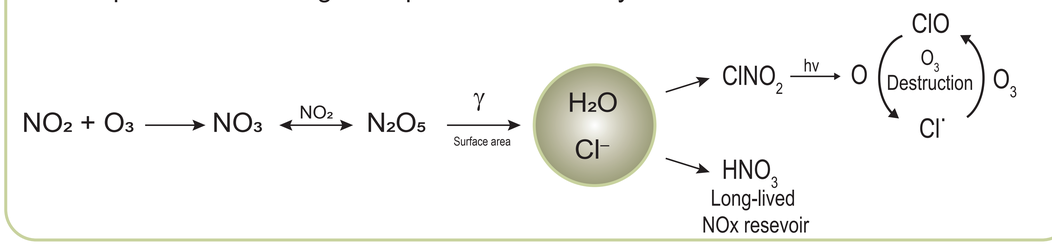
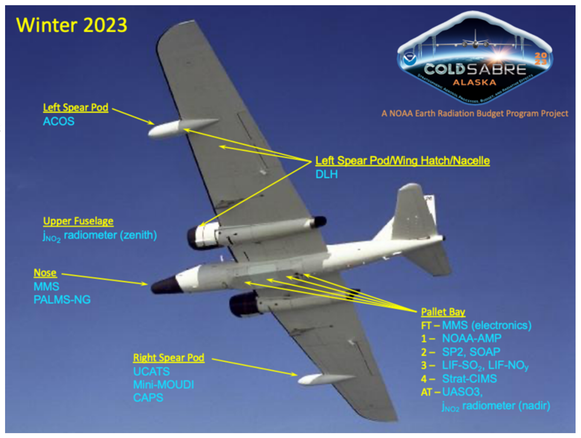
Reactive Nitrogen Influences Stratospheric O_3

The formation and fate of N_2O_5 influences the total reactive nitrogen (NO_y) budget. Heterogeneous (gas / particle) processing of N_2O_5 transfers Nitrogen Oxides (NO_x) into HNO_3 (a long-lived NO_x reservoir) or nitryl chloride ($ClNO_2$, a source of Cl radicals) which in turn influence stratospheric ozone (O_3) destruction. Yet, the N_2O_5 uptake coefficient (γ) of stratospheric aerosol has yet to be directly constrained by stratospheric observations and understanding of this parameter is instead based on laboratory and tropospheric field studies. As such, there is uncertainty in global climate models with respect to N_2O_5 influences and how future changes in stratospheric aerosol might couple to O_3 chemistry.



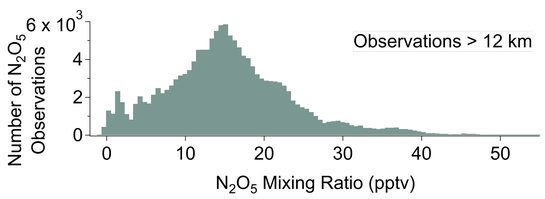
The SABRE Alaska Campaign

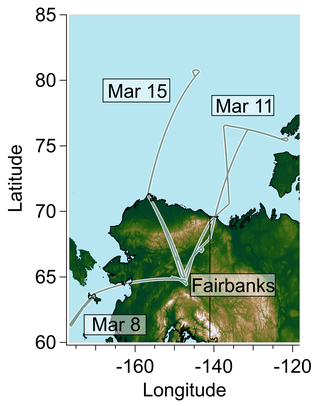
In 2023 the NOAA Stratospheric Aerosol Processes, Budget, and Radiative Effects (SABRE) campaign achieved comprehensive observations of stratospheric gasses and aerosol from the NASA WB-57 high-altitude research aircraft.



- Includes 20 flights (12 at latitudes > 65°)
- Altitudes range between 10 – 17 km
- Sampled in & out of winter polar vortex

- The NOAA Stratospheric Chemical Ionization Mass Spectrometer (StratCIMS) achieved the first in-situ observations of N_2O_5 which allows the determination of $\gamma(N_2O_5)$.





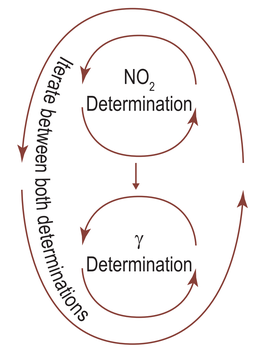
Our preliminary analysis uses SABRE data from three flights: Mar 8th, 11th, and 15th, which cover a variety of air mass types below

- Daytime and Nighttime
- Mid-latitude UTLS
- High-latitude non-vortex stratosphere
- Highly aged polar vortex

An Observationally Constrained Iterative Diel Box Model Derives $\gamma(N_2O_5)$

- The model has been used to derive $\gamma(N_2O_5)$ in the troposphere and lower-stratosphere
- The model begins 24 hours before the observation and iterates on initial conditions until the model and observations converge.
- Reactions (75 total) from the Master Chemical Mechanism are used including NO_x, HO_x, and Cl_y reactions relevant to the stratosphere.

1. For daytime observations, NO_2 can be determined from observed total NO_x. The model iterates NO_2 until modeled and observed NO are within 1 %.
2. $\gamma(N_2O_5)$ is determined by iterating γ until modeled and observed N_2O_5 match within 2%.
3. Both determinations are repeated until the derived γ remains within 5%.

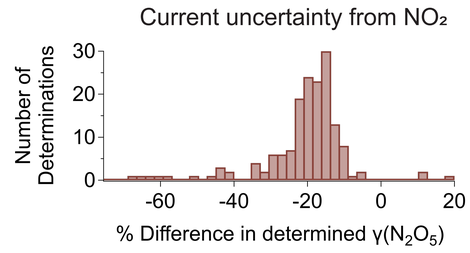


Model inputs include

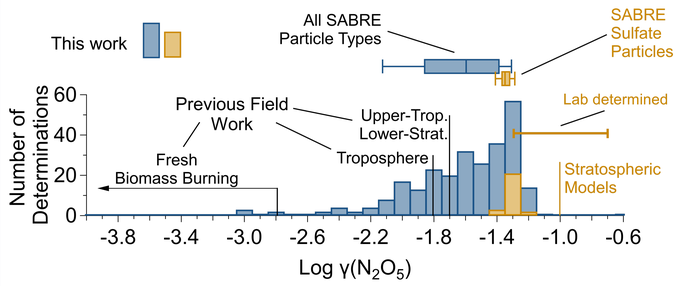
Chemical	Meteorology
• N_2O_5	• Lat / Lon / Alt
• NO	• 16 photolysis rates (TUV)
• NO_2	• Temperature
• HNO_3	• Pressure
• CO	
• O_3	
• Aerosol surface area	

Using the modeled NO_2 or observed NO_2 results in a 20 % difference in the $\gamma(N_2O_5)$ result.

SABRE data is not yet final and these differences are being investigated. Data presented below use observed NO_2.

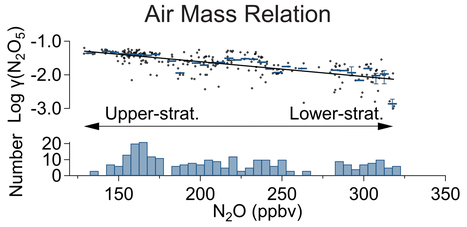


Observationally Constrained Stratospheric $\gamma(N_2O_5)$ [Preliminary Results]



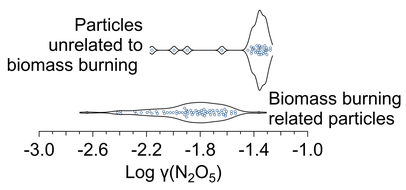
- Results suggest a median Log $\gamma(N_2O_5)$ of –1.6 (or 2.5×10^{-2}) for all particle types.
- Results are consistent with previous field determinations of UTLS and Tropospheric derived values.[1,2,3]
- Stratospheric models assume pure sulfate particles and use a value roughly ×2 greater

Air Mass Relation



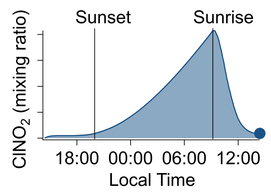
The $\gamma(N_2O_5)$ is correlated (R^2 ~ 0.44) with air mass indicators such as N_2O. This relation is caused by changes in particle content such that $\gamma(N_2O_5)$ increases as deeper regions of the stratosphere are sampled.

Biomass Burning Relation



The $\gamma(N_2O_5)$ on particles associated with biomass burning is consistently lower (a 33% median difference) consistent with field and laboratory studies.

Potential for $ClNO_2$ formation



Solomon et al. suggest organics increase HCl stratospheric particle solubility. With available particle chloride, $ClNO_2$ formation is possible but currently unconfirmed.

Next Steps

The implications of a lower $\gamma(N_2O_5)$ in stratospheric models is being investigated. Specifically, what are the implications for O_3 ? How sensitive are O_3 outcomes to $\gamma(N_2O_5)$ in a stratospheric aerosol injection geoengineering scenario? Further, observations of $ClNO_2$ from the SABRE campaign will be used to determine if an upper-bound $ClNO_2$ yield can be determined.

References

1: Novak et al. *in prep*
2: Decker et al. *Geophys. Res. Let.*, **2024**
3: McDuffie et al. *JGR Atmos.*, **2018**
4: Solomon et al. *Nature*, **2023**