Investigation Into Daytime NO_3 Through Steady State Approximation and Global Modeling

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I. Abstract

The nitrate radical (NO_3) is a key oxidizing agent in the atmosphere and participates in numerous oxidative reactions. Importantly, NO_3 reacts with volatile organic compounds (VOCs) to form secondary pollutants, which can have many harmful effects on human health and the climate[1]. Although NO_3 is generally a nocturnal species due to rapid photolysis, some instances allow for daytime NO_3 to be observed[2,3]. In this study, a steady state approximation is applied to estimate daytime NO_3 in Salt Lake City during summer months, revealing daytime NO_3 levels to be around 1 pptv in the hours leading up to sunset. Further analysis of data from the global chemical transport model, GEOS-Chem, was conducted to pinpoint areas with heightened daytime NO_3 levels and evaluate the global significance of this phenomenon. Results from this analysis showed daytime NO_3 to be most considerable in the hours before sunset, particularly in highly urban areas, and can be responsible for up to 85% of the losses of major VOCs.

II. Introduction

Atmospheric NO_3

- NO_3 Radical is an important atmospheric oxidizing agent (as well as O_3, OH, Cl)
- Converts volatile organic carbons (VOCs) to harmful secondary pollutants
- Nocturnal Species: Often considered negligible during the day
- High ozone environments can allow for NO_3 to be seen during the day[2]
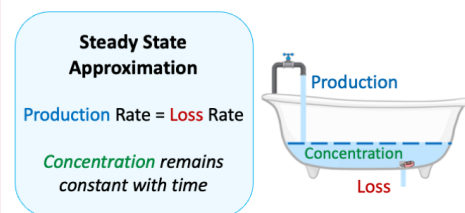
SLC Measurements
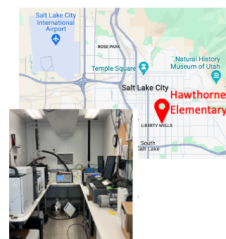
Hawthorne Elementary DEQ Site

- Trace gas measurements for steady state analysis
- Solar Irradiance measurements
- Data from 6/01/2021 – 08/31/2021 and 6/01/2022-8/31/2022

☀ = Photolysis
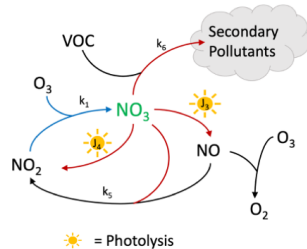
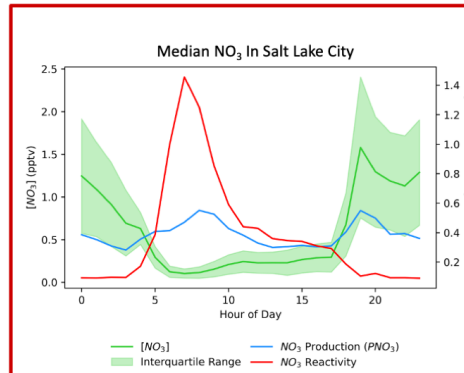**What environments allow for heightened daytime NO_3 and what is the global significance?**

III. Steady State Analysis

Steady State Approximation

Production Rate = Loss Rate

Concentration remains constant with time

Production

Concentration

Loss

NO_3 Production Rate = $k_1 [O_3][NO_2]$

NO_3 Loss Rate = $J_3[NO_3] + J_4[NO_3] + k_5[NO] + [NO_3]\sum k_6 [alkenes]$

$$[NO_3] = \frac{k_1 [O_3][NO_2]}{J_3 + J_4 + k_5[NO] + \sum k_6 [alkenes]}$$

Median NO_3 In Salt Lake City

— $[NO_3]$
Interquartile Range
— NO_3 Production (PNO_3)
— NO_3 Reactivity

Fractional Loss of NO_3 In Salt Lake City

NO
Photolysis
Monoterpenes
Isoprene
Other VOC

- Loss rate (reactivity) drives NO_3 concentration in Salt Lake City
- Majority lost to NO and photolysis
- Approximately 1 pptv of NO_3 in hours before sunset
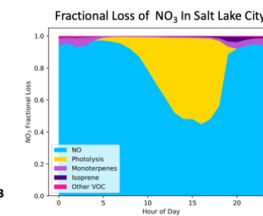
IV. Global Model Analysis

GEOS-Chem Model: NO_3

Daytime NO_3 a Few Hours Before Sunset In January and June

- Time before sunset is normalized by adding 5 hours to peak photolysis (solar noon) in each grid box
- Model estimates are averaged over the month
- Low photolysis rates displayed as hatching (right) to visualize areas where the sun has began setting

Daytime NO3 Concentrations

NO_3 Concentrations June 2017
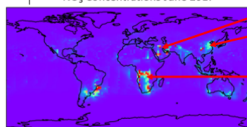
Anthropogenic Emissions
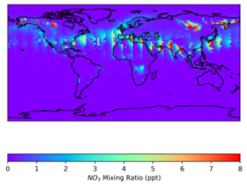
Biomass Burning

NO_3 Mixing Ratio (ppt)

Isoprene Loss by NO_3

Isoprene: Common VOC

$$\text{Fractional loss by } NO_3 = \frac{\text{Loss by } NO_3}{\text{Total loss by all oxidants}}$$

NO_3 Concentrations January 2017

NO_3 Mixing ratio (ppt)

- Compare how much isoprene is lost by NO_3 in comparison to other oxidative reagents
- Evaluate significance of daytime NO_3 by exploring its role in forming secondary pollutants from isoprene
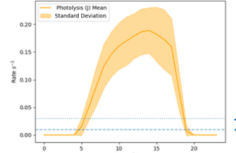- **Areas with high NO_3 concentrations are responsible for large fractions of isoprene loss**

Loss of Isoprene to NO_3 January 2017

Fractional Loss of Isoprene to NO_3
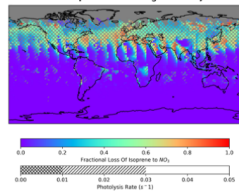
Photolysis Rate (s^{-1})

Loss of Isoprene to NO_3 June 2017

Fractional Loss Of Isoprene to NO_3
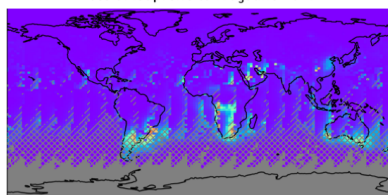
Photolysis Rate (s^{-1})

Summer NO3 Photolysis Rates In Salt Lake City

Photolysis (J) Mean
Standard Deviation

V. Conclusions and Future Work

Conclusions

- Daytime NO_3 is seen in Salt Lake City, at about 1 pptv in the hours before sunset
- Daytime NO_3 hotspots are seen in highly urban areas and areas of burning biomass
- NO_3 is responsible for large percentages of isoprene loss in hours before sunset in certain environments

Future Work

- Investigation into central Africa's NO_3 hotspot
- Higher resolution GEOS-Chem models to explore drivers to daytime NO3 hotspots
- Application of steady state approach to additional urban background sites

VI. Acknowledgements

REALM

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2. Hamilton, J. F.; Bryant, D. J.; Edwards, P. M.; Ouyang, B.; Bannan, T. J.; Mehra, A.; Mayhew, A. W.; Hopkins, J. R.; Dunmore, R. E.; Squires, F. A.; Lee, J. D.; Newland, M. J.; Worrall, S. D.; Bacak, A.; Coe, H.; Percival, C.; Whalley, L. K.; Heard, D. E.; Slater, E. J.; Jones, R. L.; Cui, T.; Surratt, J. D.; Reeves, C. E.; Mills, G. P.; Grimmond, S.; Sun, Y.; Xu, W.; Shi, Z.; Rickard, A. R. Key Role of NO 3 Radicals in the Production of Isoprene Nitrates and Nitrooxyorganosulfates in Beijing. Environ. Sci. Technol. 2021, 55 (2), 842–853. https://doi.org/10.1021/acs.est.0c05689.
3. Khan, M. A. H.; Morris, W. C.; Watson, L. A.; Galloway, M.; Hamer, P. D.; Shallcross, B. M. A.; Percival, C. J.; Shallcross, D. E. Estimation of Daytime NO 3 Radical Levels in the UK Urban Atmosphere Using the Steady State Approximation Method. Advances in Meteorology 2015, 2015, 1–9. https://doi.org/10.1155/2015/294069.