



Observing NO₂ and HNO₃ from Space: Effects of revised a priori profiles based on DC-3 and SEAC4RS measurements of CH₃O₂NO₂

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Introduction

- Lightning is a major source of NO_x to the upper troposphere and thus affects the concentrations of upper tropospheric O₃ and HO_x.
- Recent studies using satellite observations of NO₂ and/or HNO₃ interpreted using standard photochemical transport models have constrained the lightning NO_x emissions to within a factor of 2.^{1,2,3}
- However, recent modeling⁴ and field studies⁵ have shown that CH₃O₂NO₂ chemistry reduces NO_x and HNO₃ concentrations in areas of lightning. Currently, most models do not include this chemistry. The issue is important because the CH₃O₂NO₂ lifetime is greatest where lightning NO_x emissions typically occur and where the satellite is most sensitive to NO₂ (Fig. 1).

We investigate the impact of CH₃O₂NO₂ chemistry on the interpretation of satellite observations of NO₂ and HNO₃ as a constraint on lightning NO_x emissions.

Conclusions

- During DC-3 and SEAC4RS, we observed similar concentrations of CH₃O₂NO₂ and NO₂ ~12 – 24 hours downwind from deep convection.
- Production of CH₃O₂NO₂ reduces the lightning enhanced NO₂ column density by a large enough amount that it affects interpretation of the column observed by OMI as a constraint on lightning NO_x.
- CH₃O₂NO₂ chemistry also reduces HNO₃ by amounts large enough to affect interpretation of space-based HNO₃ measurements as constraints on lightning NO_x.
- We conclude that lightning NO_x constrained by space-based observations and interpreted without taking into account CH₃O₂NO₂ measurements and changes to our understanding of the production rate of HNO₃ are biased high. A quantitative assessment of the magnitude of the bias is in progress.

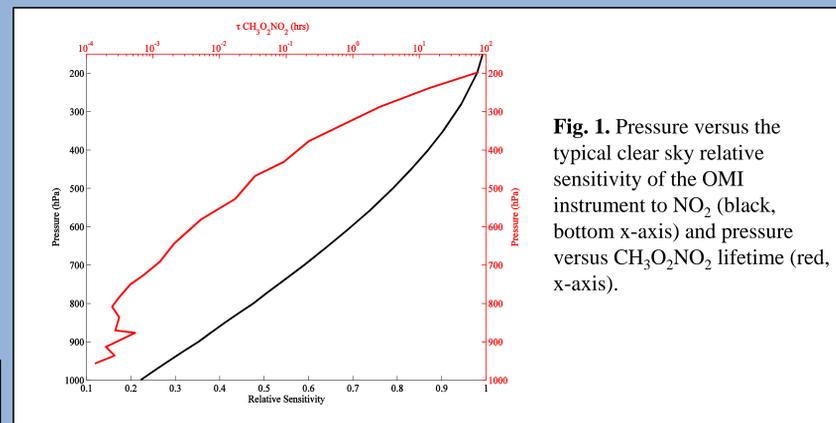


Fig. 1. Pressure versus the typical clear sky relative sensitivity of the OMI instrument to NO₂ (black, bottom x-axis) and pressure versus CH₃O₂NO₂ lifetime (red, x-axis).

Measurements of NO₂ and CH₃O₂NO₂ during DC-3 and SEAC4RS

Measurements of CH₃O₂NO₂ and NO₂ during DC-3 and SEAC4RS have been described elsewhere.^{5,6} Briefly, NO₂ is excited with a 585 nm tunable dye laser, and we measure the red shifted photons. CH₃O₂NO₂ is thermally dissociated at ~60°C to NO₂ and its parent radical, and the NO₂ is subsequently excited. The concentration of CH₃O₂NO₂ is the difference between the ambient NO₂ and the

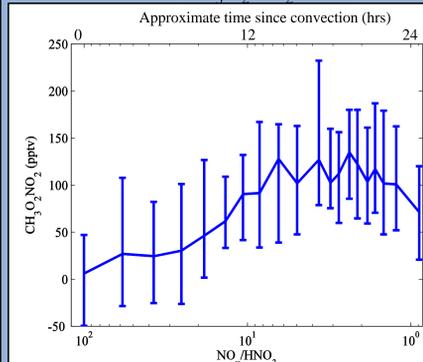


Fig. 2. Observed CH₃O₂NO₂ mixing ratios versus NO_x/HNO₃ ratios (bottom x-axis) and calculated time since convection (top x-axis) during DC-3. Bars are the inter-quartile measurements and the line is the median measurements.

We use NO_x/HNO₃ ratios as a chemical clock since convection completely removes HNO₃.⁷ After ~12 hours, the CH₃O₂NO₂ has reached a steady state concentration of ~100 pptv. This indicates that an extra 100 pptv of NO_x has been removed from the air parcel that models are not accounting for.

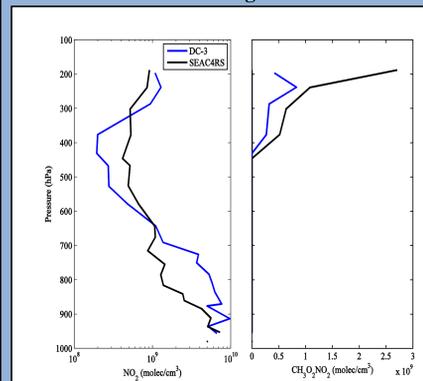
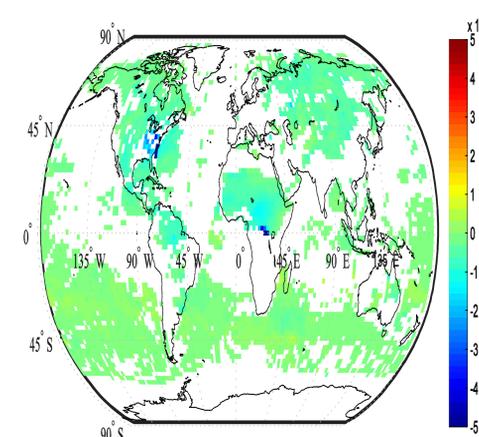


Fig. 3. Observed NO₂ (left) and CH₃O₂NO₂ (right) profiles during DC-3 (blue) and SEAC4RS (black). The data shown are medians all observations except for the upper three points which are medians restricted to air masses with NO_x/HNO₃ ratios between 2 and 10 (~12 – 24 hours old).

During DC-3 and SEAC4RS we observed enhanced NO₂ at high altitudes due to lightning. At these altitudes, CH₃O₂NO₂ is in excess of 0.5 × 10⁹ molecules/cm³, and ranges from 50%–250% of NO₂

Effects of CH₃O₂NO₂ chemistry on lightning NO_x and NO₂ Vertical

Fig. 4. The effect of CH₃O₂NO₂ chemistry on the lightning enhanced NO₂ column (molecules/cm²) averaged in the month of July from GEOS-Chem. The change is calculated as the difference between the lightning enhancement of NO_x with and without CH₃O₂NO₂ chemistry in the model: (NO_{2,with lightning and with CH3ONO2} – NO_{2,without lightning and with CH3ONO2}) – (NO_{2,with lightning and without CH3ONO2} – NO_{2,without lightning and without CH3ONO2}). Only regions where lightning NO_x emissions dominate (greater than 60% of the emissions) are shown.



The model indicates that decreases in the NO₂ column due to including CH₃O₂NO₂ are as high as ~2 × 10¹⁴ molecules/cm², values which are detectable by OMI.

Similar decreases in the NO₂ column density are calculated for the months of June and August.

The largest changes in the NO₂ column occurs at high lightning NO emissions. This indicates that including CH₃O₂NO₂ chemistry has a noticeable impact in the interpretation of NO₂ columns near high lightning source regions (e.g., Southeast U.S.).

Impacts on Satellite Retrieved HNO₃

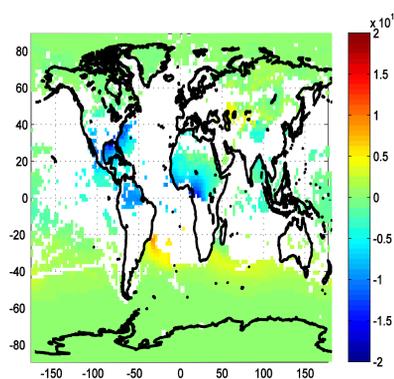


Fig. 5. The absolute change in the HNO₃ column (molecules/cm²) averaged in the month of July from GEOS-Chem. The change is calculated as: HNO_{3,with CH3ONO2} – HNO_{3,without CH3ONO2}. Only regions where lightning NO_x emissions dominate (greater than 60% of the emissions) are shown.

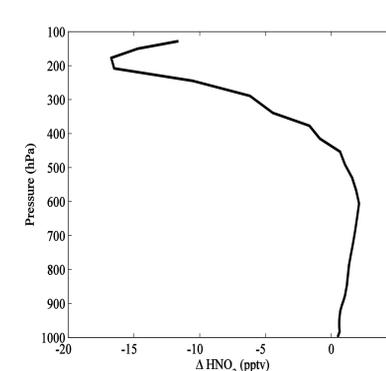


Fig. 6. The absolute change in the HNO₃ profile (pptv) averaged in the month of July from GEOS-Chem over central Africa. The change is calculated as: HNO_{3,with CH3ONO2} – HNO_{3,without CH3ONO2}

Satellite measurements of HNO₃ have also been used to constrain lightning NO_x emissions.^{1,2,3} Browne et al. showed that including CH₃O₂NO₂ chemistry decreased HNO₃ concentrations by 15 – 40 pptv at pressure levels lower than 400 hPa.⁴

We calculate decreases of HNO₃ as a result of CH₃O₂NO₂ chemistry of as much as 2 × 10¹⁴ molecules/cm², which is on order 10 – 20% of the HNO₃ column density observed by Cooper et al.³ and calculated with GEOS-Chem.

In addition to the effects of CH₃O₂NO₂ recent work^{8,9} and our own analysis of DC-3 observations has shown that the HNO₃ production rate in current models is faster than in the atmosphere, especially in the upper troposphere. We expect larger decreases in the column density and concentrations of HNO₃ from this effect than from CH₃O₂NO₂ chemistry. Both changes to our understanding of the chemistry of the upper troposphere will reduce the amount of lightning NO_x required for the models to be consistent with satellite based remote sensing of HNO₃

Acknowledgements

The authors would like to acknowledge NASA Grant Number NNX08AR13G and NSF GRFP under Grant No. DGE 1106400.

We also acknowledge Jack Dibb for the use of HNO₃ measurements and Tom Ryerson for use of NO measurements.

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