NO_x emission and PAN formation in boreal forest fire smoke observed during ARCTAS

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1. Introduction

Emissions of NO_x and PAN from boreal forest fires can enhance the formation of O_3 in the Arctic [*e.g., Leung et al.*, 2007]. Current estimates of the emission ratios for NO_x and PAN (relative to CO) from boreal forest fires are highly uncertain and based on few studies [*Nance et al.,*1993; *Goode et al.,* 2000; *McKeen et al.,* 2002].

In this work we used the data gathered during the DC8 flights of the summer ARCTAS campaign to calculate the enhancement ratios of NO_x and PAN in biomass burning plumes and to explore how these enhancement ratios change with the age of the smoke plume.

2. Plume Identification and Classification

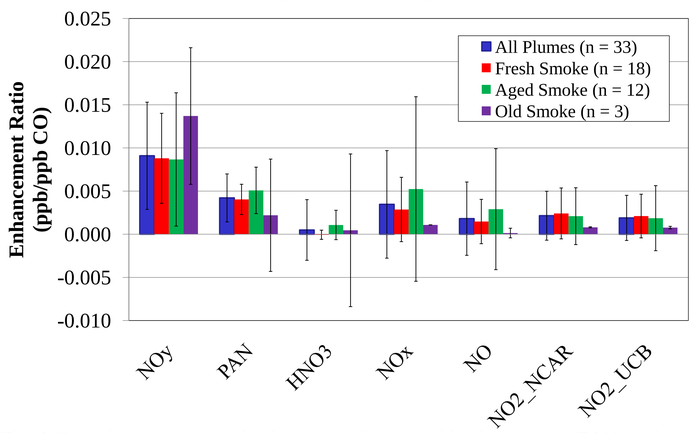
We examined the DC8 merged data sets (1 minute average) between June 29 and July 8, 2008 for evidence of biomass burning plumes. A plume was assumed to be from biomass burning when the CO concentration rose at least 20 ppb above the background level, and the enhancement of CO was correlated ($r^2 > 0.3$) with an enhancement in HCN. DC8 flight reports and back trajectories provided by H. Fuelberg (FSU) were also used to identify plumes.

33 plumes were identified, some of which were sampled more than once. The relative age of these plumes was classified based on the correlation of CO with several short-lived organic species. The categories are:

Fresh – CO correlated with propene (r^2>0.3)
Aged – CO correlated with ethene or toluene, but not propene
Old – CO correlated with butane, propane, or benzene, but not propene, ethene or toluene

3. NO_x and PAN Enhancement Ratios

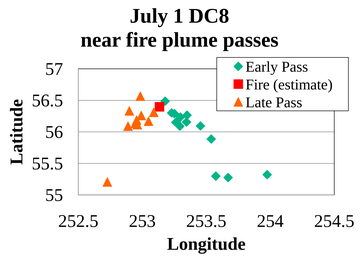
Enhancement ratios of various NO_y species versus CO were determined from the slope of the linear regression between CO and the species during the plume sampling. NO_x concentrations were estimated using the formula NO_x = NO + 0.5*(NO2_NCAR + NO2_UCB)

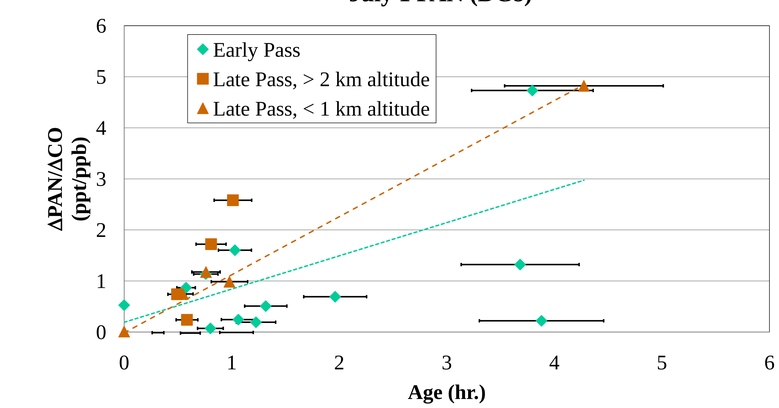


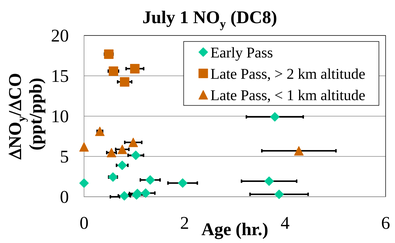
The NO_y enhancement ratio does not change with plume age. PAN and NO_x both show slight, but not statistically significant, increases with age. The variability of the estimated enhancement ratios between plumes is very high.

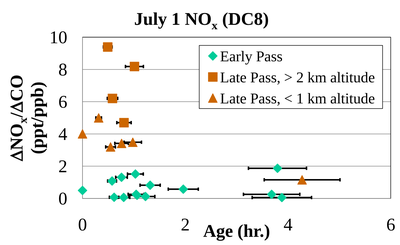
4. Rapid Local Change in PAN Enhancement Ratios

The DC8 flight of July 1 sampled a fresh smoke plume at several distances downwind from the fire source at the beginning (Early Pass, 13:00-15:00 LT) and end (Late Pass, 18:20-19:40 LT) of the flight. We used this data to explore how the enhancement ratios of PAN and NO_x changed with plume age near the fire. We estimated the Lagrangian age for each plume sample using the distance from the highest measured CO concentration and the average measured wind speed.



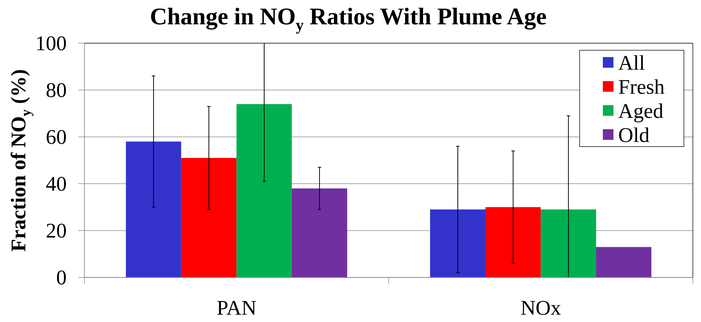




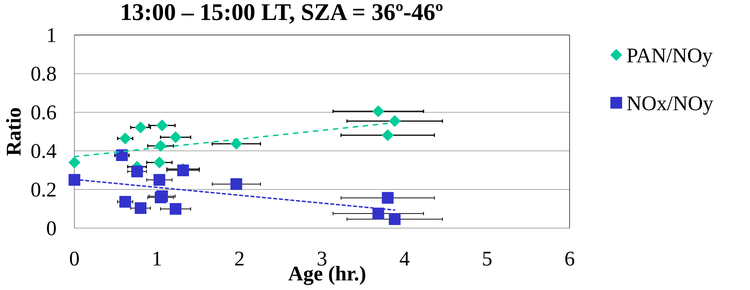


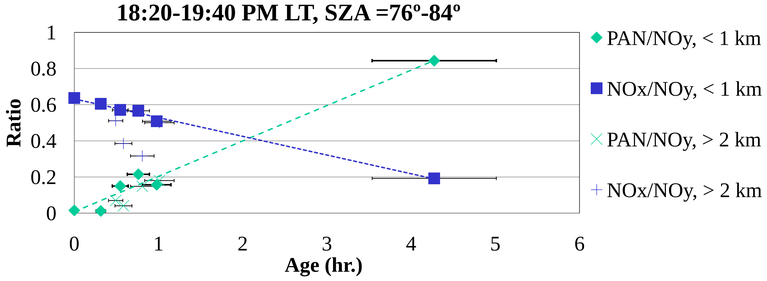
- The PAN enhancement ratio increased with plume age in both the early and late pass. This suggests that PAN is rapidly formed within boreal forest fire smoke plumes.
- Total NO_y appears fairly constant in the late pass. In the early pass, two of the > 3 hour samples suggest no change, but the third shows the highest NO_y ratio for the pass.
- The NO_x enhancement ratios are fairly constant in the early pass, but appear to have decreased with time in the late pass.
- Plume samples above 2 km in the late pass have higher enhancement ratios of NO_x and NO_y.
- Modified combustion efficiencies were much higher in the high altitude late pass samples (0.95 vs. 0.85) than in the low altitude samples, consistent with more flaming combustion.

5. Change in NO_y Partitioning with Age



NO_x fraction shows no significant change with age. PAN increases from 50% of NO_y in fresh plumes to 70% of NO_y in aged plumes, but the large variability between plumes suggests that the increase is not significant.





The PAN/NO_y ratio increases with age in both passes, while the NO_x/NO_y ratio decreases with age.

6. Conclusions and Future Work

- NO_y enhancement ratio is 9(±6)x10^{-3} ppb/ppb CO. This is consistent with the *McKeen et al.* [2002] estimate of 7x10^{-3} for NO_y.
- NO_x is 30±24% of NO_y in the identified biomass plumes with an enhancement ratio of (3±3) x10^{-3} ppb NO_x/ppb CO. This is well below the *Nance et al.* [1993] estimate of 1.2x10^{-2} and the *Goode et al.* [2000] estimate of 1.4-1.8x10^{-2} for Alaskan fires.
- PAN is 51±22% of initial NO_y, with an average PAN enhancement ratio (4.6±3.7)x10^{-3} ppb/ppb CO.
- The fraction of NO_y as PAN increased, and the PAN enhancement ratio increased, within the first few hours after emission in the fresh smoke plumes sampled on July 1.
- Future work will explore how these new estimates of boreal forest fire NO_x and PAN emission ratios affect the simulation of atmospheric chemistry in the Arctic in GEOS-Chem.

REFERENCES

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Leung et al. [2007] JGR 112, D10313.
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ACKNOWLEDGEMENTS

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