APAN Formation in Biomass Burning Plumes During SENEX

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Photo Credit: Joost de Gouw

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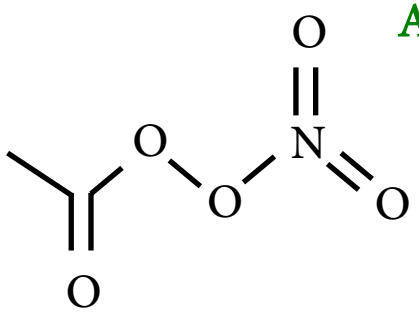
Measurement of acyl peroxynitrates [$RC(O)OONO_2$] during SENEX aboard the NOAA P3

Acyl peroxynitrates are typically the most abundant NO_y species in the mid to upper-troposphere and are the main pathway for NO_x transport from source regions. Additionally acyl peroxynitrates uniquely reflect the photochemical history (more generally chemical history) of an air mass.



Acetyl Peroxynitrate (PAN), $CH_3C(O)OONO_2$

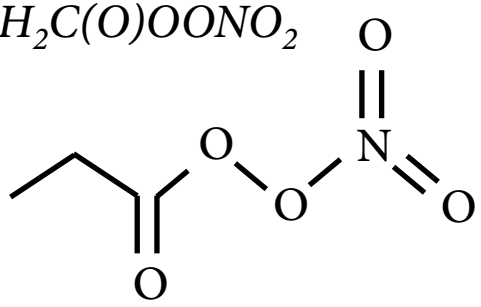
- Anthropogenic VOCs
- Isoprene Chemistry
- Biomass Burning

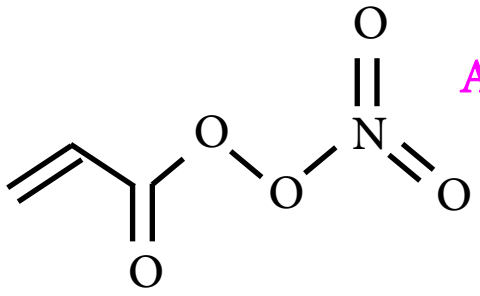
- Acetone
- Acetonitrile
- Methylglyoxal

Propionyl Peroxynitrate (PPN), $CH_3CH_2C(O)OONO_2$

- Anthropogenic VOCs
- Biomass Burning

- Propanal



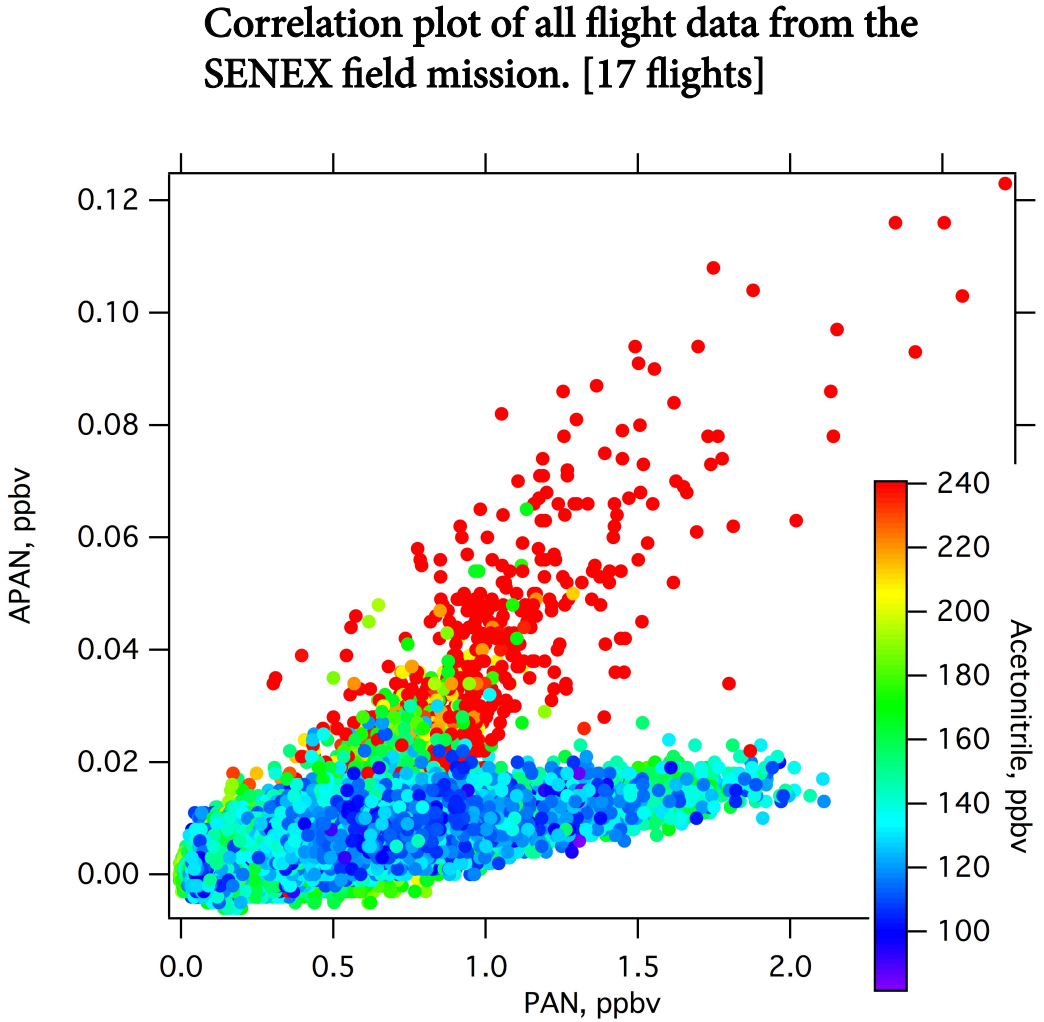


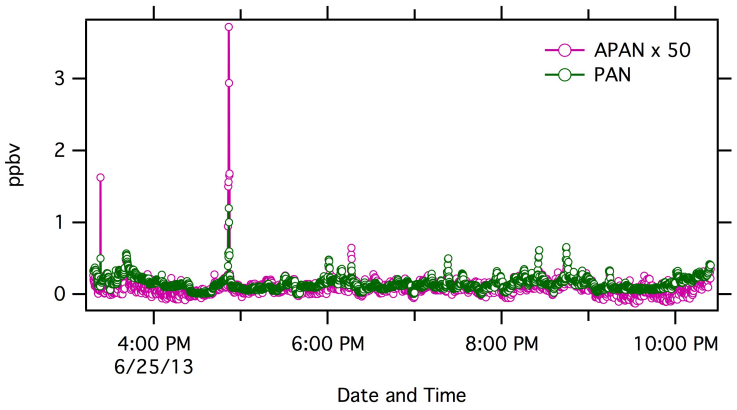
Acryloyl Peroxynitrate (APAN), $CH_2CHC(O)OONO_2$

- Biomass Burning
- *Small Urban Source?*

- Acrolein
- 1,3-dienes

Acyl peroxynitrates [$RC(O)OONO_2$] observed in biomass burning plumes during SENEX.



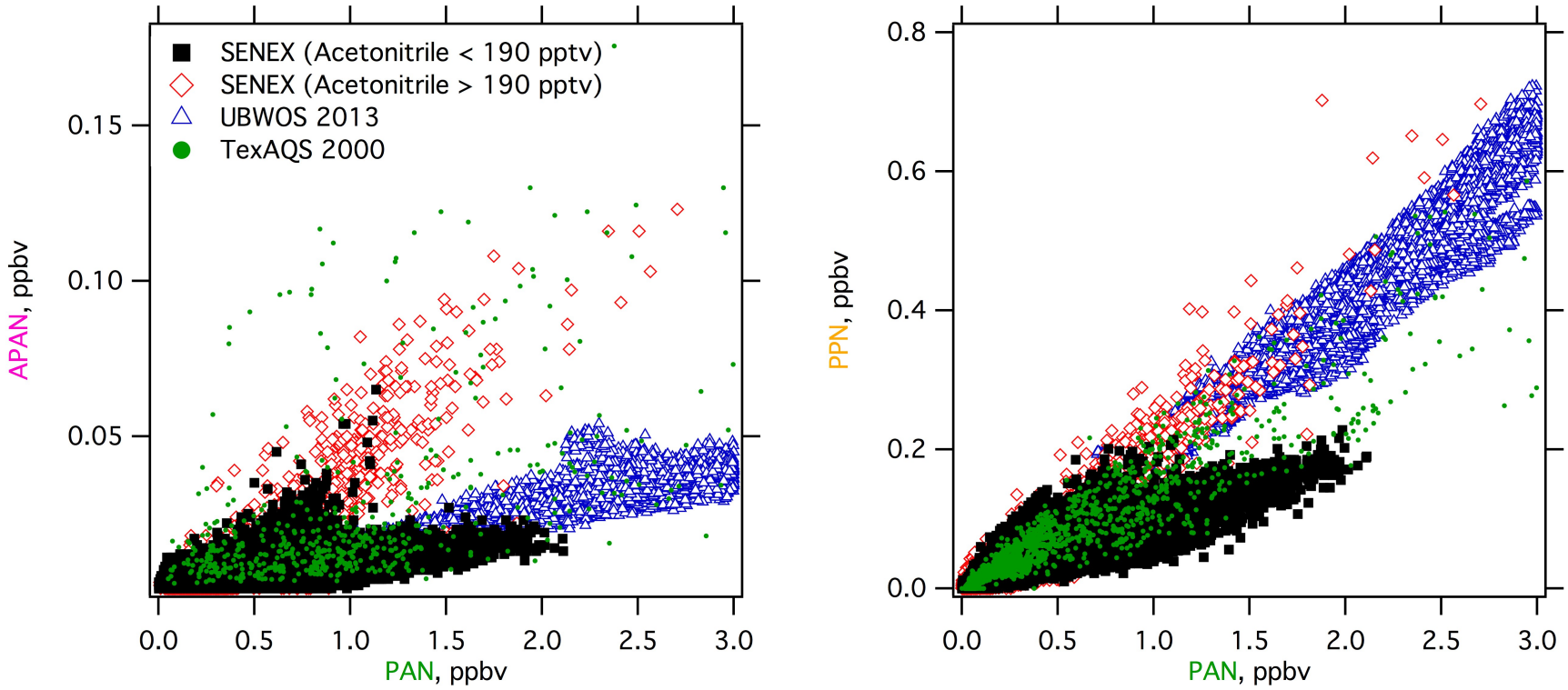


The plot on the right illustrates that APAN:PAN shows a distinct, and largely constant biomass burning signature during SENEX.

APAN, almost exclusively a product of biomass burning plume chemistry, can potentially serve as an indicator of plume age.

Field Intercomparison of acyl peroxynitrates

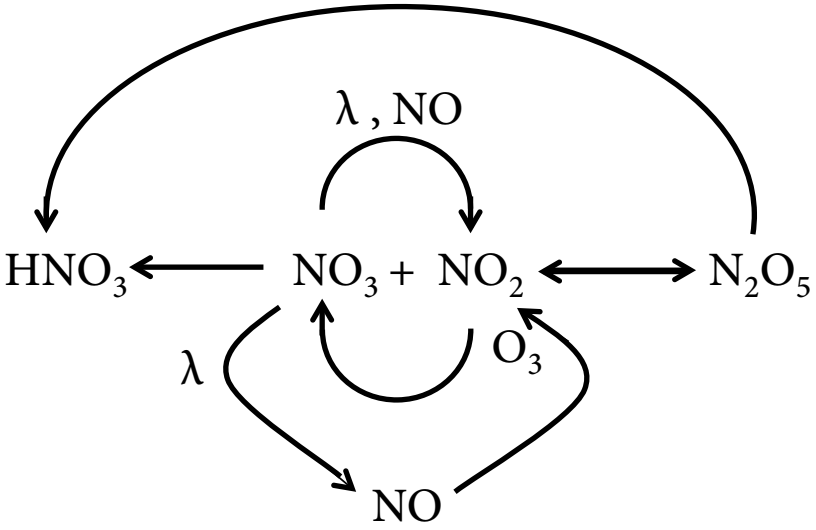
SENEX 2013, UBWOS 2013, and TexAQS 2000



While APAN:PAN can be used to identify a distinct biomass burning influence, PPN:PAN shows no obvious difference between SENEX measured biomass burning and previous measurements of these two species.

Fire Plume Box Model

36 Reactions, APAN, PAN, PPN
VOC precursors: Acrolein, Acetone, Acetaldehyde, Methylglyoxal, Propanal



APAN Formation

$$\text{Acrolein} + \text{NO}_3/\text{OH} \longrightarrow \text{ACO}_3$$

$$\text{Acrolein} + \text{ACO}_3 \xrightarrow{\text{O}_2,\ \text{NO}_2} \text{APAN}$$

APAN Loss

$$\text{APAN} + \text{OH} \longrightarrow \text{HOCH}_2\text{CHO} + \text{NO}_2$$

$$\text{APAN} \xrightarrow{\Delta} \text{ACO}_3^{\cdot} + \text{NO}_2$$

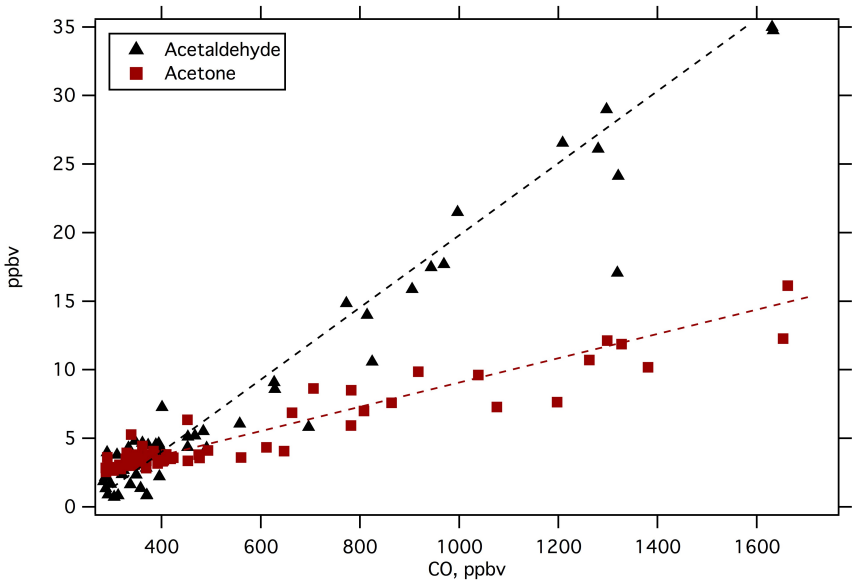
$$\text{ACO}_3 + \text{NO}/\text{NO}_3 \longrightarrow \text{HCHO, C}_2\text{H}_3 + \text{NO}_2$$

Fire Plume Box Model

36 Reactions, PAN, APAN, PPN
VOC precursors: Acrolein, Acetone, Acetaldehyde, Methylglyoxal, Propanal

Fire emission factors for unmeasured species are taken from a study of prescribed burn fuels from the Southeastern US (*Yokelson et al. 2013, Warneke et al. 2011).*

*Literature recommendation for propanal is 1.20 ppbv @ 1500 ppbv CO. However, the best APAN/PPN agreement was found with 5.7 ppbv propanal.



	Species	$[X]_0$, ppbv
Literature	Acrolein	0.82
	Propanal*	5.7
	NO	14.6
	NO_2	31.9
SENEX Measured	CO	1500
	Acetaldehyde	28
	Acetone	11
	Methylglyoxal	8
	PAN	0.3
	PPN	0.08
	APAN	0.005
	N_2O_5	0
	NO_3	0

Fire Plume Box Model:

Initialized with SENEX Measurements

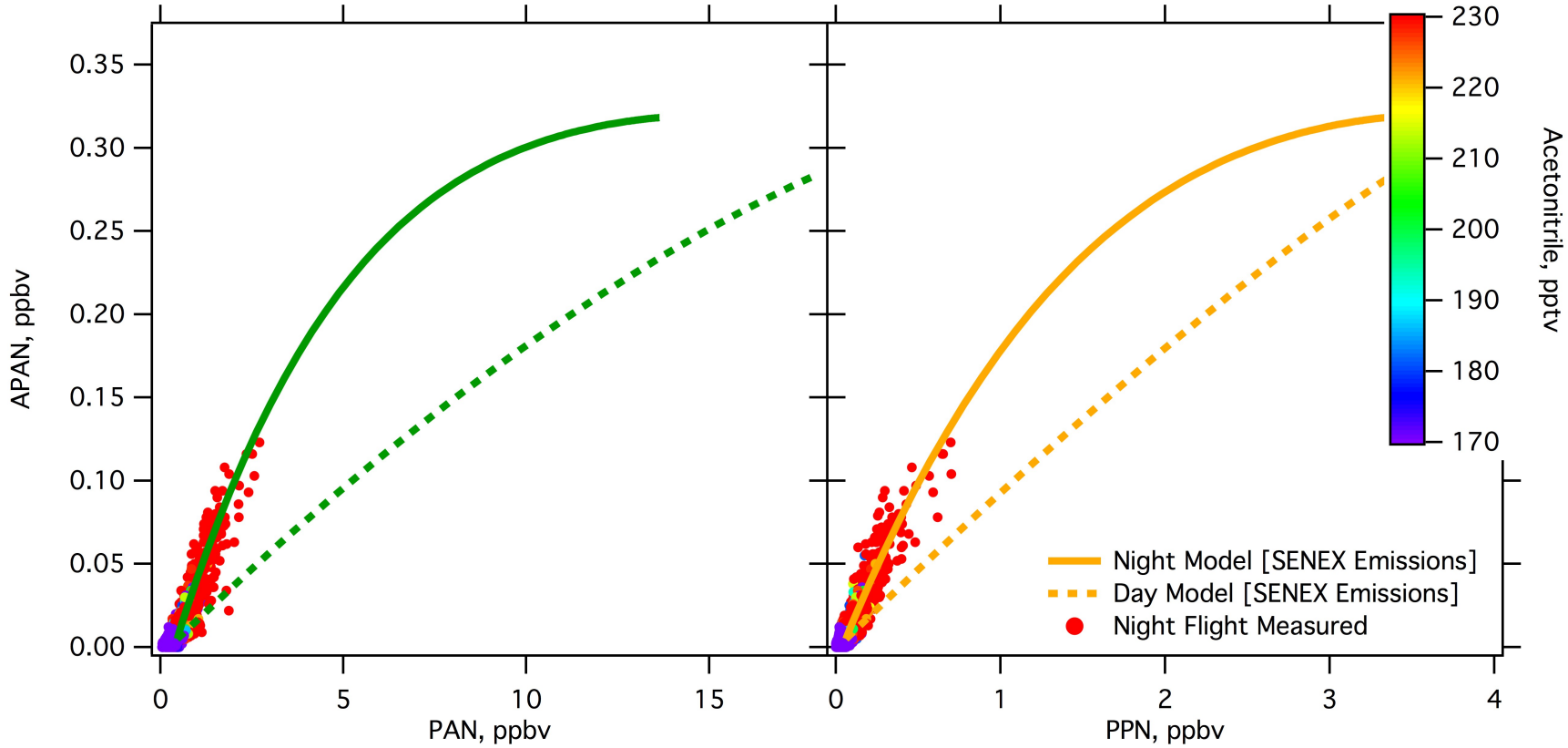
$[X]_0$ for PAN, APAN, PPN, methylglyoxal, Acetone, Acetaldehyde, and CO were set according to measurements from the 07/03/2013 SENEX flight.

$[X]_0^{DAY} = [X]_0^{NIGHT}$

$T_{atm} = 298$ K

$[OH] = 1 \times 10^6$ (constant)

Photolysis @ solar max

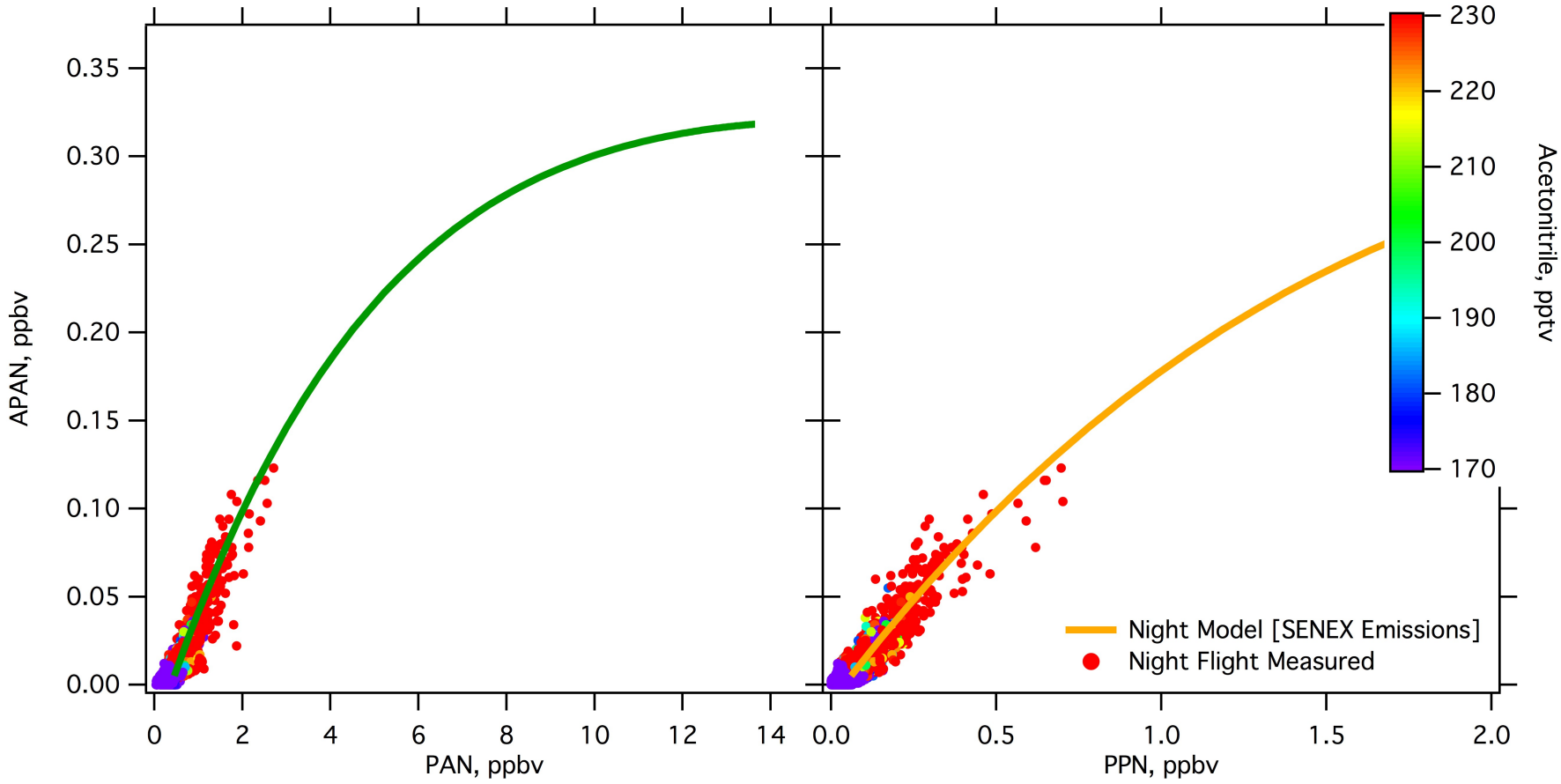


Model comparisons shown for measurements from the 07/03/2013 flight, 01:00 – 08:00 hours.

Fire Plume Box Model:

Nighttime, SENEX Initialized

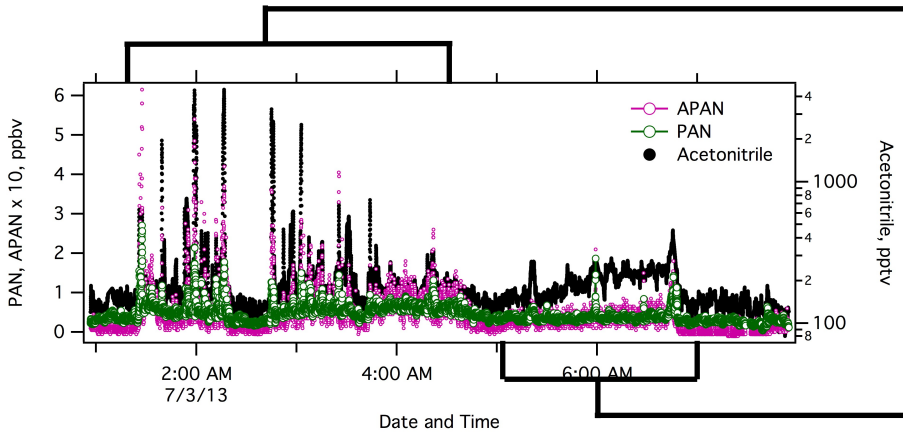
For the remainder of this talk, data will be compared to the nighttime model output initialized with SENEX measurements for all possible species.



Model comparisons shown for measurements from the 07/03/2013 flight, 01:00 – 08:00 hours.

SENEX Flight 07/03/2013 (01:00 – 08:00)

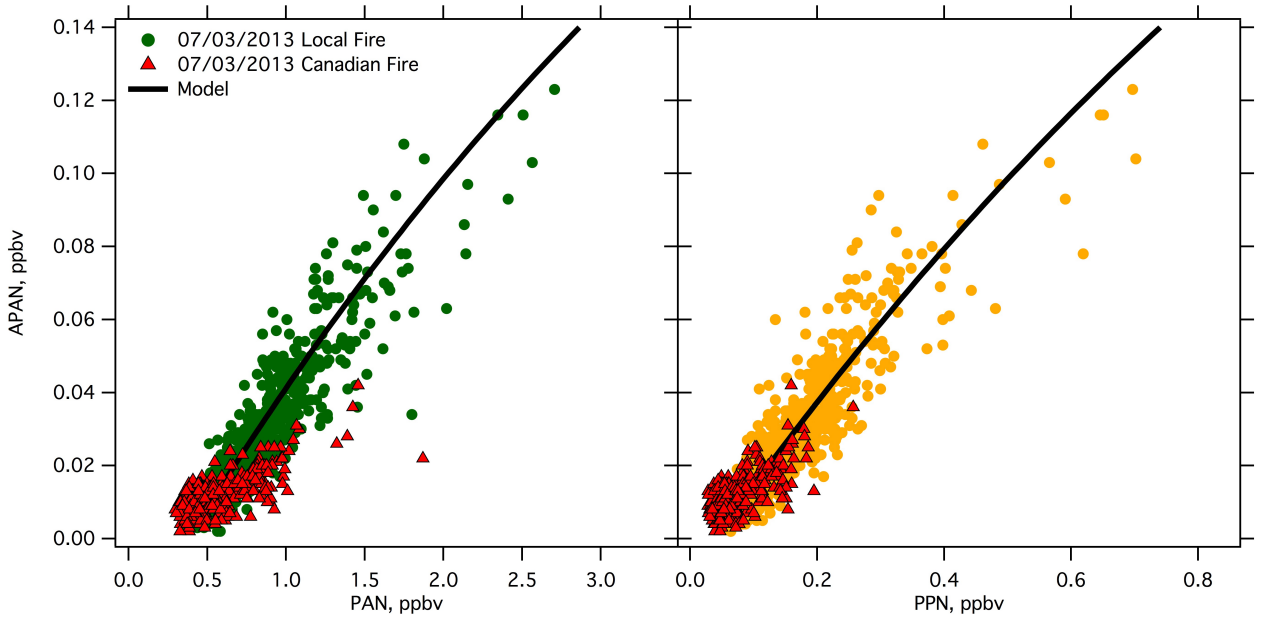
Northwest Tennessee/Arkansas



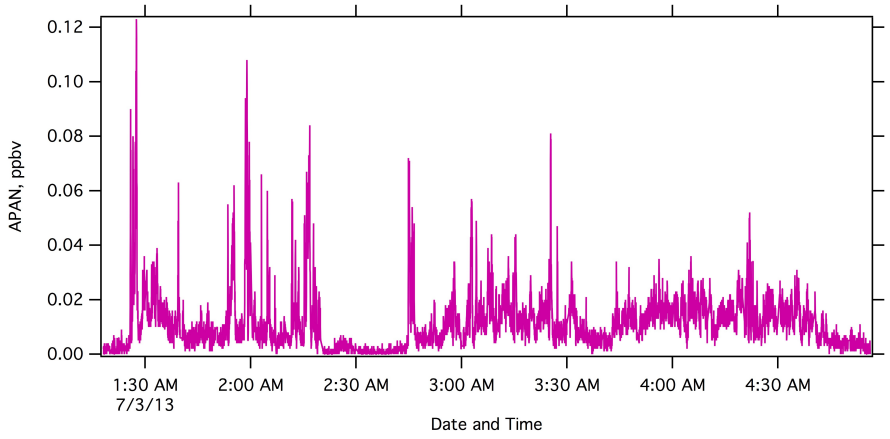
Local controlled biomass burning in NW Tennessee.

Long range transport of Canadian biomass burning emissions.

A lack of consideration of dilution and mixing as well as difference in fuel types can account for the lack of agreement between the model output and the Canadian fire measurements.

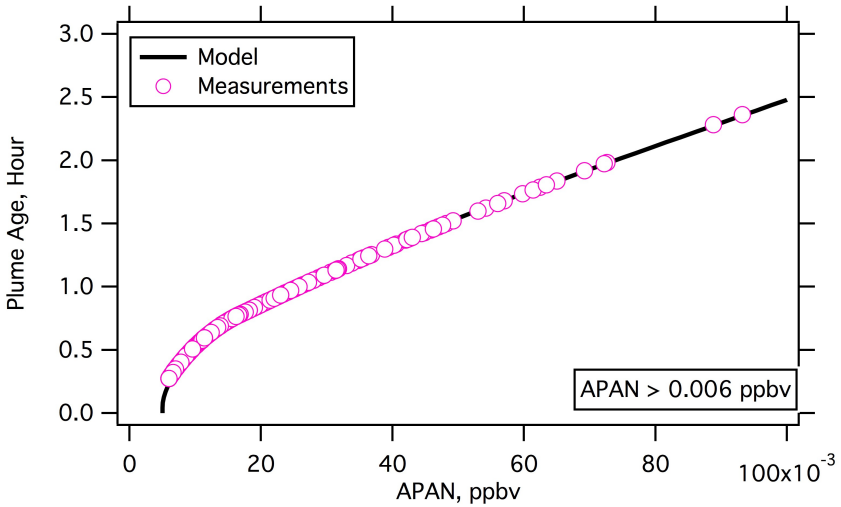


Plume Age Approximation



Observed APAN concentrations are matched to the APAN model output to determine an approximate plume age.

In the case of the Tennessee flight (07/03/13), plume ages range from 0 – 3 hours for the local controlled burn observed.



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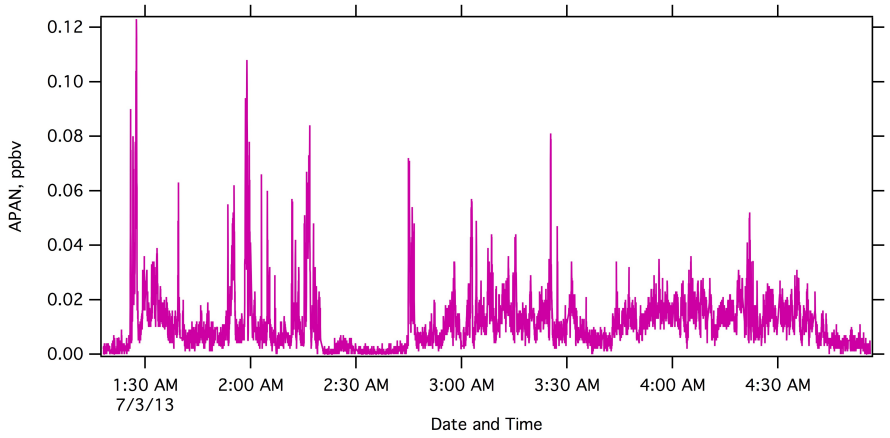

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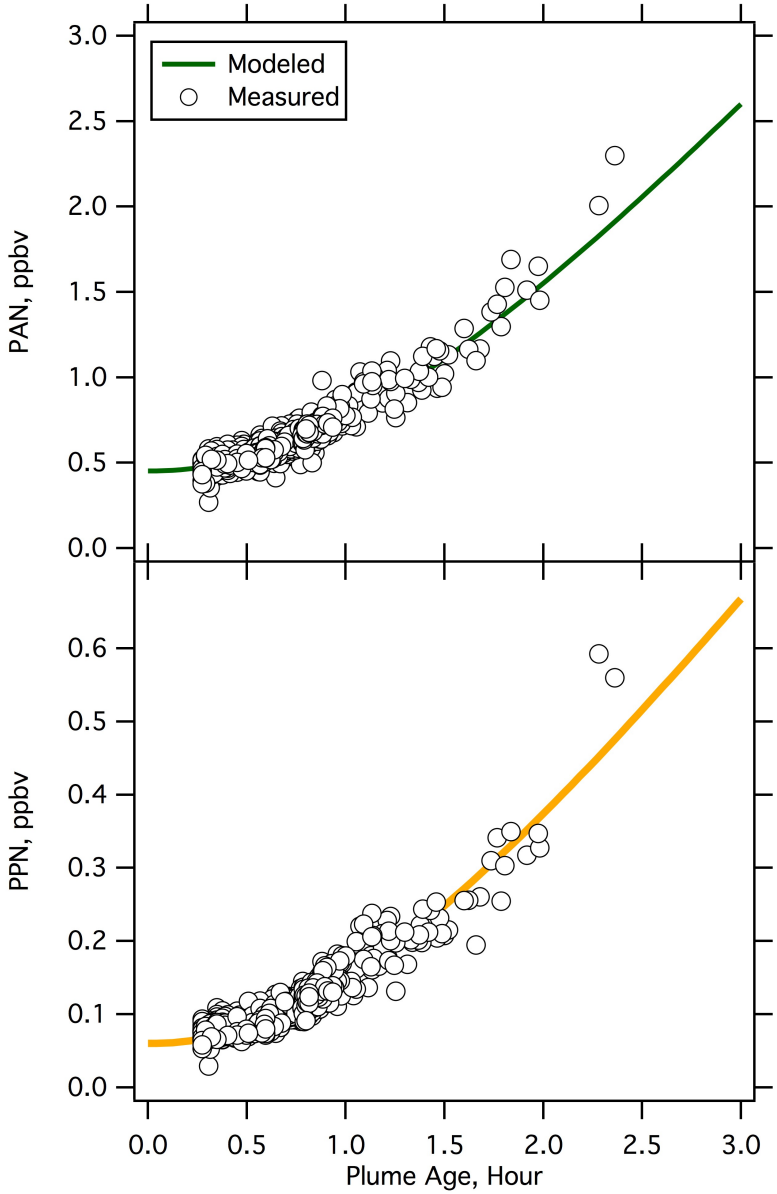
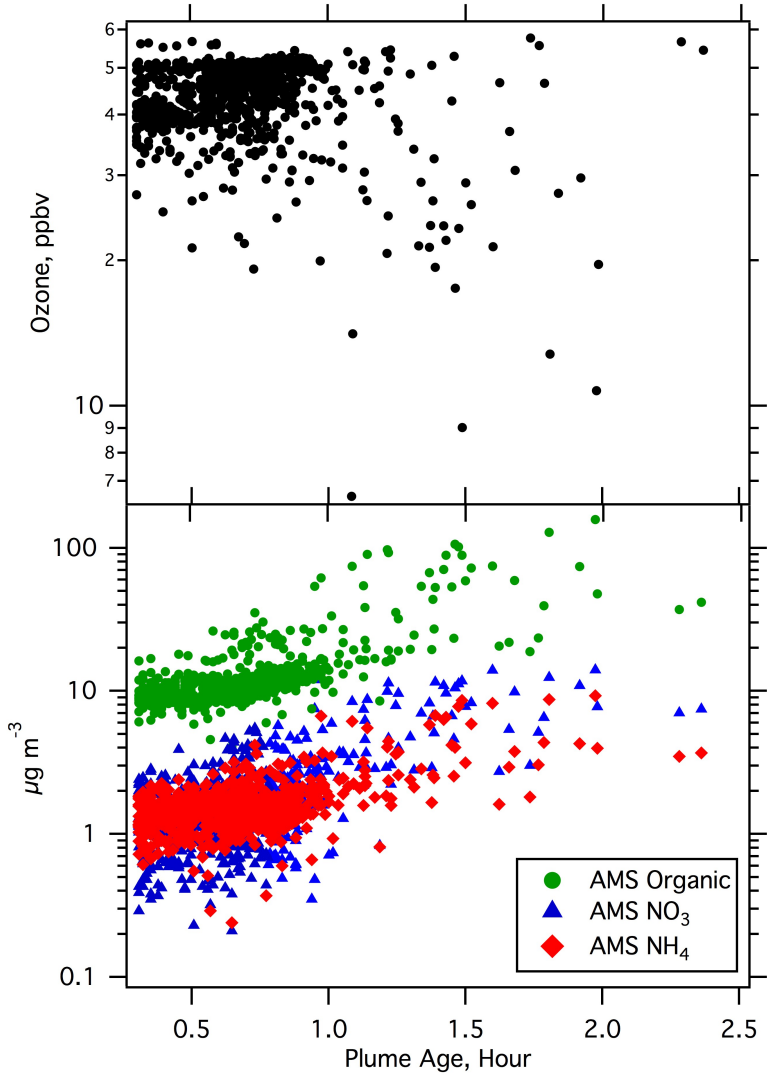


Plume Age Applications:

Insights into Biomass Burning Plume Chemistry

07/03/2013 Night Flight



No net production of ozone is observed as these plumes age. Considering sampling was performed at night, this is not necessarily a surprising result.

We do observe, however, potential production of organic aerosol mass as the plumes ages. Additionally, both aerosol NO_3 and NH_4 show enhancements with plume age.

These results are very preliminary and more work is needed to understand these complex relationships and validate the observed trends!!!

Conclusions

- PAN, APAN, and PPN were measured aboard the NOAA P3 during the SENEX 2013 field mission. Biomass burning plumes were observed during several research flights.

- A simple box model incorporating 36 chemical reactions was developed to simulate plume chemistry relevant to the production of PAN, APAN, and PPN.

- Using model outputs, plume age can be approximated from measurements of APAN.

Future work will focus on improving the performance of this model and attempts to validate calculated plume ages. This model has the potential to be extremely useful for any future measurement efforts focused on the impacts of biomass burning emissions.

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Thank you for your time!