Annual Workshop
Pickle Research Campus
University of Texas, Austin
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Project 14-026

Quantifying ozone production from light alkenes using novel measurements of hydroxynitrate reaction products in Houston during the NASA SEAC^{4}RS project

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Project 14-026 - Quantifying ozone production from light alkenes using novel measurements of hydroxynitrate reaction products in Houston during the NASA SEAC^{4}RS project

Today:

- Briefly summarize SEAC^{4}RS data sets
- Briefly review O_3 production from alkene oxidation
- Demonstrate utility of hydroxynitrates as tracers of photochemistry
- Discuss difficulty arising from rapid atmospheric loss of hydroxynitrates and other secondary products
- Discuss need for and status of modeling

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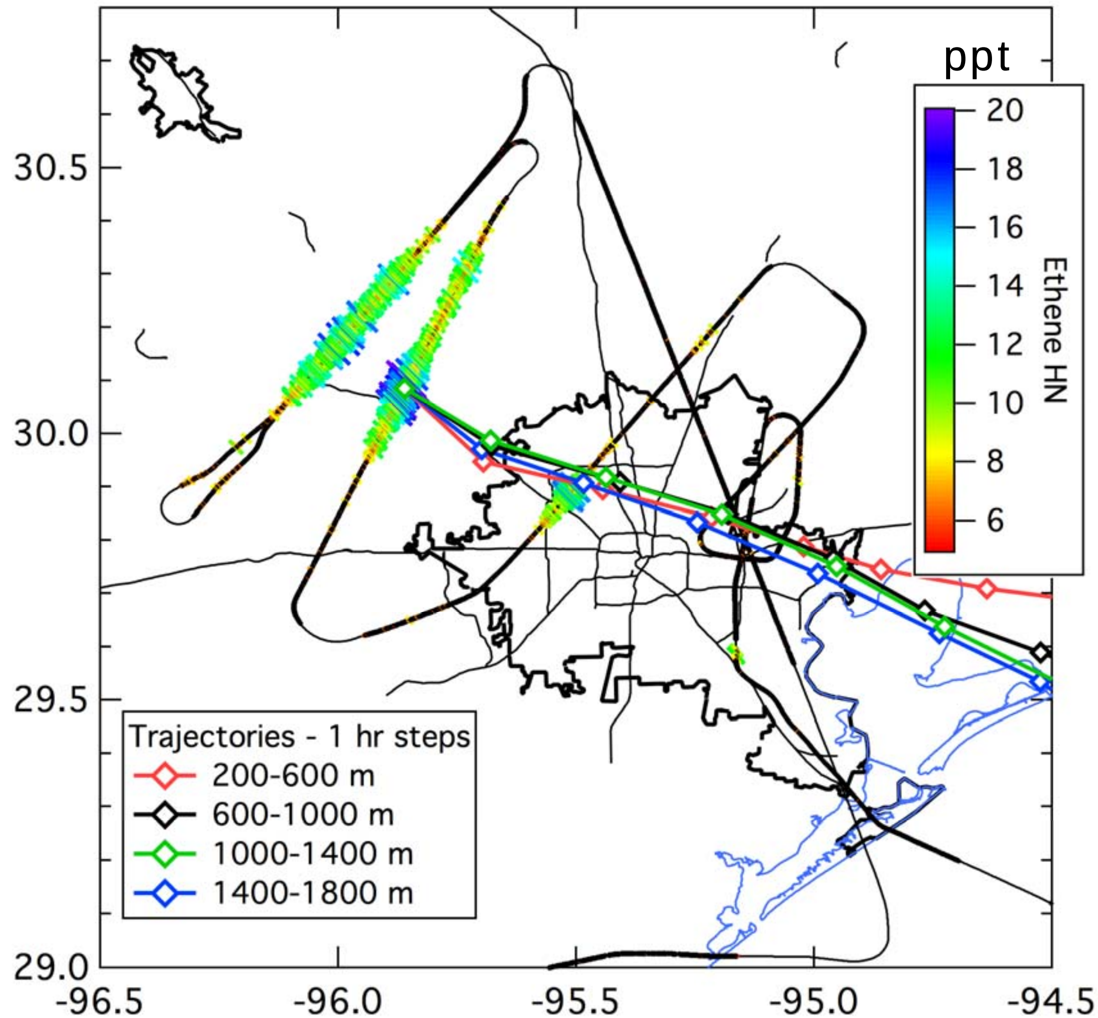
Summary of SEAC⁴RS data sets

One hour of one flight (18 September 2013) with repeat sampling downwind of the Houston Ship Channel area

- Hydroxynitrates form downwind of ship channel
- Back trajectories verify origin of plume



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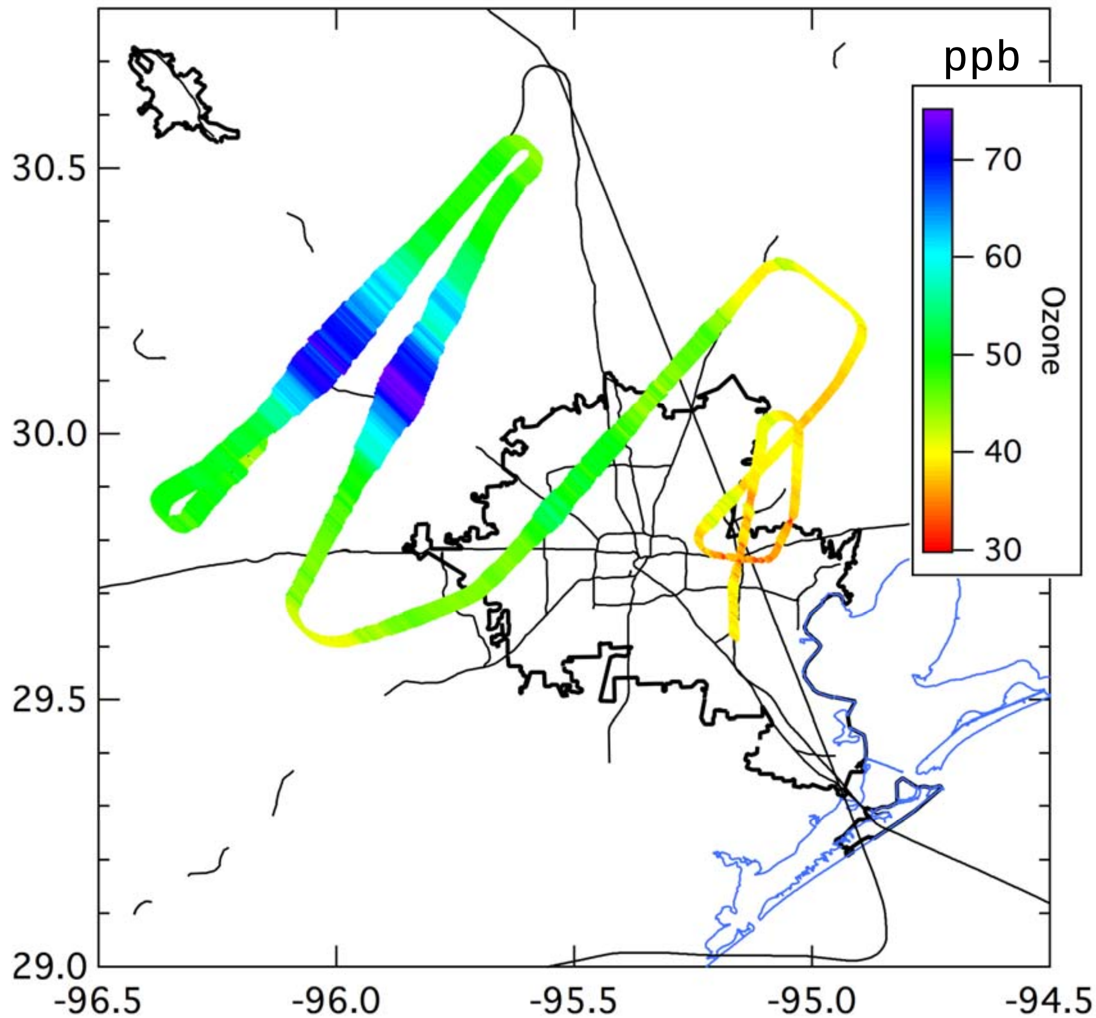

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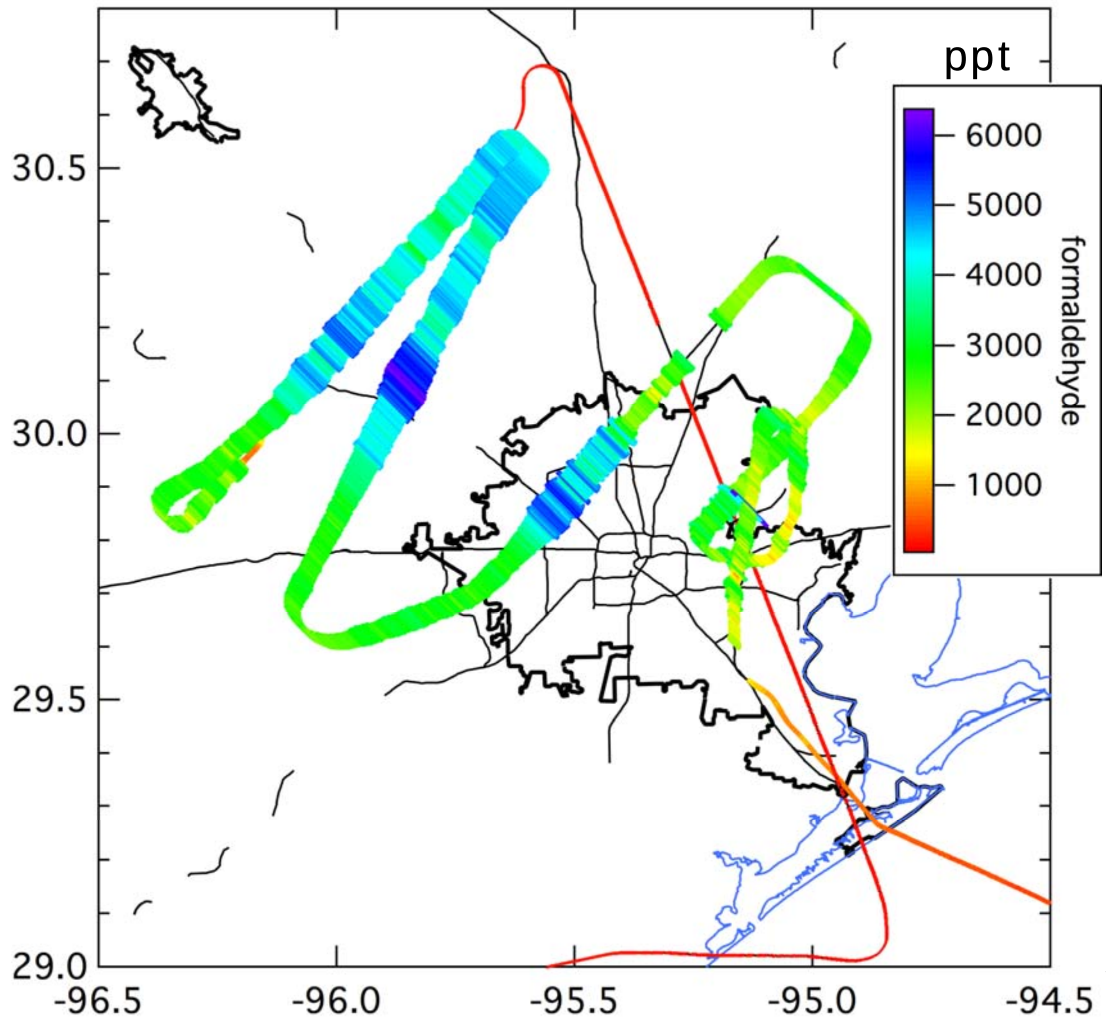

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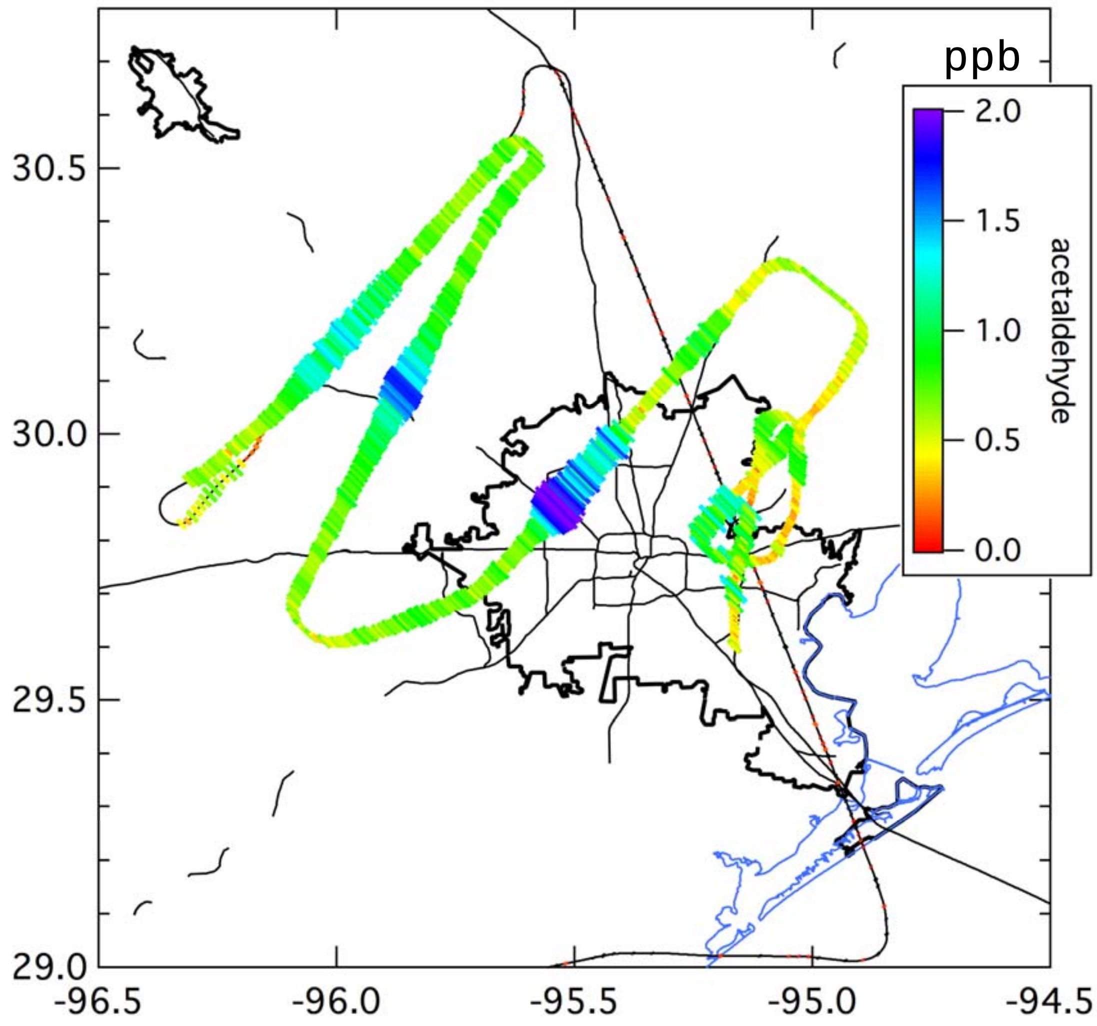

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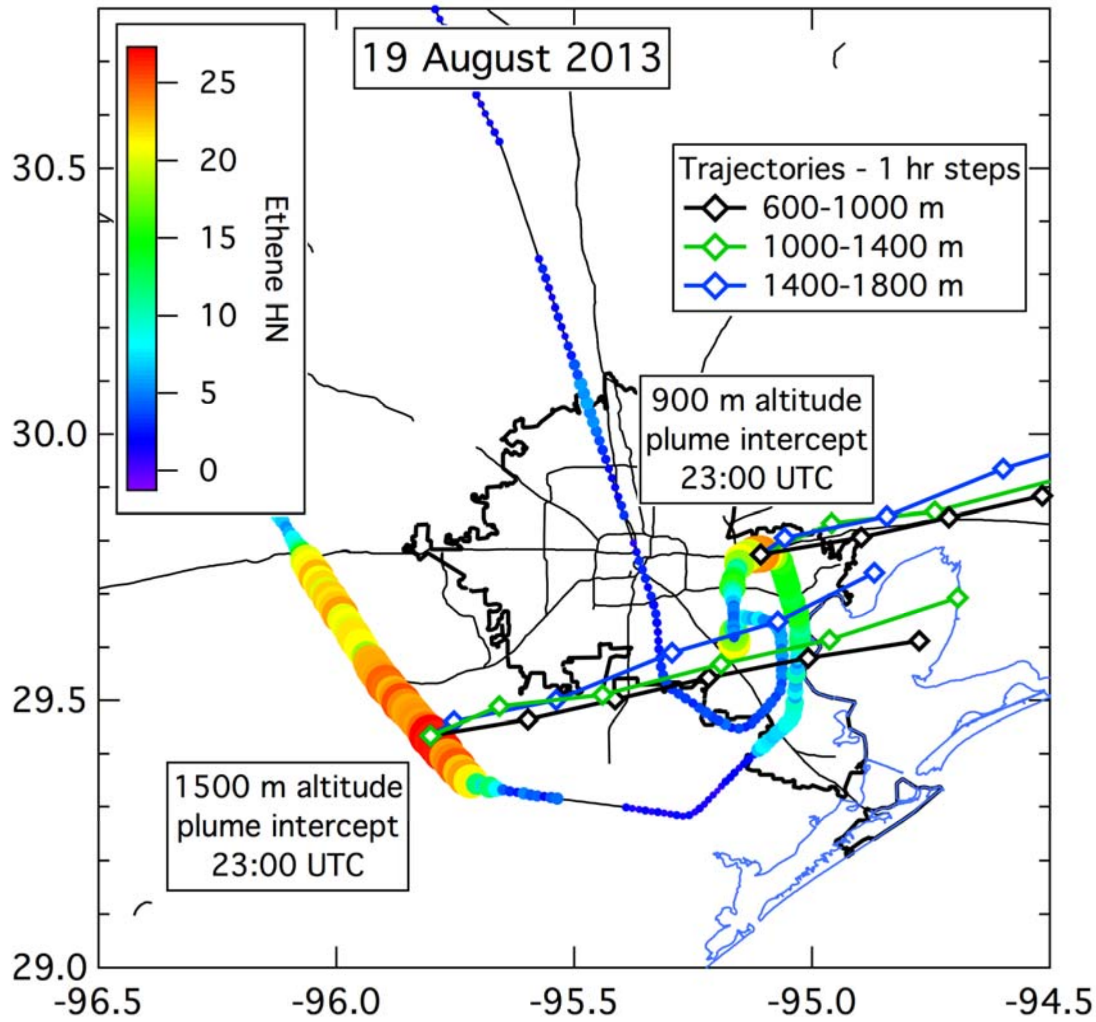
Ship Channel plumes were serendipitously intercepted on 10 additional SEAC4RS flights (e.g. 19 August 2013)



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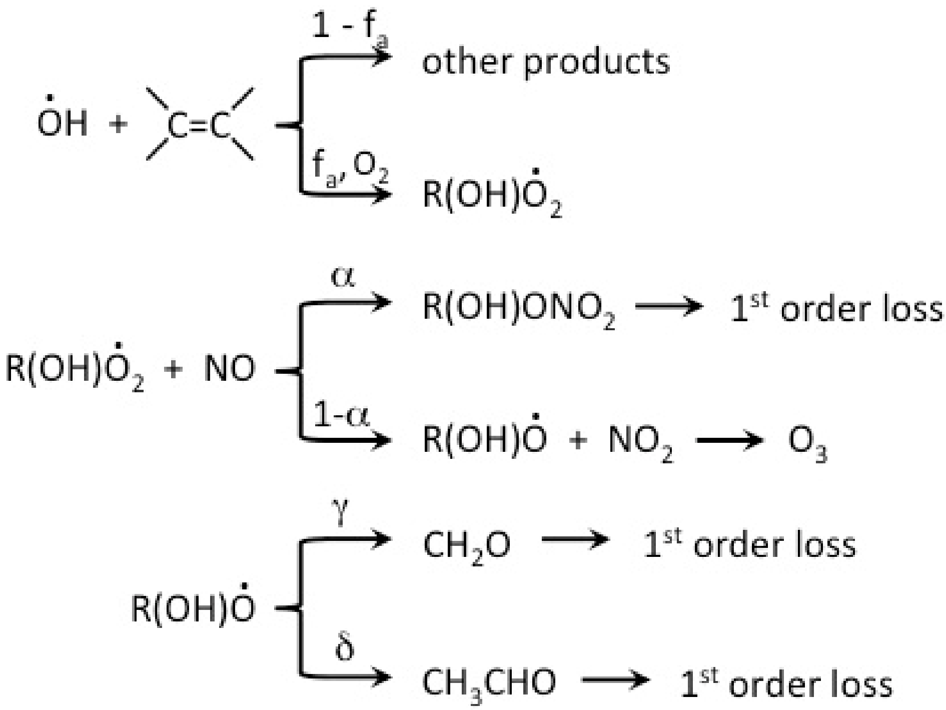
Expected O_3 production from alkene oxidation

Simplified Chemical Scheme



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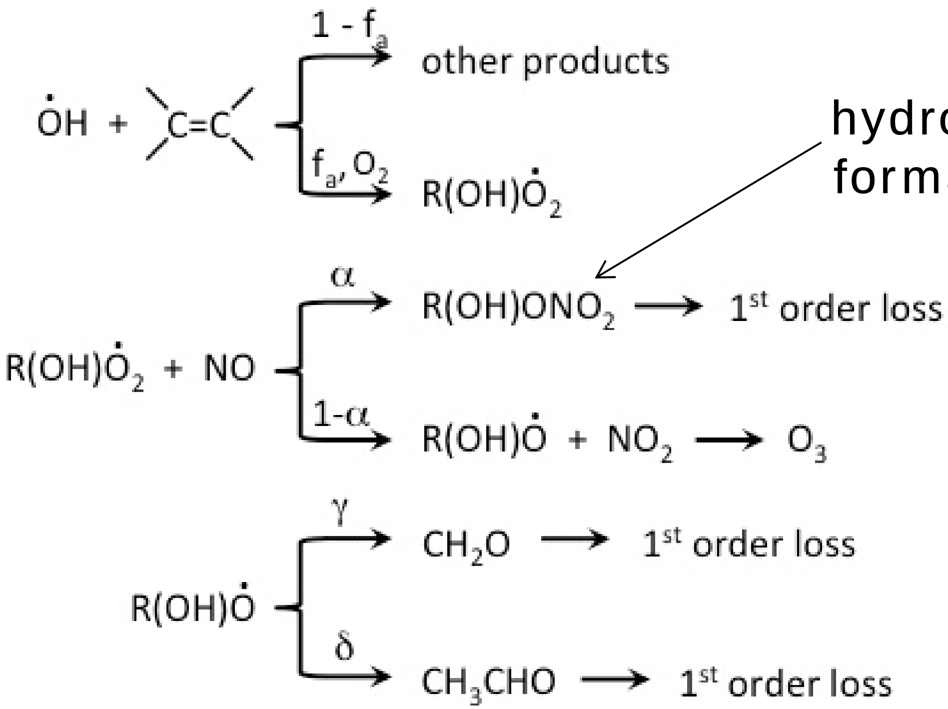
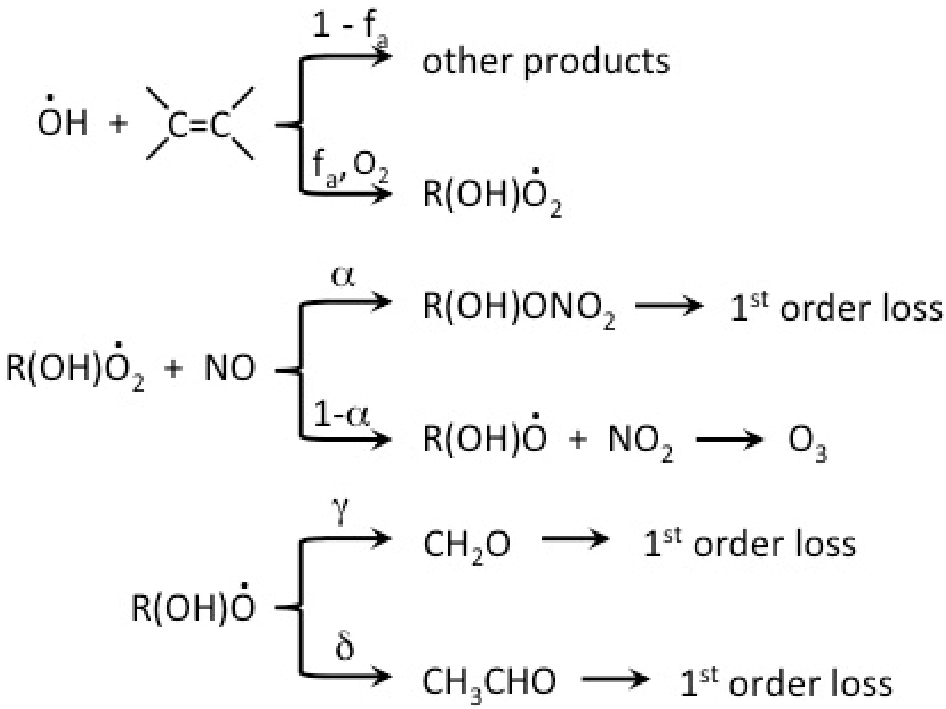


hydroxynitrate formation

Expected O_3 production from alkene oxidation

Simplified Chemical Scheme



Expected product relationships

$$\Delta[O_3] = \sum_i \frac{O_3yield_i}{f_{ai}\alpha_i} \times [HN]_i$$

$$\Delta[CH_2O] = \sum_i \frac{\gamma_i(1-\alpha_i)}{\alpha_i} \times [HN]_i$$

$$\Delta[CH_3CHO] = \sum_i \frac{\delta_i(1-\alpha_i)}{\alpha_i} \times [HN]_i$$

(index *i* identifies alkene)

Scheme parameters for each alkene

alkene	f_a	α	γ	δ	O_3 yield
ethene	1	0.023	1.6	0	1.95
propene	0.97	0.053	1	1	1.87
butene	0.97	0.106	1	1	1.76
butadiene	0.97	0.104	1	0	1.77
isoprene	0.92	0.12	1	0	1.69

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Utility of hydroxynitrates as tracers of photochemistry

- Three downwind plume transects, plus sampling over ship channel

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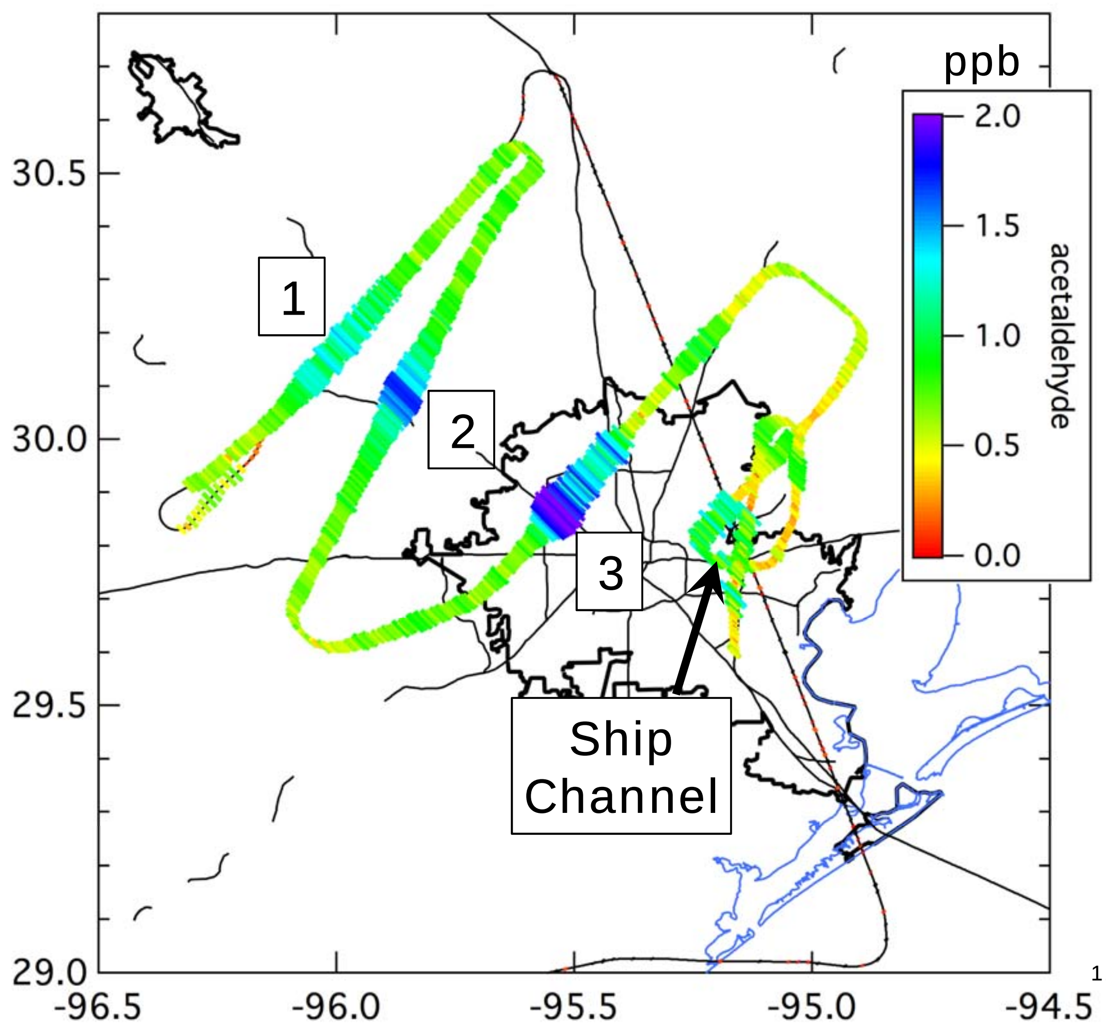

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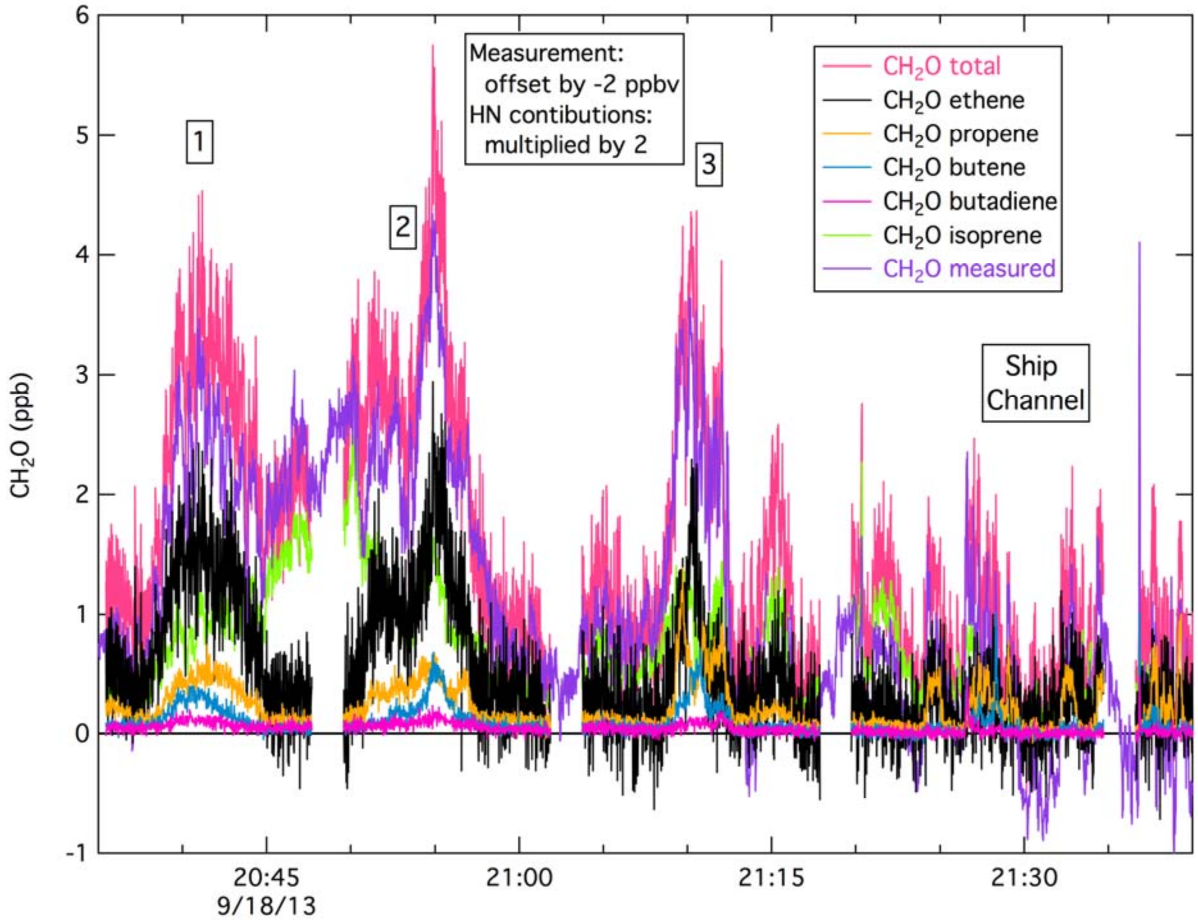
Utility of hydroxynitrates as tracers of photochemistry

- Three downwind plume transects, plus sampling over ship channel
- Hydroxynitrates correlate well with CH_2O
- All 5 alkenes contribute to CH_2O
- <u>However</u>, need factor of 2 to explain magnitude of CH_2O observed

$$\Delta[CH_2O] = \sum_i \frac{\gamma_i (1-\alpha_i)}{\alpha_i} \times [HN]_i$$



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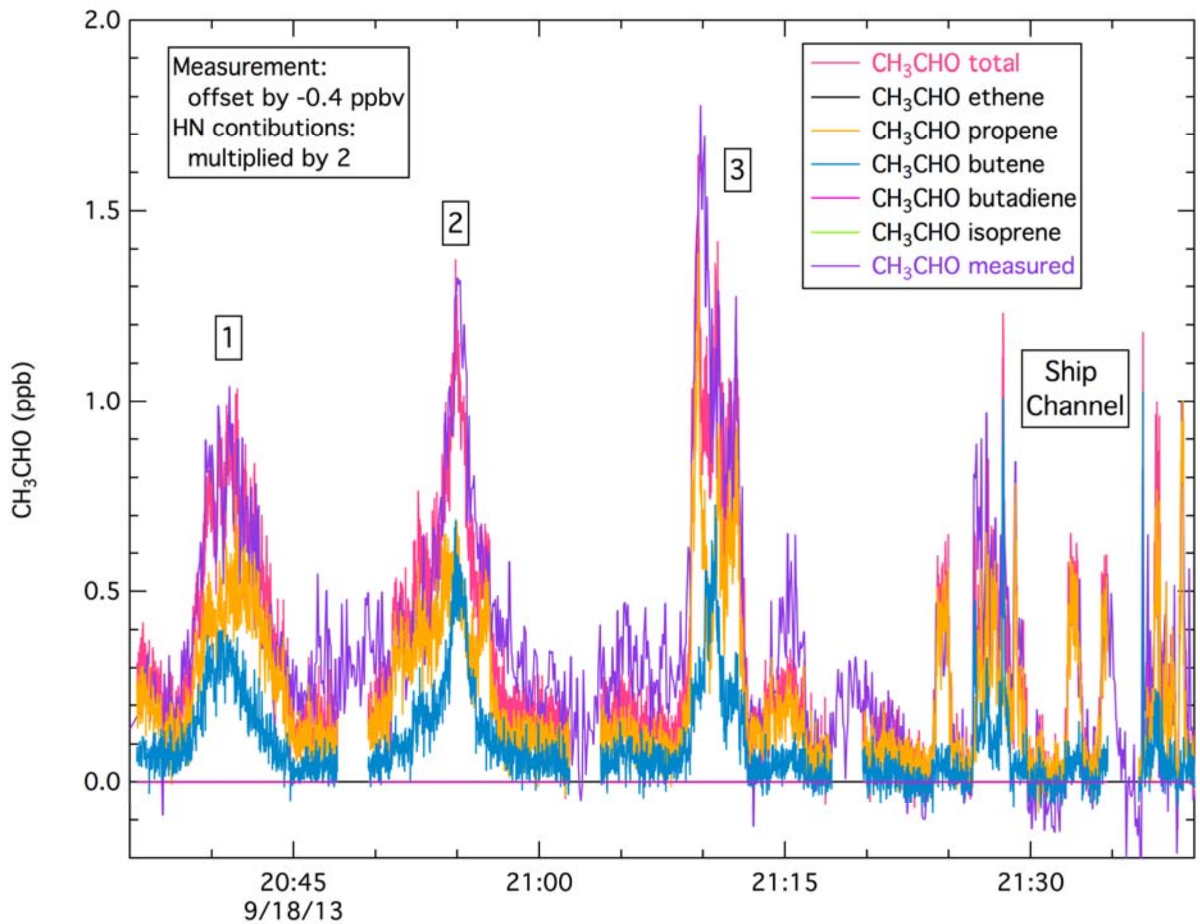
Utility of hydroxynitrates as tracers of photochemistry

- Three downwind plume transects, plus sampling over ship channel
- Hydroxynitrates correlate well with CH_2O and CH_3CHO
- All 5 alkenes contribute to CH_2O
- Only propene and butenes contribute to CH_3CHO
- <u>However</u>, need factor of 2 to explain magnitude of aldehyde observed

$$\Delta[CH_3CHO] = \sum_i \frac{\delta_i(1-\alpha_i)}{\alpha_i} \times [HN]_i$$



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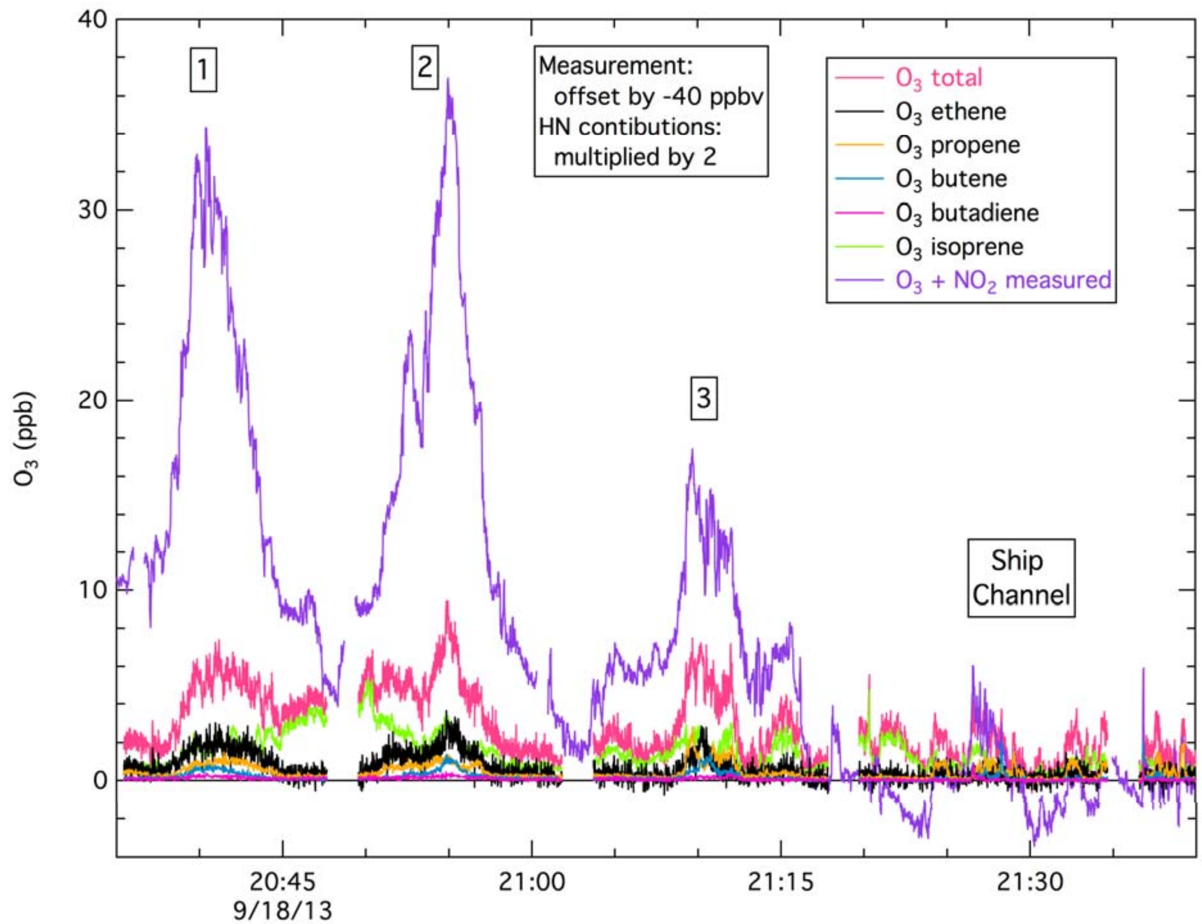
- However, need factor of 2 to explain magnitude of aldehyde levels
- <u>A much greater factor</u> necessary to explain O_3 observed

Evidently, hydroxynitrates and aldehydes are rapidly lost on the time scale of hours!!

$$\Delta[O_3] = \sum_i \frac{O_3 yield_i}{f_{ai}\alpha_i} \times [HN]_i$$



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- However, need factor of 2 to explain magnitude of aldehyde levels
- <u>A much greater factor</u> necessary to explain O_3 observed. That factor is ~10

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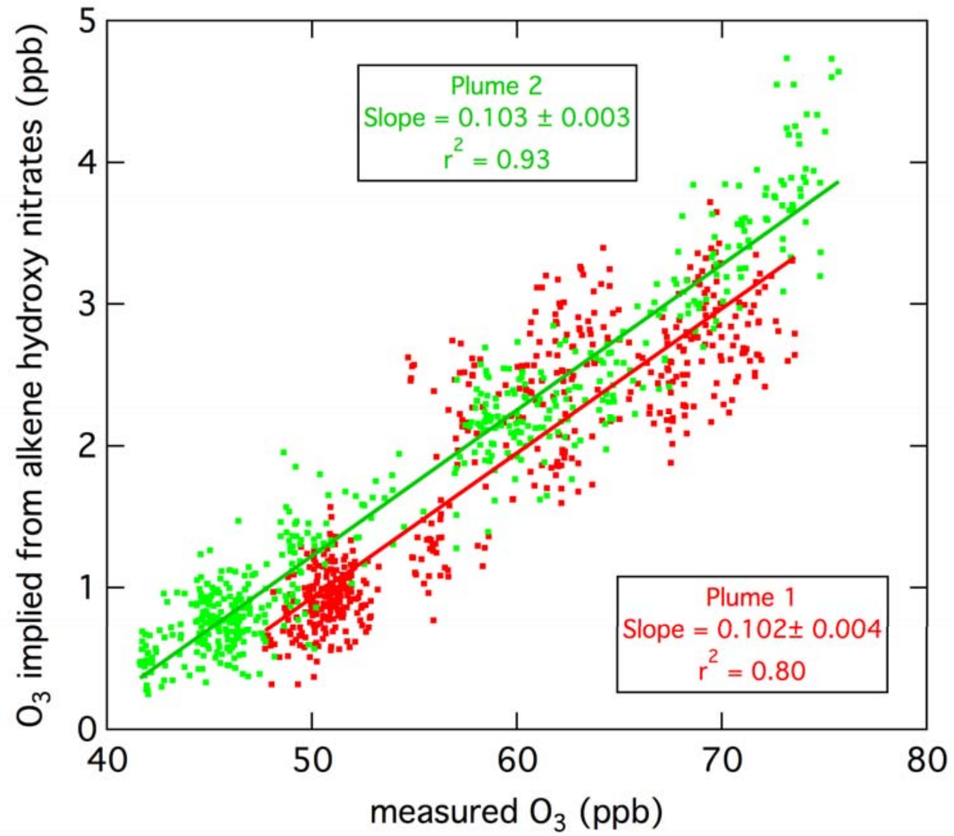
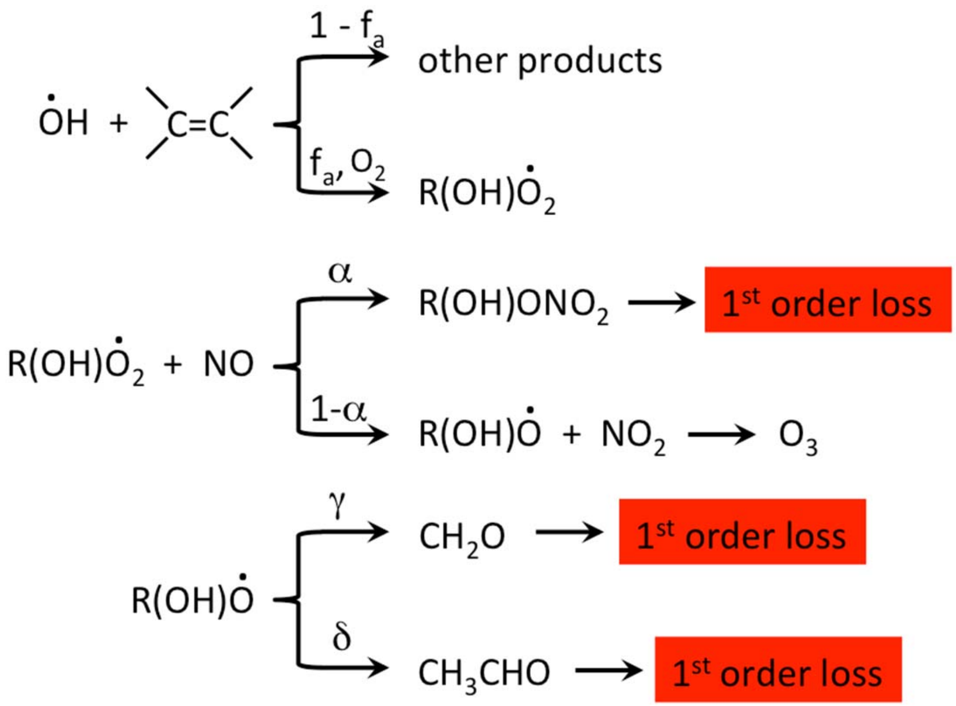


Rapid atmospheric loss of hydroxynitrates and other secondary products

- Loss processes are equally important as production in determining concentrations of photochemical products



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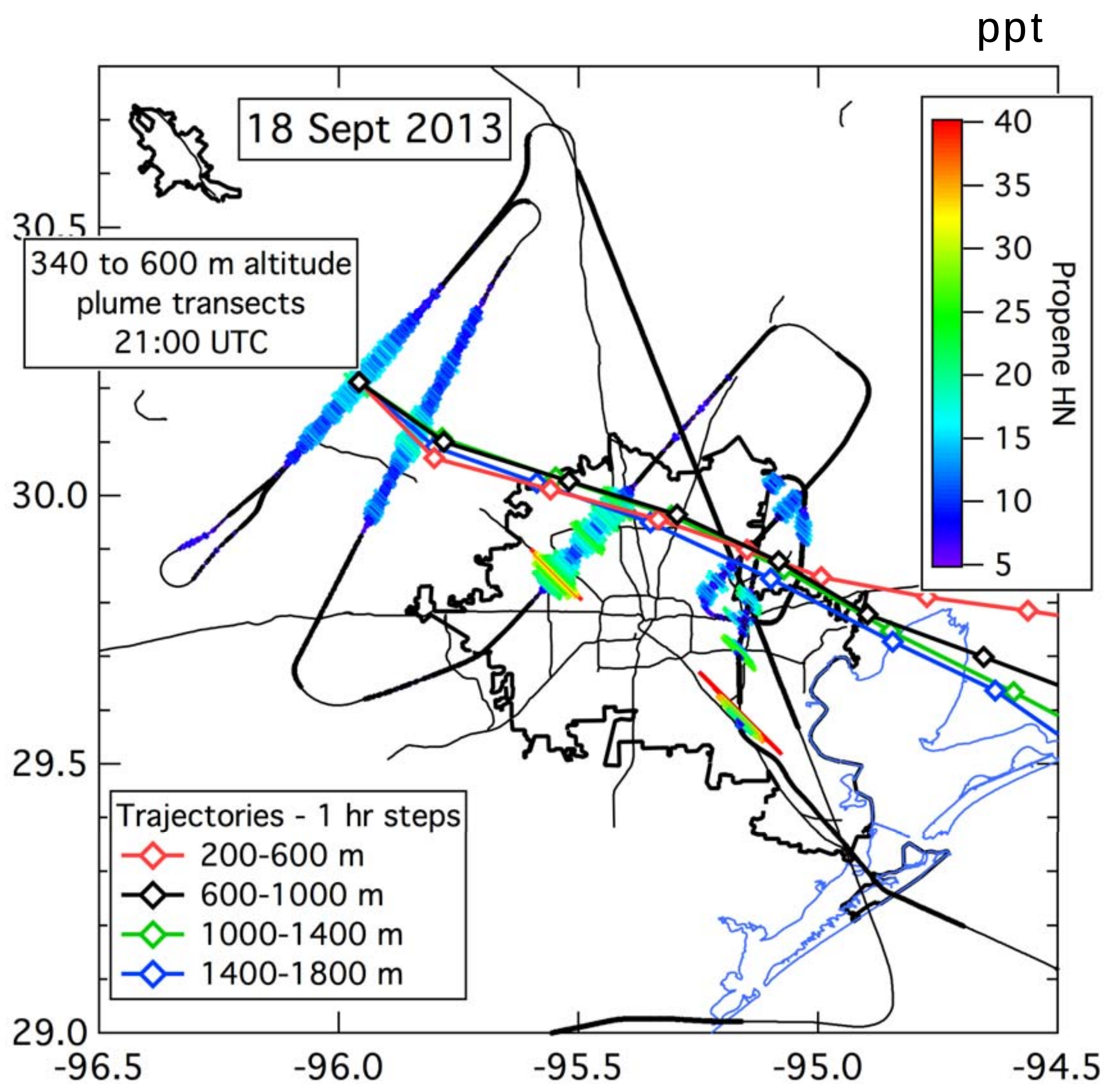
Rapid atmospheric loss of hydroxynitrates and other secondary products

- Loss processes are equally important as production in determining concentrations of photochemical products
- Plume transport is 4 to 5 hours at furthest downwind transect
- Most of hydroxynitrates and aldehydes have been lost, while O_3 accumulates
- Plume modeling required to quantitatively treat evolution of photochemical products



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- Plume modeling required to quantitatively treat evolution of photochemical products
- Reaction with OH, photolysis, and take up on aerosols are all important, but contributions vary between species – Critical to quantify in modeling

Species	Reaction with OH	Photolysis	Aerosol take up
formaldehyde	√	√	
acetaldehyde	√		
hydroxynitrates			√

Relationships between photochemical products will vary with plume composition and meteorological conditions!!

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Need for and status of modeling

- Quantitative assessment of HRVOC sources and their impacts on the Houston atmosphere
- Evaluate chemical mechanism for alkene oxidation and ozone and hydroxynitrate formation in HRVOC plumes
- Investigate how to model the Houston Ship Channel HRVOCs

Need for and status of modeling

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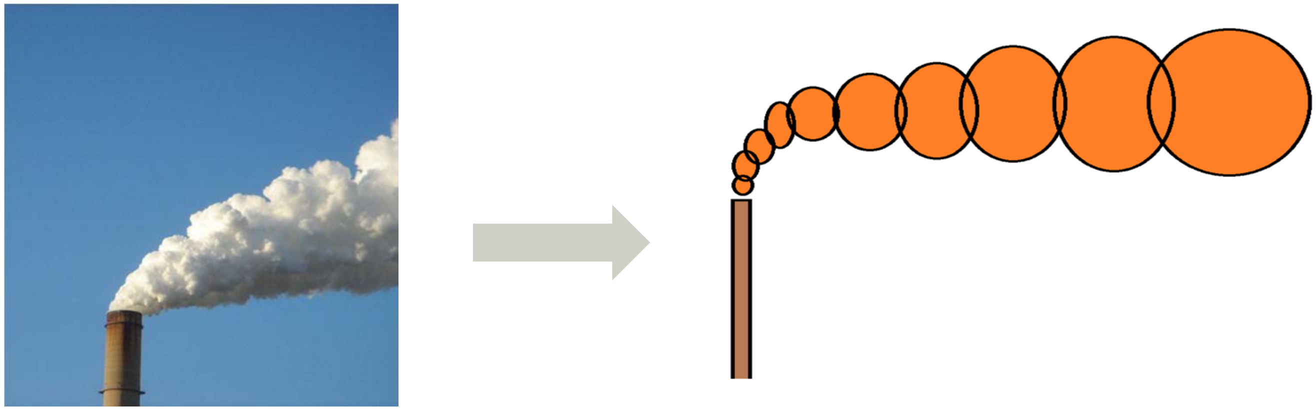
- Reactive plume modeling with SCICHEM 3.0
- Results for 18 September 2013 flight
- Preliminary simulations conducted to characterize Ship Channel emissions based on peak NO_2 plume concentrations
- Initial results shown here
- Refined modeling and analysis in progress

SCICHEM: SCIPUFF with Chemistry



- Plume represented as a succession of puffs
- Puff dispersion based on SCIPUFF (Second Order Closure Integrated Puff Model)
- Full chemistry treatment, comparable to CAMx and CMAQ
- Latest version, SCICHEM 3.0, completed in June 2015
- Older version used in a previous AQRP project (10-020) to simulate Oklaunion power plant plume at night
- For AQRP 14-026, CB6r2 implemented for SCICHEM 3.0 and hydroxynitrate mechanism added

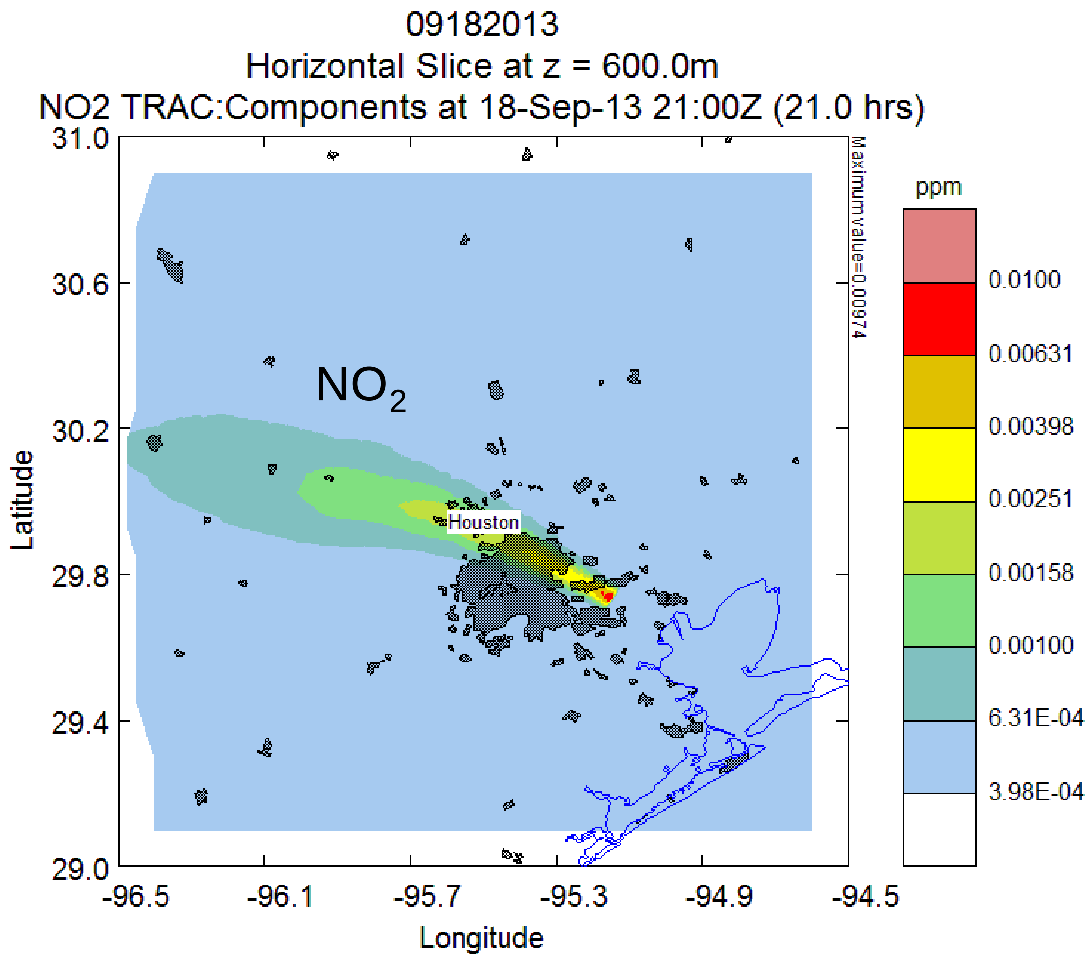
September 18, 2013 Plume

- Surface meteorology from KHOU (Houston Hobby) and KIAH (George Bush Intercontinental Airport)
- Upper air meteorology from KCRP (Corpus Christi) and DC-8 measurements during September 18, 2013 flight
- Initial width (~6 km) and height (600 m) of Ship Channel plume based on plume measurements over the channel
- Ship Channel Emissions:
  - — Initial estimates of ship channel emissions for NOx, ethene, propene and alkanes based on SOF (Johansson et al., 2014)
  - — Regression analysis of DC-8 ship channel plume measurements for other HRVOCs, aromatics and aldehydes with NOy and ethene measurements to estimate emissions of these species
  - — Adjust emissions of NOx and other species to match peak measured NOy concentrations near the Ship Channel

*Johansson, J. K. E., J. Mellqvist, J. Samuelsson, B. Offerle, B. Lefer, B. Rappenglück, J. Flynn, and G. Yarwood (2014), Emission measurements of alkenes, alkanes, SO_2, and NO_2 from stationary sources in Southeast Texas over a 5 year period using SOF and mobile DOAS, *J. Geophys. Res. Atmos.*, **119**, doi:10.1002/2013JD020485.

Preliminary Results from September 18, 2013 Simulation: Plume NO_2

- Modeled plume direction agrees with measurements
- NOx concentrations consistent with observations near ship channel and downwind



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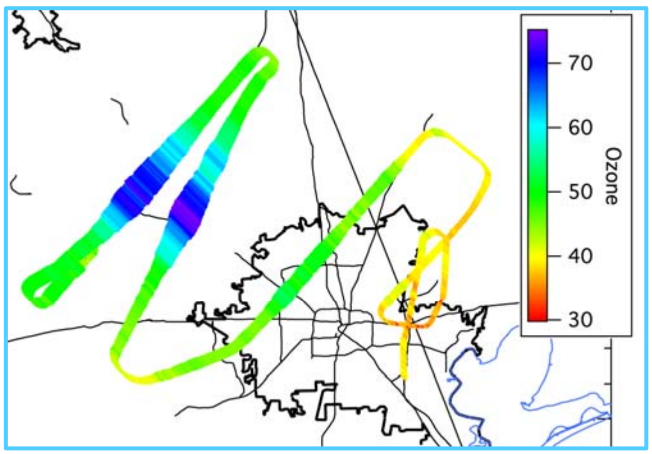
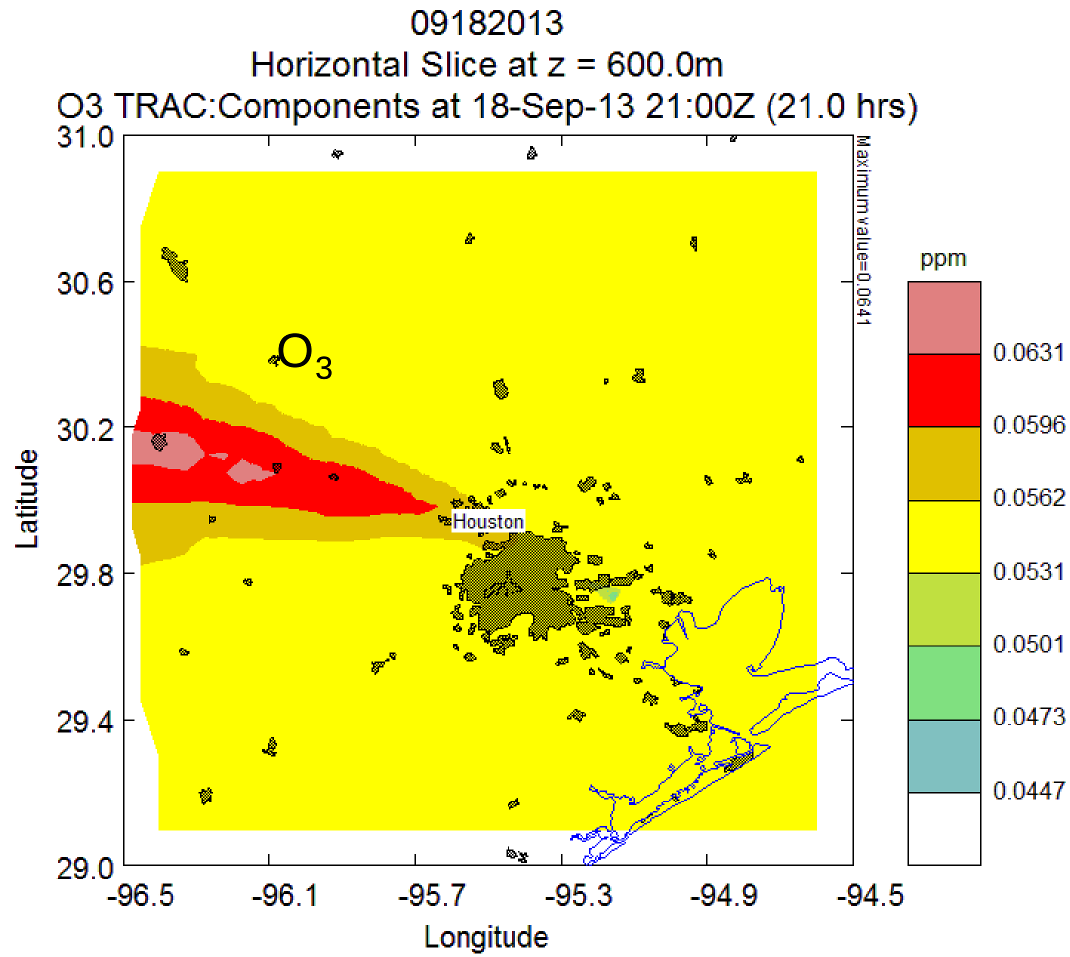
Preliminary Results from September 18, 2013 Simulation: Plume O_3

- O_3 titration at ship channel consistent with measurements
- O_3 production downwind qualitatively consistent with measurements





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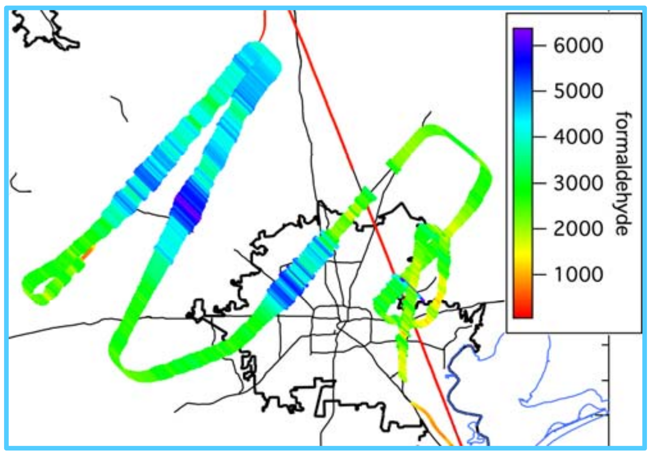
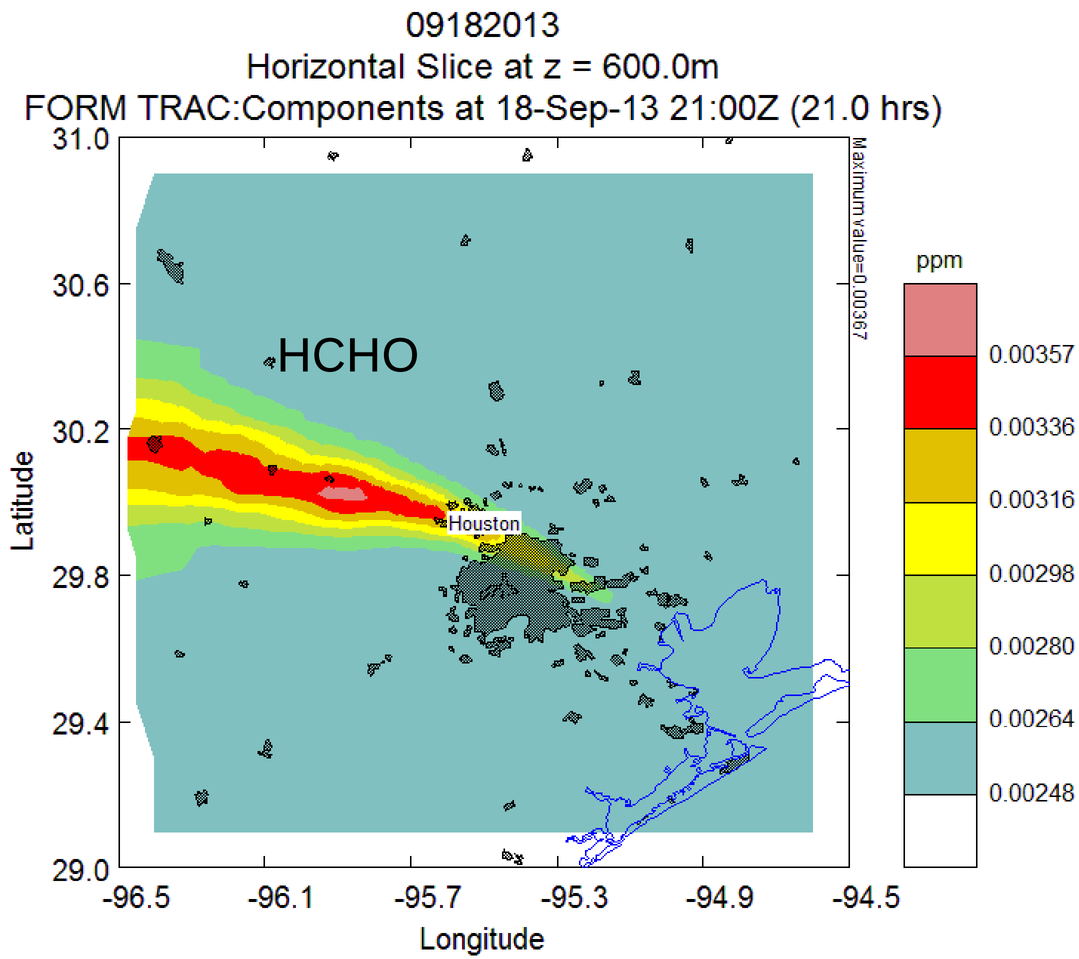
Preliminary Results from September 18, 2013 Simulation: Plume HCHO

- Modeled HCHO behavior consistent with measurements: HCHO levels initially increase and then decrease at the furthest downwind transect





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Project 14-026

Quantifying ozone production from light alkenes using novel measurements of hydroxynitrate reaction products in Houston during the NASA SEAC^{4}RS project

Summary:

- Hydroxynitrates provide useful tracers of photochemical products from alkene oxidation including O_3 and aldehydes
- The rapid atmospheric loss of the hydroxynitrates (and the aldehydes) compared to O_3 complicates the analysis
- Modeling will provide an indispensible complement to the observational analysis
- Preliminary modeling results are encouraging

Project 14-026

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Work to be done:

- Complete analysis of observations from all 11 SEAC^{4}RS flights that sampled Ship Channel plumes to get as complete a picture as possible of production and loss of hydroxynitrates, aldehydes and O_3
- Complete modeling of 18 September and other selected flights