Physical Processes in Convection: Chemistry

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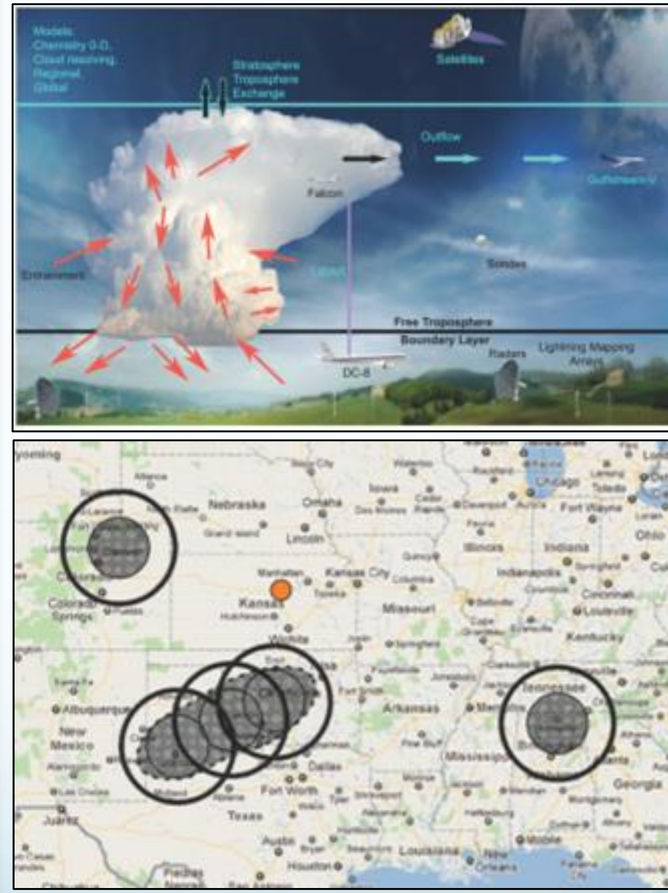
Outline

- Chemical tracer transport in convection
- Lightning NO_x production
- Effects of convection on ozone
    - In-cloud
    - Downwind
    - Wrapping of stratospheric air
- Convective transport of short-lived halogen species
- Wet scavenging of soluble gases
- New particle formation in convective outflow
- Pyroconvection

DEEP CONVECTIVE CLOUDS & CHEMISTRY (DC3)

- **Field campaign** to **simultaneously** use extensive ground & airborne instrumentation to investigate midlatitude deep convection
  - May-June 2012
  - 3 sampling regions
- Focus on storm behavior, lightning, surface emissions, **LNO_x, anvil chemistry, and scavenging of chemical species**
- DC3 objectives:
  - Investigate active convection and its outflow post-event (12-48 hrs)
  - Study impact on composition and chemistry of upper troposphere



Experimental design (top); Sampling regions (bottom)

(Barth et al., 2015)

The CONTRAST Experiment (Guam, Jan-Feb 2014)

An example of how model, satellite and in situ observations work together to accomplish the science goals

Science Question:

- How important is halogen chemistry to ozone destruction and the associated chemistry-climate interaction?

NCAR Model:

- CAM-chem (CCM) predicts 25% of the chemical ozone loss in the tropical UT is represented by halogen chemistry.
- Halogen chemistry is important to stratospheric ozone depletion, but the injection of halogens into the stratosphere is poorly known; convective lifting of VSLS into TTL can only be provided by in situ observations

The Field Campaign- CONTRAST "CONvective TRansport of Active Species in the Tropics"

- Unprecedented halogen data from ocean surface to the tropopause
- CAM-chem was run in forecast mode to provide chemical forecast for the flights
- Post-campaign comparison in progress

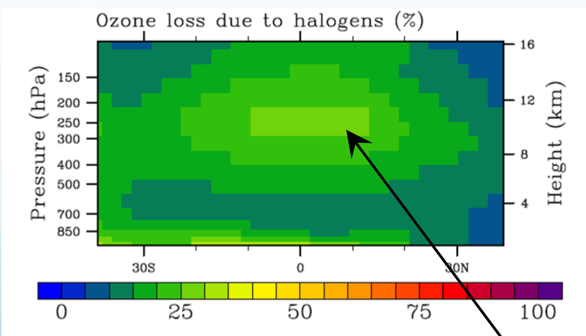
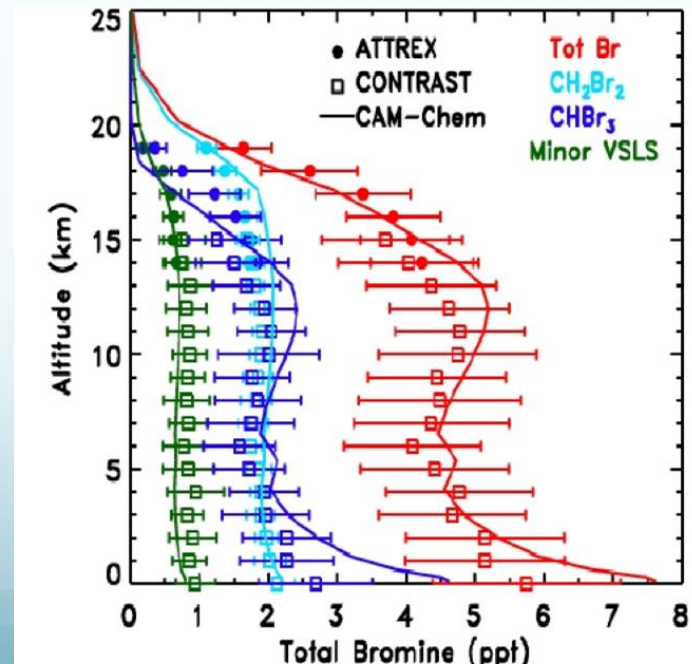


Fig. 6. Percentage of the annually integrated chemical ozone loss from HO_x, O_x and halogen photochemistry as simulated by CAM-Chem.

Saiz-Lopez et al., 2012

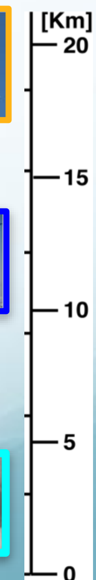
Ozone destruction of by halogens in the tropical UT



NASA Global Hawk

NCAR GV

UK BAe146

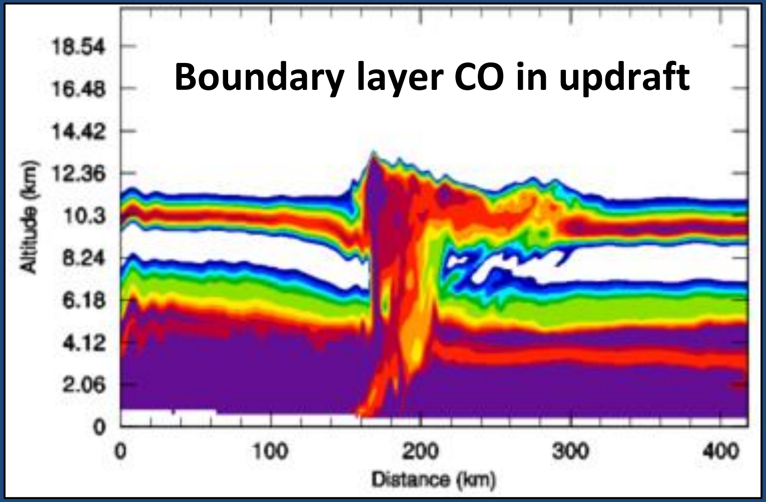


Chemical Tracers as Diagnostics of Convective Transport

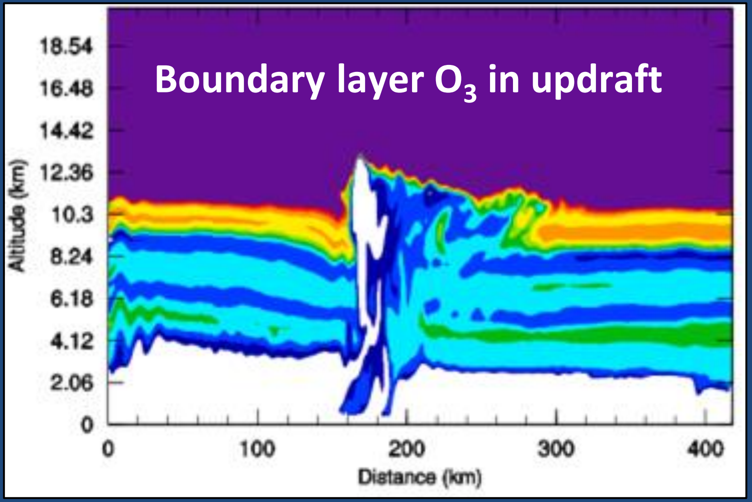
- Trace gases can be used to illustrate the magnitude and direction of transport within a convective cloud.
- Use gases that have chemical lifetimes much longer than the duration of the convective event.
- Typical examples: CO, O_3, C_2H_6, C_3H_8, CH_3I

Additional gases ? Need to sample at numerous altitudes.

May 29-30, 2012 DC3



~50 ppbv increase due to upward transport

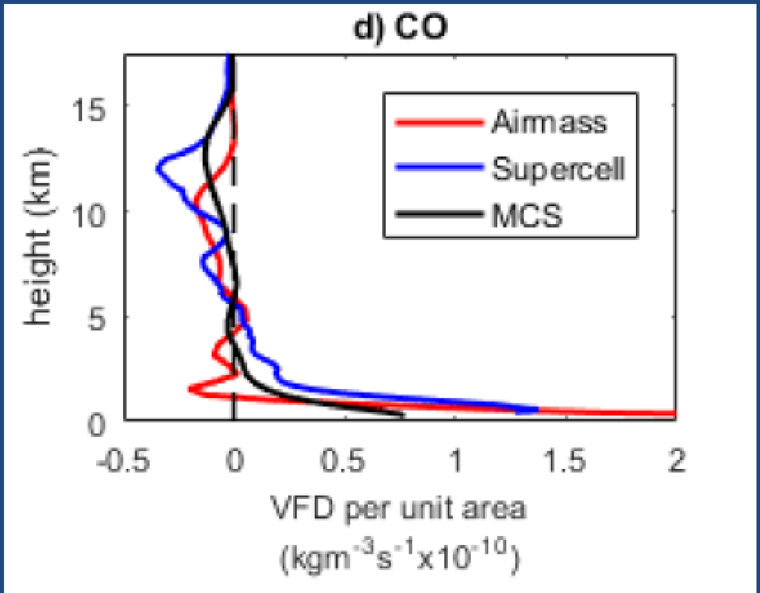


~40 ppbv decrease due to upward transport
~2 ppbv loss due to chemistry

Cummings et al., 2017, in prep.

Tracers Used for Model Evaluation

DC3 Storm		Low level inflow		Upper levels			
				Affected by storm outflow		Unaffected by storm outflow	
		CO	O3	CO	O3	CO	O3
May 21st	Aircraft	150.5 (±9.6)	71.4 (±3.0)	100.2 (±4.5)	143.4 (±25.2)	75.1 (±3.4)	214.3 (±7.6)
	WRF-Chem	152.5 (±2.2)	61.8 (±2.3)	94.2 (±6.7)	147.3 (±25.2)	79.7 (±0.4)	213.0 (±14.3)
May 29th	Aircraft	132.3 (±3.1)	32.6 (±0.4)	123.1 (±3.6)	80.0 (±4.8)	104.4 (±5.4)	82.2 (±7.0)
	WRF-Chem	136.3 (±0.3)	44.1 (±3.6)	123.2 (±14.2)	84.7 (±12.9)	96.3 (±3.4)	97.1 (±6.4)
June 11th	Aircraft	117.5 (±4.3)	33.9 (±3.5)	107.9 (±5.0)	111.1 (±16.0)	72.6 (±3.1)	155.3 (±20.2)
	WRF-Chem	112.0 (±7.8)	45.9 (±4.2)	108.8 (±2.1)	101.4 (±14.4)	69.8 (±0.7)	161.8 (±6.1)



Positive values of Vertical Flux Divergence (VFD) indicate entrainment; negative values indicate detrainment

At mature stage, supercell storm has strongest anvil level detrainment, but MCS is much longer lived storm

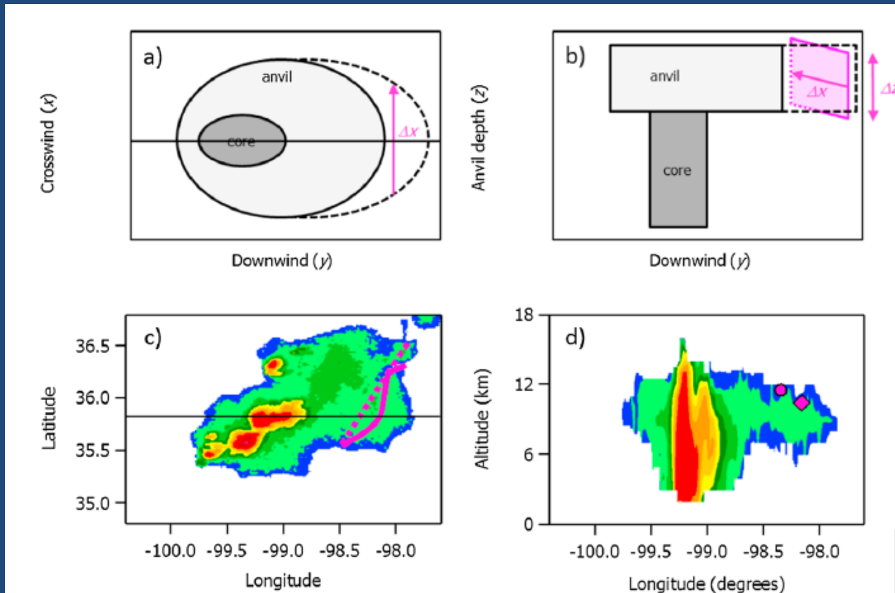
Li et al., 2017 submitted

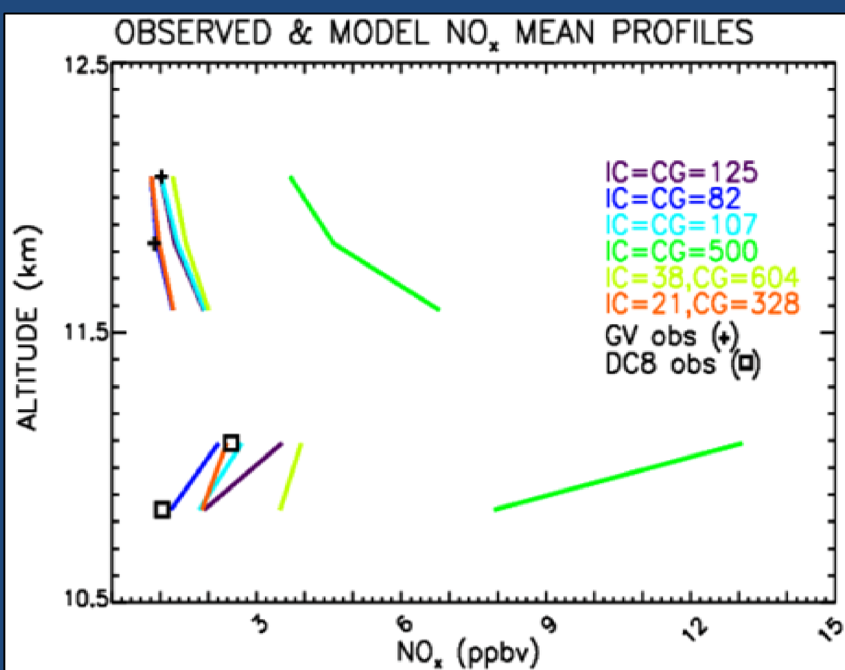
Some Literature Estimates of LNO_x Production Per Flash

Method	Moles NO/flash (Notes)	Reference
Theoretical	1100 (CG), 110 (IC)	Price et al., 1997
Laboratory	~103	Wang et al., 1998
A/C data, cloud model	345-460 (STERAO-A)	DeCaria, et al., 2005
A/C data, cloud model	590-700 (CRYSTAL-FACE)	Ott et al., 2010
	500 (Mean midlat. model)	Ott et al., 2010
A/C data, cloud model	500 - 600 (Hector)	Cummings et al., 2013
A/C data, cloud model	82 (DC3 OK supercells)	Cummings, 2017
Aircraft data	70-210 (TROCCINOX)	Huntrieser et al., 2008
Aircraft data	121-385 (SCOUT-Darwin)	Huntrieser et al., 2009
Aircraft data	70-179 (AMMA)	

Best estimate: 250 moles/flash → Globally, 2 – 8 TgN/yr (Schumann and Huntrieser, 2007) – factor of 4 uncertainty

LNOx Production in DC3 Storms





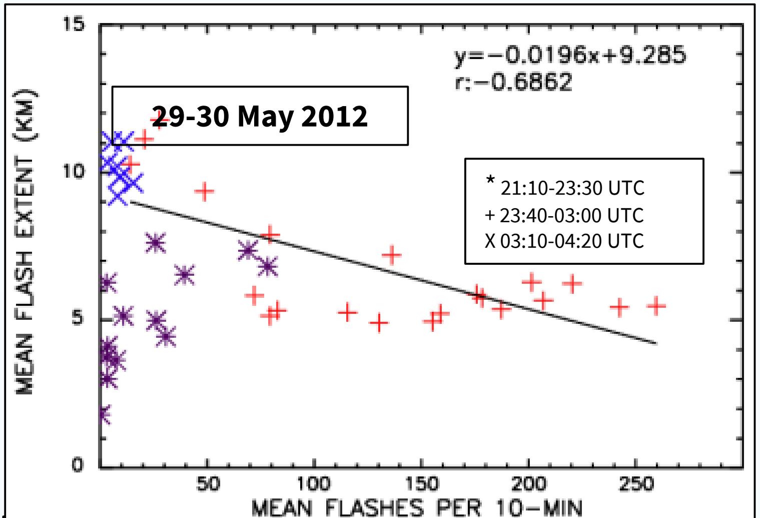
Pollack et al., (2016) estimated mean LNOx production per flash in 3 DC3 storms using volume- and flux-based approaches.

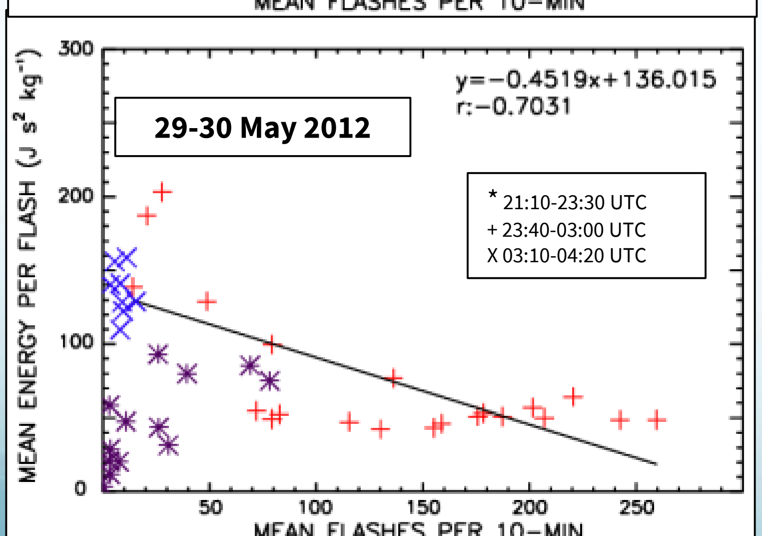
Estimates ranged from 107 to 332 moles per flash.

Cummings et al. (2017, in prep.) simulated the 29-30 May DC3 high flash rate supercell storm in Okla. using WRF-Chem and a upward ice flux flash rate prediction scheme.

Several LNOx production scenarios were tested: 82 moles per flash yielded best with anvil aircraft data; LMA: mean flash extent 7.6 km → ~10 moles/km

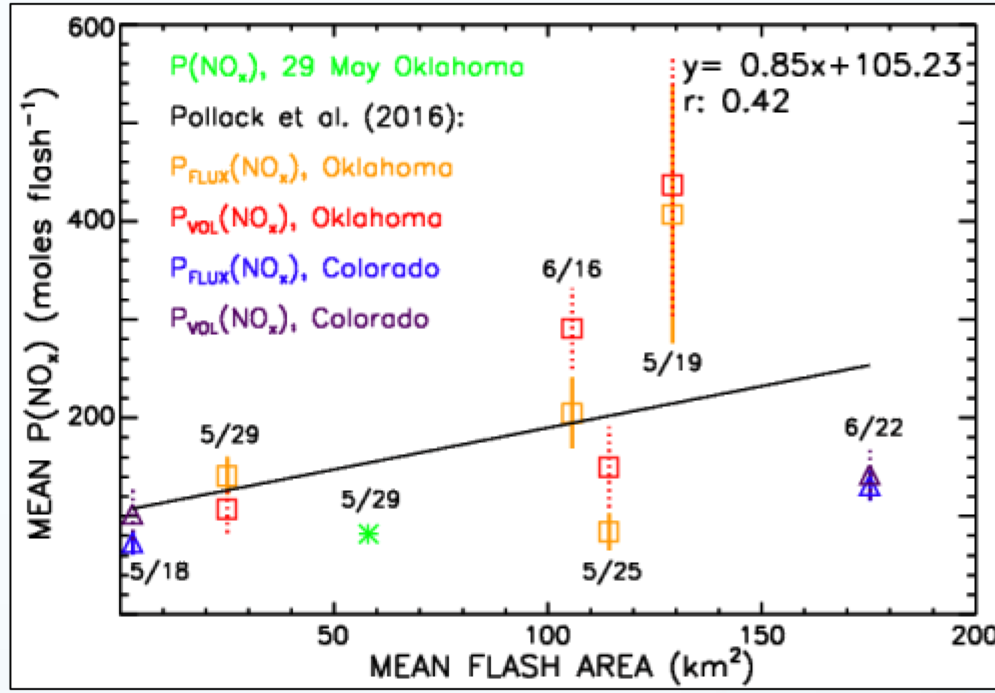
Relating LNO_x Production to Lightning Characteristics





Correlations based on data from 23:40-03:00 UTC (red +)

Cummings et al., 2017, in prep.



- Flash extent in DC3 storms ~6-15 km
- Potential to develop parameterization scheme for LNO_x production based on flash rate or flash extent.
- Need flash rate, extent, energy from LMA

Possible Underestimate of LNOx Production per Flash

- Nault et al. (2015) found that methyl peroxy nitrate, pernitric acid, nitrogen pentoxide, and alkyl nitrates are more significant sinks for NOx in convective outflow in DC3 than expected.
- Much more NOx in convective outflow was converted to higher oxides of N.
- Result is 2 – 3 hour lifetime for NOx in upper tropospheric convective outflow rather than the assumed few days.
- Nault et al. (2017, in prep.) find that reinterpretation of many previous measurements in light of the short NOx lifetime leads to greater estimates of LNOx production per flash (510 moles per flash in tropics and 550 moles/flash in midlatitudes).
- Nault et al. also show GEOS-Chem simulations with updated chemistry support 665 – 700 moles/flash over SE US when constrained by OMI NO2 column satellite data.

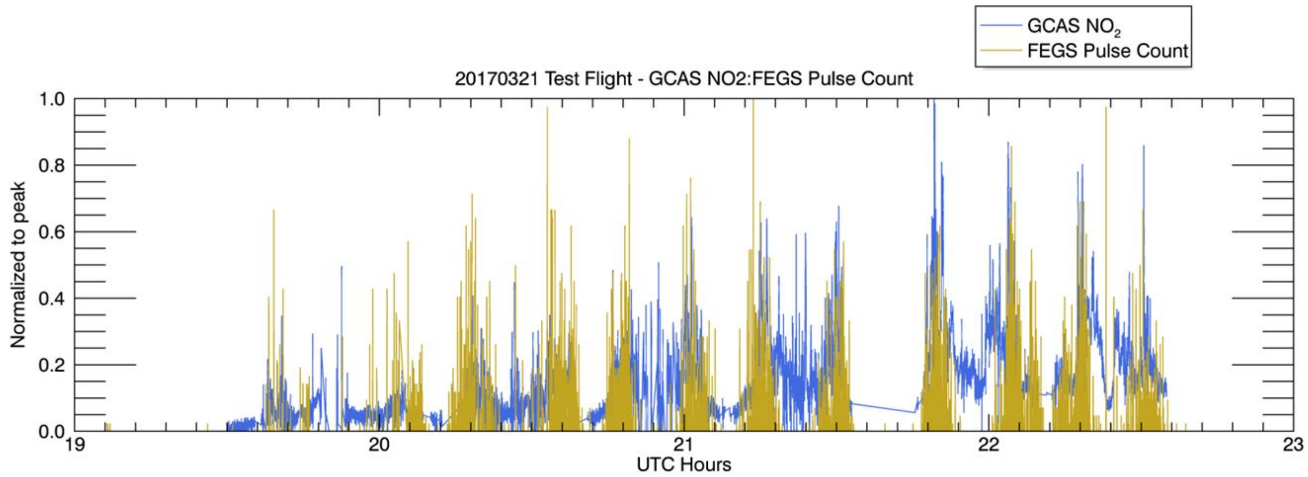
Further Investigation of Short NOx Lifetime and Larger LNOx Production/Flash Needed

- Storm penetrating aircraft (A-10) needed to sample NOx produced by lightning within or near storm core, where most lightning occurs.
- Combine the storm penetrating observations with anvil sampling (DC-8 or G-V) at a variety of altitudes and downwind distances to obtain a comprehensive view of NOx within a convective system.
- Will allow verification of the proposed 2-3 hour NOx lifetime and large LNOx production per flash.
- Alternatively, overfly storms with high-altitude aircraft to remotely sense NO2 in storm cores.
- Both methods require detailed flash information from LMAs, GLM, or aircraft.

Lightning NO_x Production During GOES-R Validation Flights March – May 2017

Scott Janz and Matt Kowalewski, NASA/GSFC
Ken Pickering and Dale Allen, Univ. of MD

- Geo-CAPE Airborne Simulator (GCAS from GSFC) and Fly's Eye GLM Simulator (FEGS from MSFC) flew on NASA ER-2 during GOES-R Validation Mission.
- Provided a preview of the synergy available when GOES-R Geostationary Lightning Mapper (GLM) and geostationary Tropospheric Emissions Monitoring of Pollution (TEMPO; 2019 or later) are both in orbit.
- Data from validation flights and from these satellite instruments will allow retrieval of co-located flash counts and NO_2 column amounts, which will lead to improved estimates of lightning NO_x production per flash.

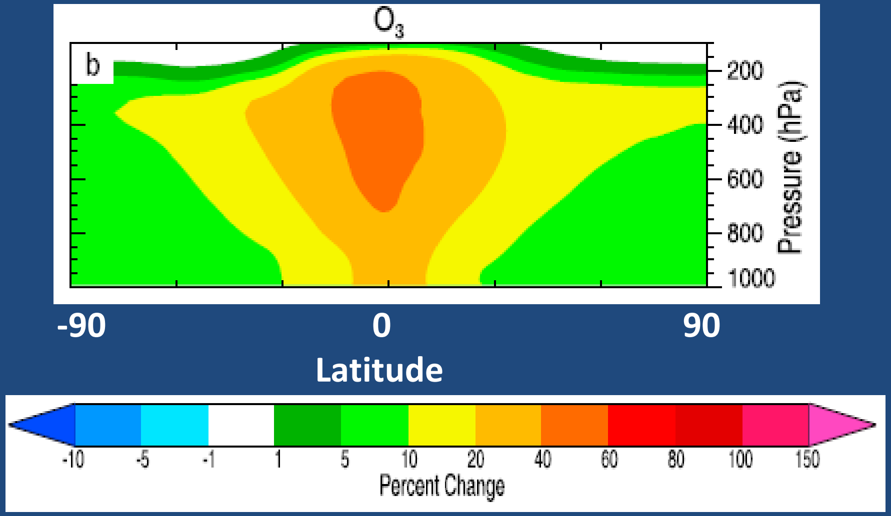


Northern California convection

FEGS:
Rich Blakeslee
Mason Quick
NASA/MSFC

Strong correlation of NO_2 columns and lightning optical pulses

Effects of LNO_x on Ozone



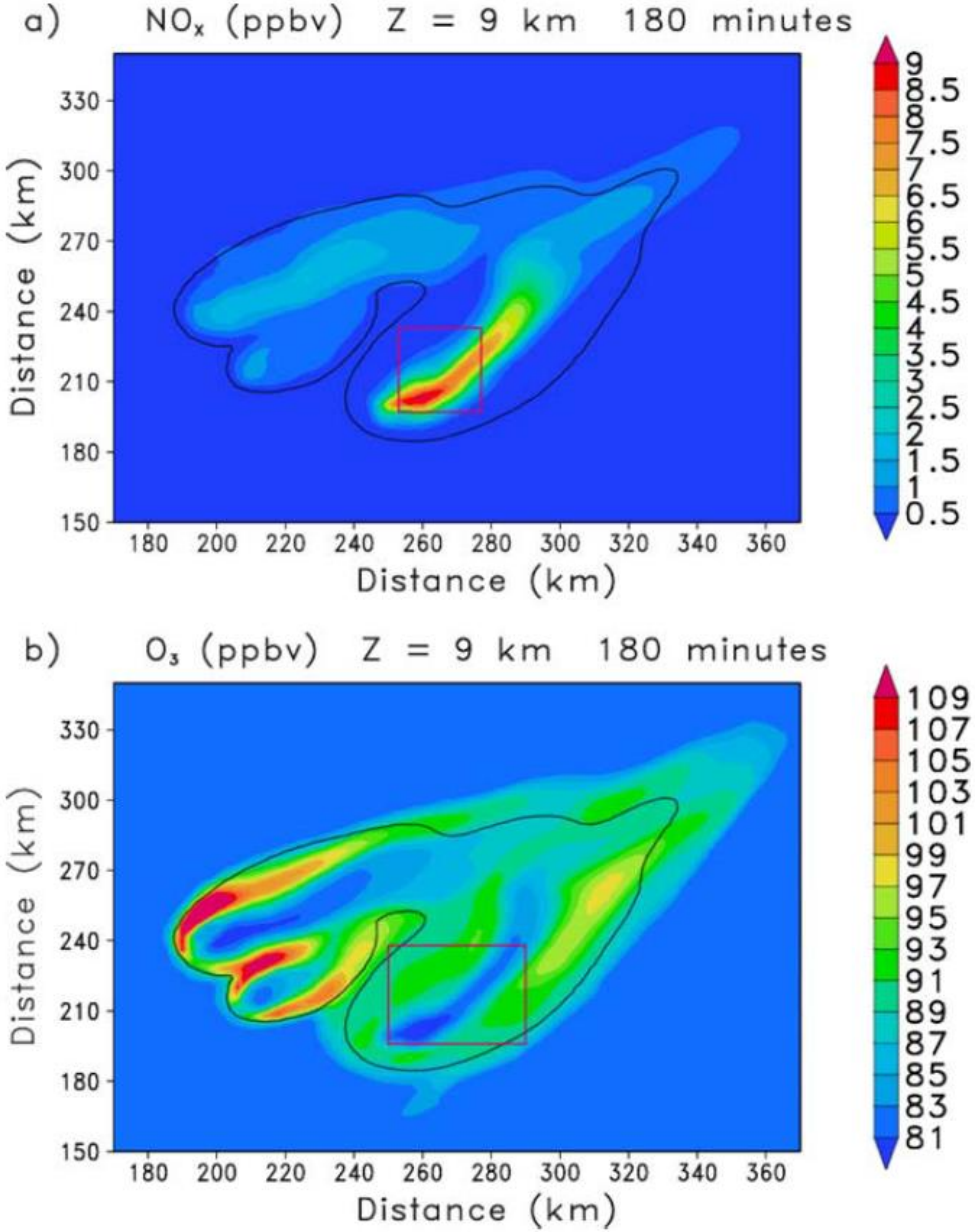
Liaskos et al. (2015) showed factor of 4 uncertainty in LNOx production leads to 40-60% uncertainty in tropical upper tropospheric O_3 in NASA GEOS-5 model

Effects to consider:

- **Short-term loss of ozone inside storm**
- **Efficient photochemical ozone production in upper tropospheric storm outflow**
- **Wrapping of stratospheric ozone downward around storm anvil**

Need storm penetrating aircraft to examine titration of ozone in storm
Need outflow sampling at several downwind transport times/distances
Need to determine how frequently stratospheric air wraps around anvil

Ozone Chemistry Within Thunderstorm Clouds



O_3 loss occurs inside highly electrified clouds due to NO + O_3 reaction in presence of large NO mixing ratios from lightning.

Ott et al. (2007) simulation of EULINOX storm near Munich, Germany using 3-D GCE model with off-line chemistry

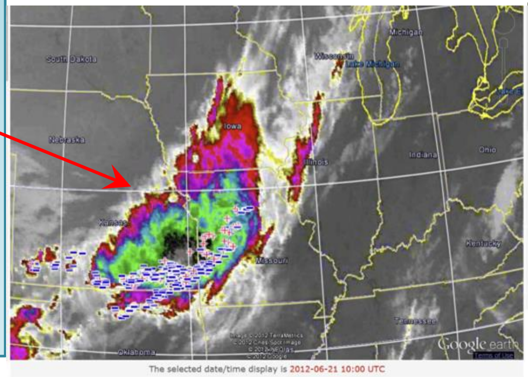
Found O_3 loss of up to 9 ppbv (avg. 4 ppbv) in regions with large NOx mixing ratios from lightning and pollution

No O_3 loss due to transport in this case.

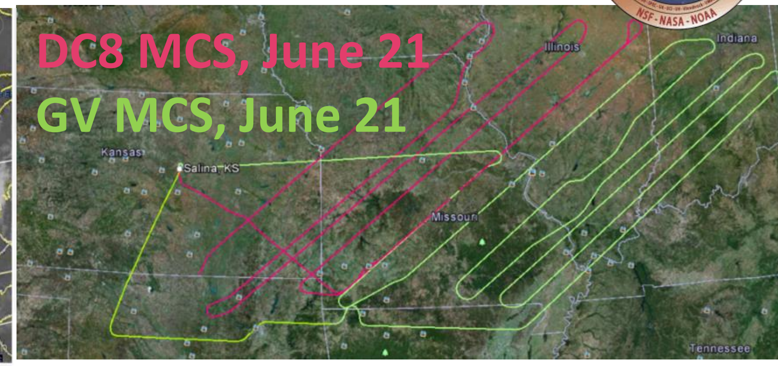
DC3 2013 June 21 MCS Flight DC-8 and GV data MM Model comparison

During the DC3 experiment we had the exceptional opportunity to study the outflow from an MCS (mesoscale convective system).

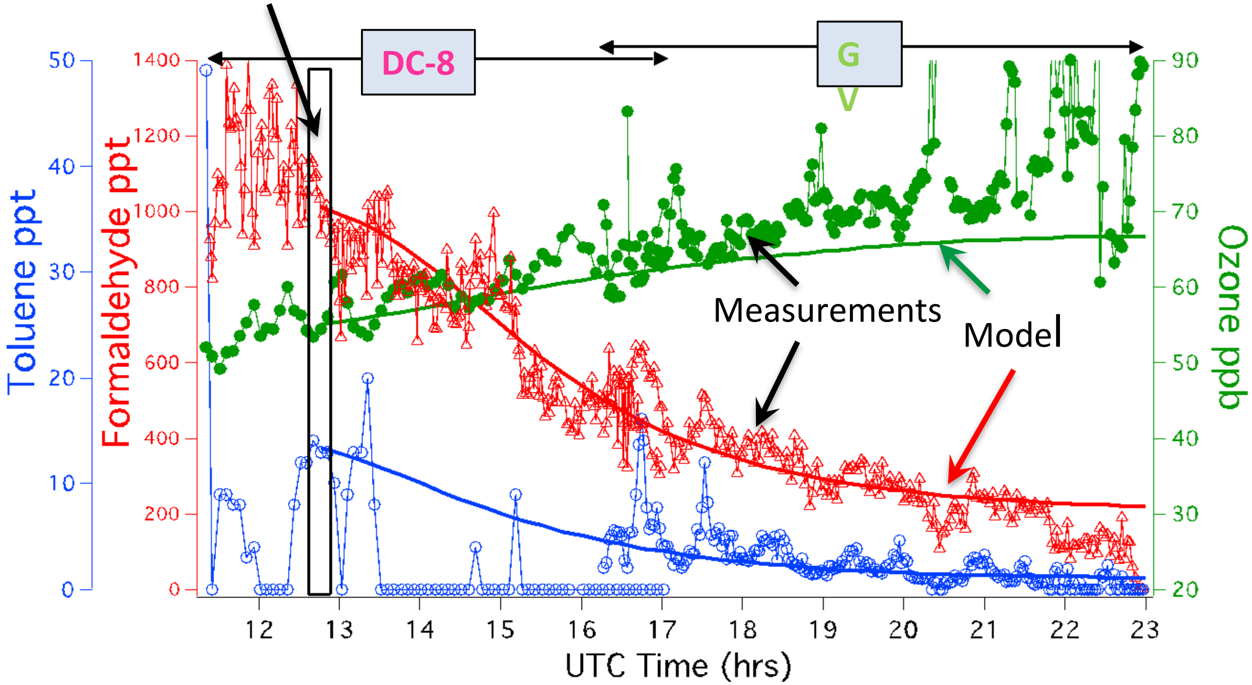
The highly instrumented GV aircraft followed the highly instrumented DC8 aircraft in a daylong study of the outflow from the previous night's MCS.



Flight tracks



Window for
Model Initial Conditions

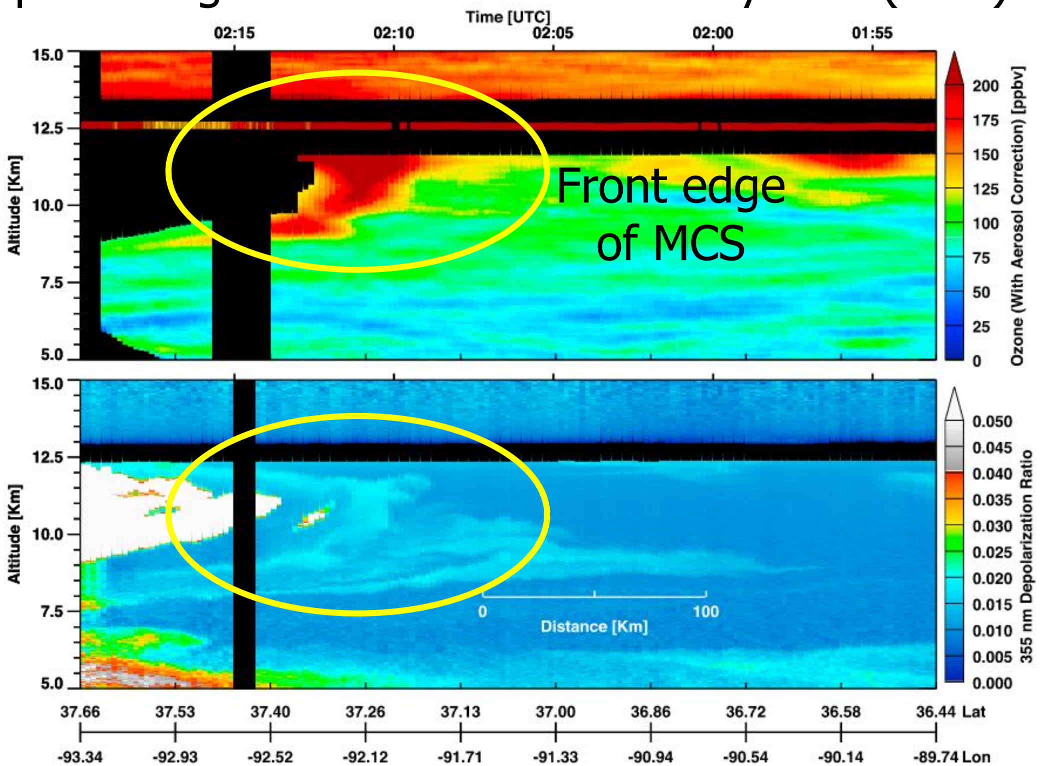


- MM agrees generally well with measurements
- Photochemistry produces ozone in outflow (at 10 km altitude) – spikes represent strat intrusion
- TOGA and WAS measured toluene and other VOCs that contribute to formaldehyde (Fried, DFGAS) and ozone (Ryerson, NOAA) formation

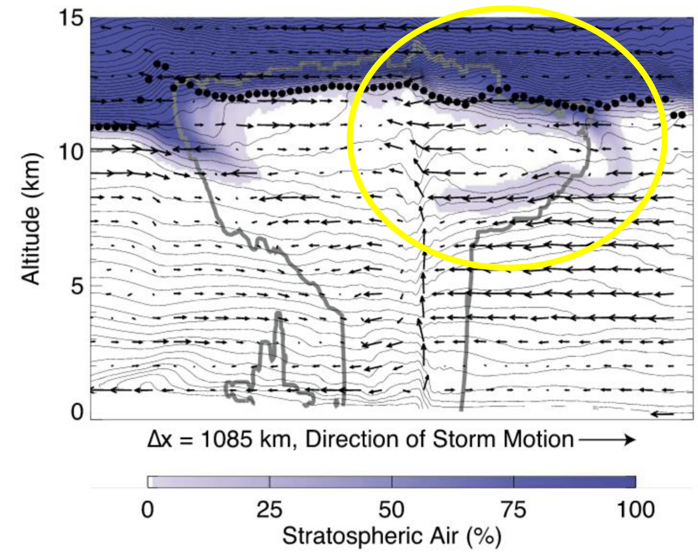
GV Measurements: VOCs – ***TOGA*** (Apel, Hills, Hornbrook, NCAR/ACD; Riemer, U. Miami), O_3 (Campos, NCAR/ACD), Formaldehyde (Fried, NCAR/EOL)
DC8 Measurements: VOCs - Whole air sampler (Blake, UC-Irvine); O_3 (Ryerson, NOAA), Formaldehyde (Fried, NCAR/EOL)
NCAR Master Mechanism: Detailed 0-D model – Chemistry – Apel, Lee-Taylor, Madronich (NCAR/ACD)

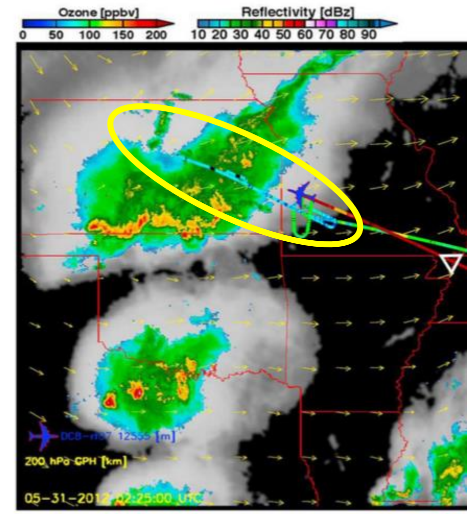
Airborne O_3 DIAL profiles directly reveal transport of stratospheric ozone near deep convective storms during DC3

Profile of ozone and depolarization (355nm) approaching Mesoscale Convective System (MCS)



Stratospheric Transport
WRF Model

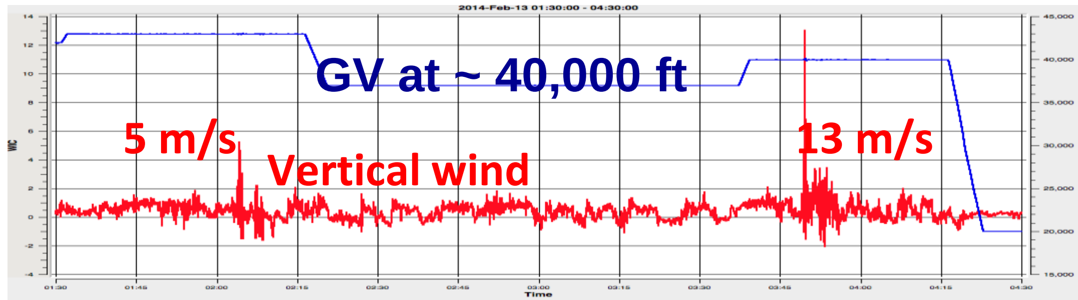


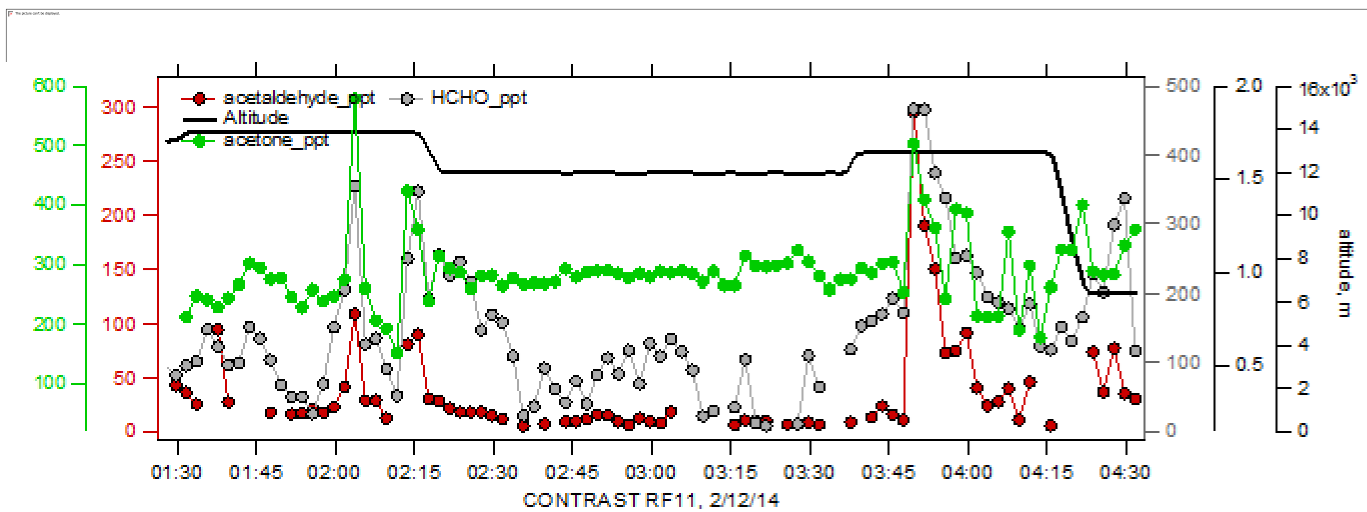


"Thunderstorms enhance tropospheric ozone by wrapping and shedding stratospheric air"
Pan, L. L., et al. (2014), Geophys. Res. Lett., 41, 7785–7790, doi:10.1002/2014GL061921

Tropical Storms – a mechanism for impacting the oxidizing capacity of the upper troposphere

Short-lived boundary layer species observed at the tropical upper troposphere on the GV near active convection





Lifetime:

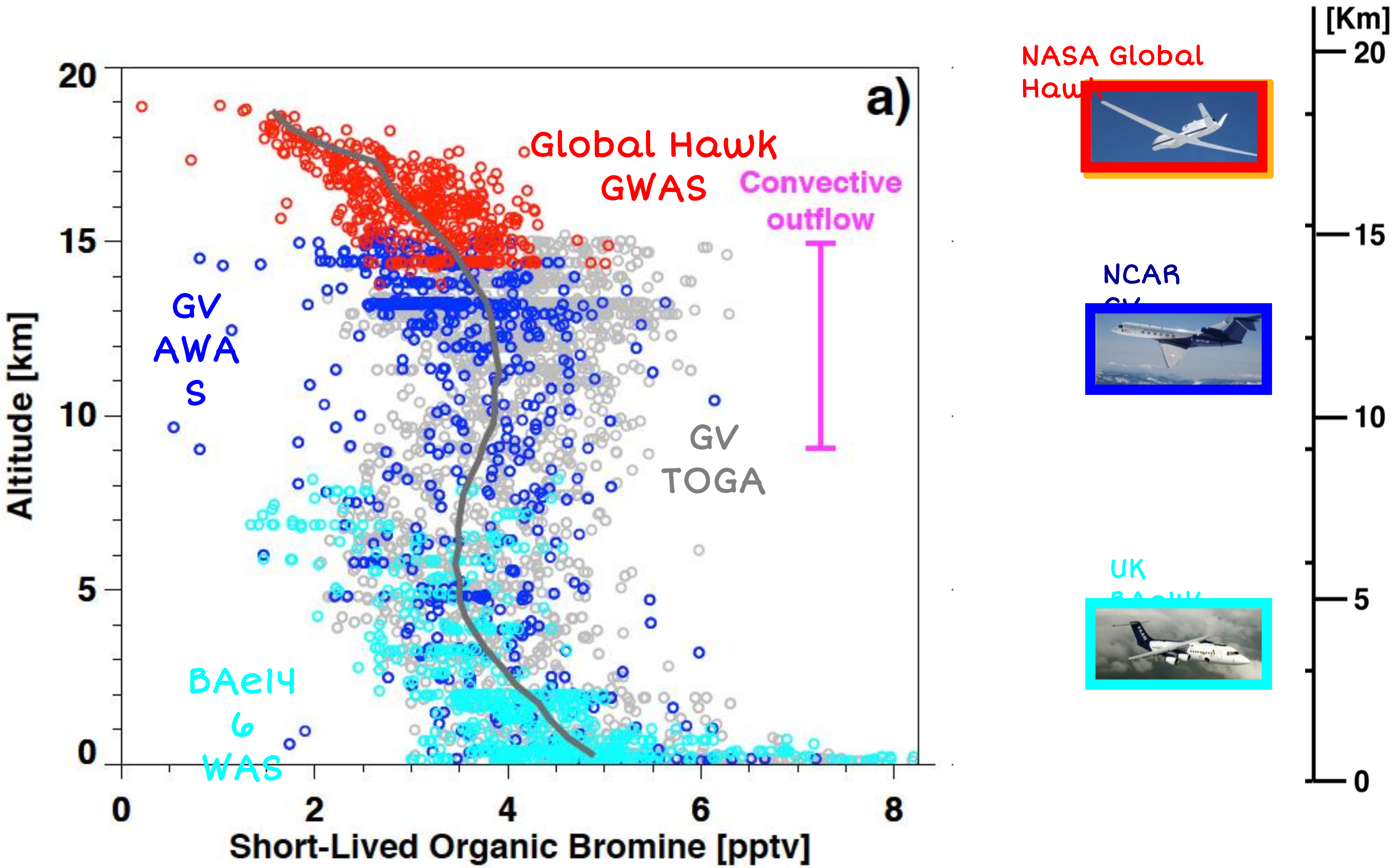
Acetone ≈ weeks

Formaldehyde ≈ hours

Acetaldehyde ≈ hours

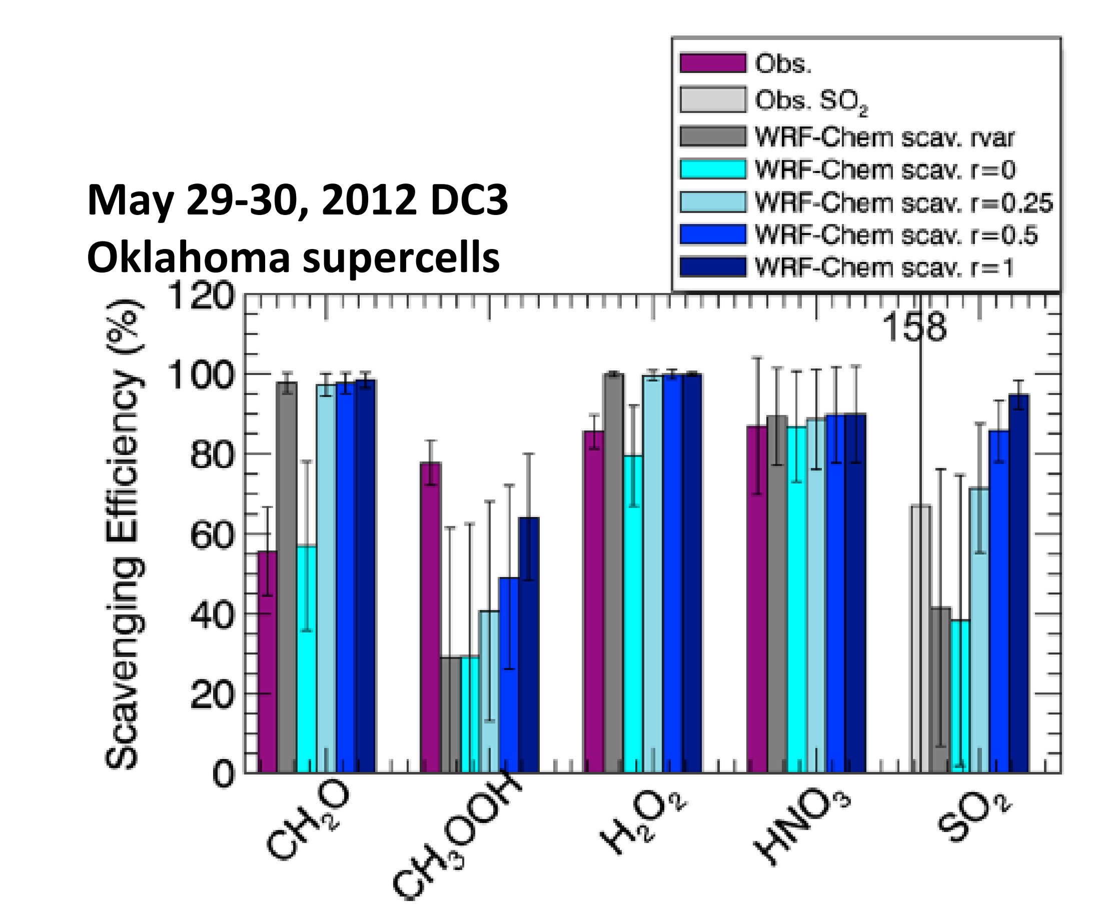
Tropical Convection – a link between oceanic biology and global ozone chemistry

- Collaborative observations from the GV, the Global Hawk, and the BAe146
- First complete measurements of this kind over western Pacific
- Provide quantitative constraints for global chemistry climate models



Wet Scavenging of Soluble Species

- Scavenging efficiencies (SE) between inflow and outflow can be calculated from aircraft observations and from cloud-resolved storm/chemistry simulations.
- Amount of soluble gas incorporated into cloud water is dependent on the degree of solubility of the gas (Henry's Law coefficient)
- But, SE is also dependent on the fraction of the gas that is retained on ice upon freezing of cloud water.



Bela et al. (2016) used the WRF-Chem model to determine SE for several soluble gases and the fraction of the gases retained on cloud ice

SE for all soluble species except HNO3 are highly sensitive to the ice retention fraction that is assumed.

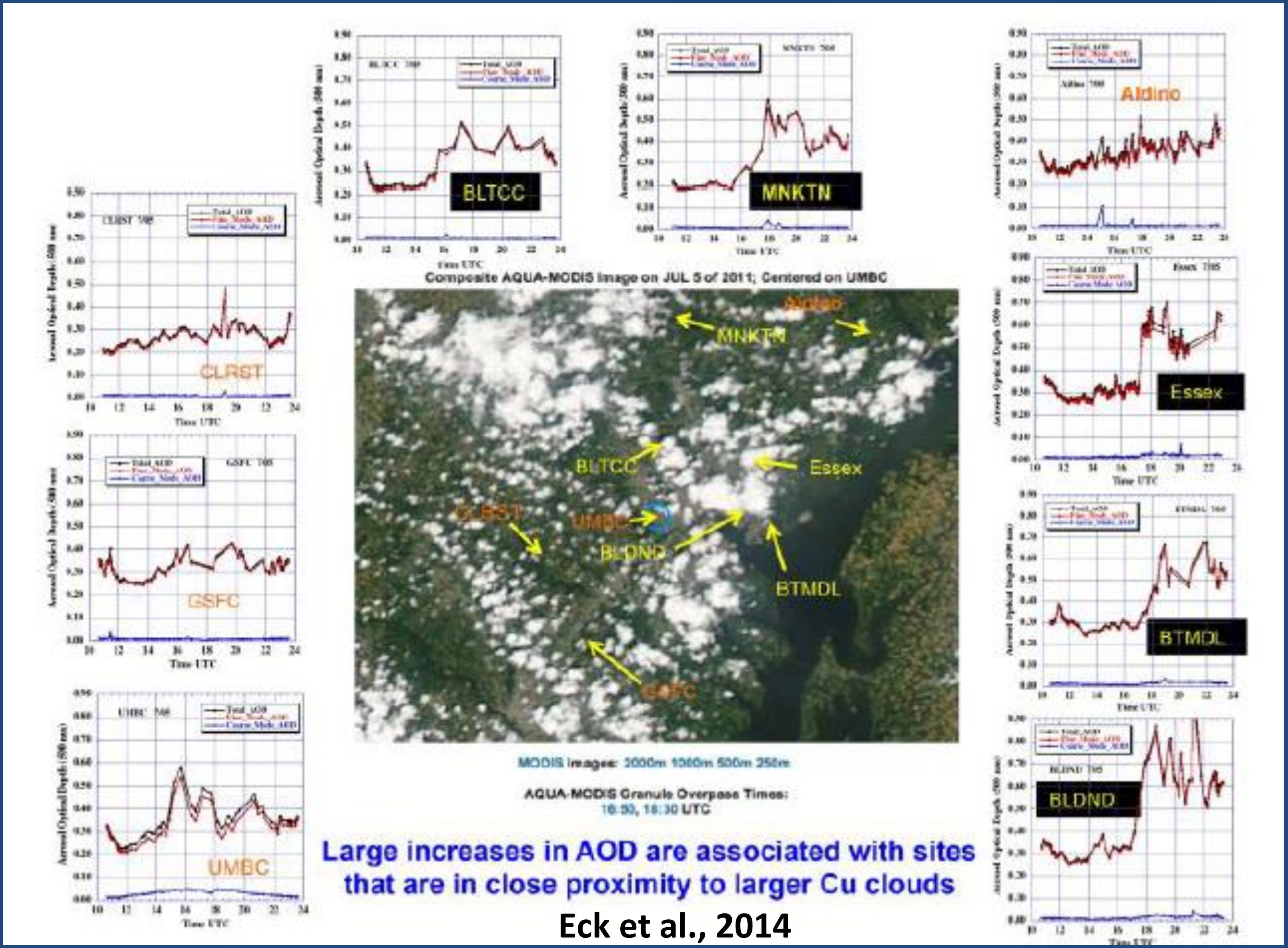
Best match aircraft obs:
0% retention: HCHO, H2O2
100% retention: CH3OOH, SO2

Storm-penetrating aircraft needed to make observations of gases, cloud water, cloud ice in storm cores (where freezing is taking place;
Can ice particles be collected and later analyzed for gas content?

New Particle Formation in Convective Outflow

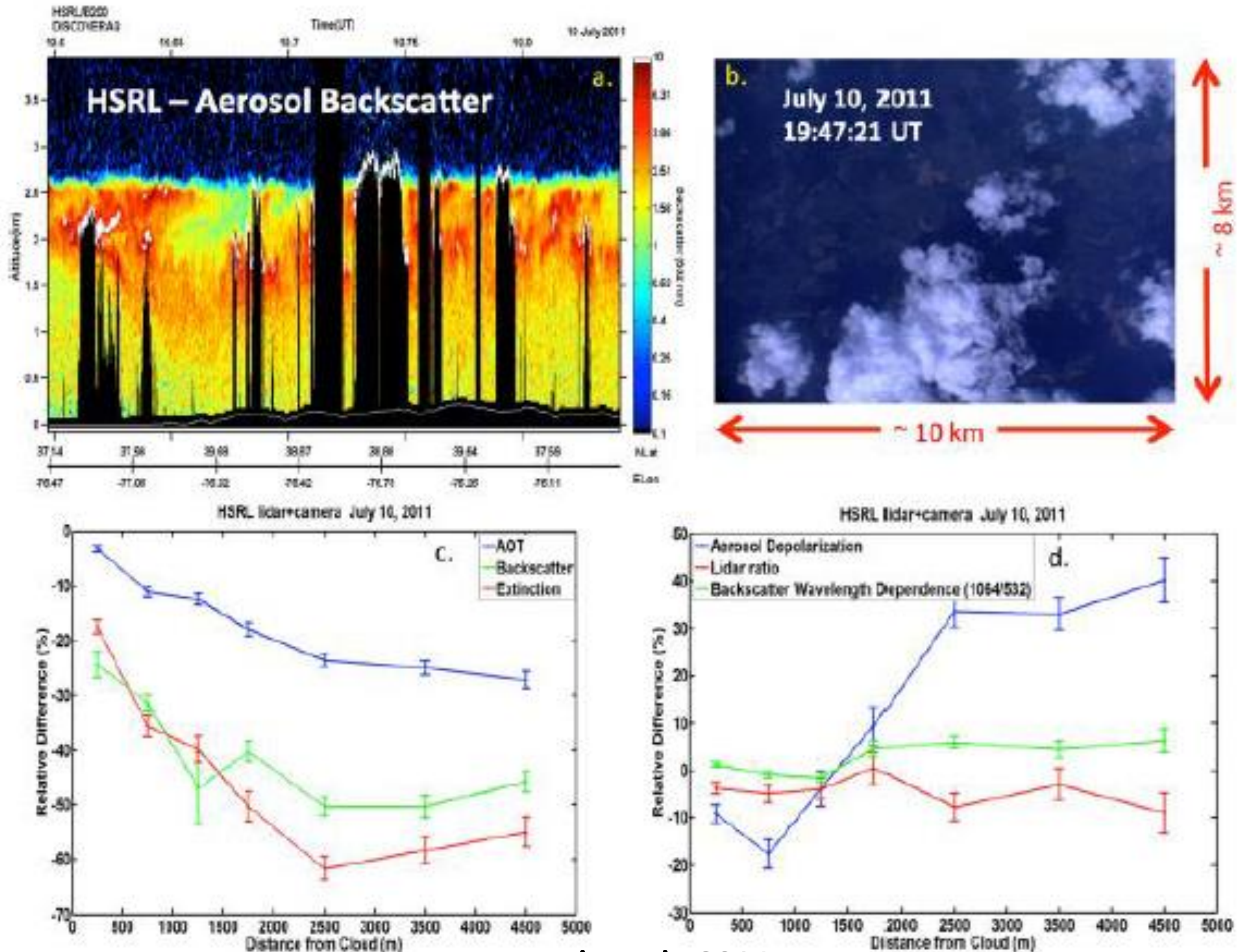
- During DISCOVER-AQ field experiment in Maryland (July 2011) Eck et al. (2014) found enhanced aerosol optical depth (AOD) in the vicinity of fair weather cumulus clouds from surface AERONET sun photometer data.
- Surface Micropulse Lidar (MPL) and airborne High Spectral Resolution Lidar (HSRL) also measured large increases in aerosol signal (backscatter, extinction, AOD) at altitudes of fair weather cumulus clouds.
- In situ aircraft observations during vertical profiling also yielded enhanced aerosol scattering and volume after cumulus formation compared with before.
- Humid environment likely enabled easy detection.
- Need further case studies of this process; need new particle speciation; investigations of ability of these aerosols to aid new cloud formation.

AERONET Detection of New Particle Formation



Eck et al., 2014

HSRL Detection of New Particle Formation



Eck et al., 2014

Pyroconvection

- Convective clouds often form in association with biomass fires due to the large quantities of heat and water vapor released.
- Extreme cases of pyroconvective clouds reaching into the stratosphere and/or containing lightning can result from large fires.
- Also plumes from fires can become entrained into otherwise relatively clean thunderstorm events (ARCTAS, DC3, SEAC4RS)

- Needs:

  Can composition of pyroconvection be determined only by remote sensing?

  How often do fire-induced clouds occur?

Summary

- Storm penetrating aircraft (A-10) is needed for :

  chemical tracer measurements

  better characterization of lightning NOx

  determining magnitude of ozone titration due to LNOx

  better understanding of wet scavenging

We won't know much about storm core chemistry without it!

- Role of remote sensing should be expanded for:

  estimates of LNOx in storm cores

  investigation of new particle formation

  composition of pyroconvective clouds

- Need close collaboration with lightning observation and cloud physics measurement communities.