Assessing anthropogenic impact on secondary pollutant formation in the South Eastern US via airborne formaldehyde measurements

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UW-Madison, JCET UMBC, NASA GSFC, UMD, Harvard,

CIRES, CU Boulder, NOAA ESRL, NOAA GFDL, UW-Seattle, Princeton,
Caltech, Hendrix College, UW-Seattle, University of Oslo, Georgia Tech

This research is funded by
U.S. EPA - Science To Achieve Results (STAR) Program
Grant # 83540601

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NASA-ISAF (HCHO) Instrument

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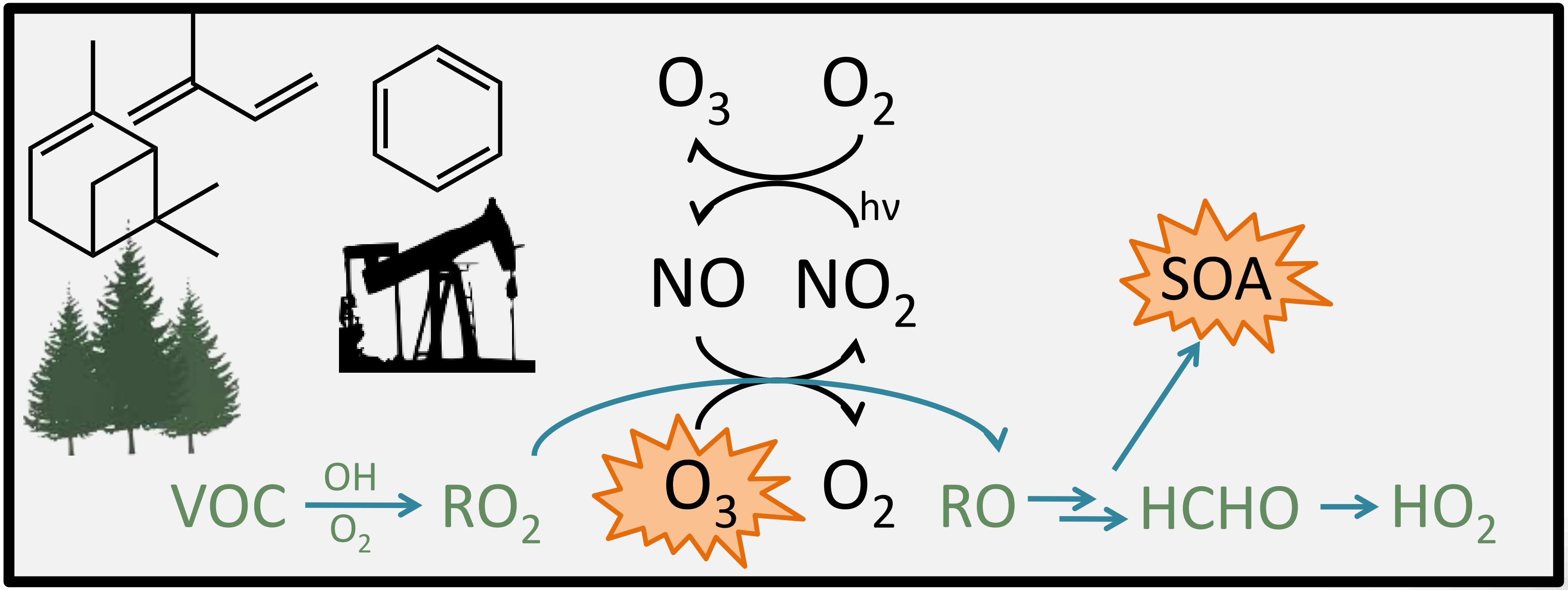
NSF GRFP

Jen Kaiser

Why Formaldehyde?

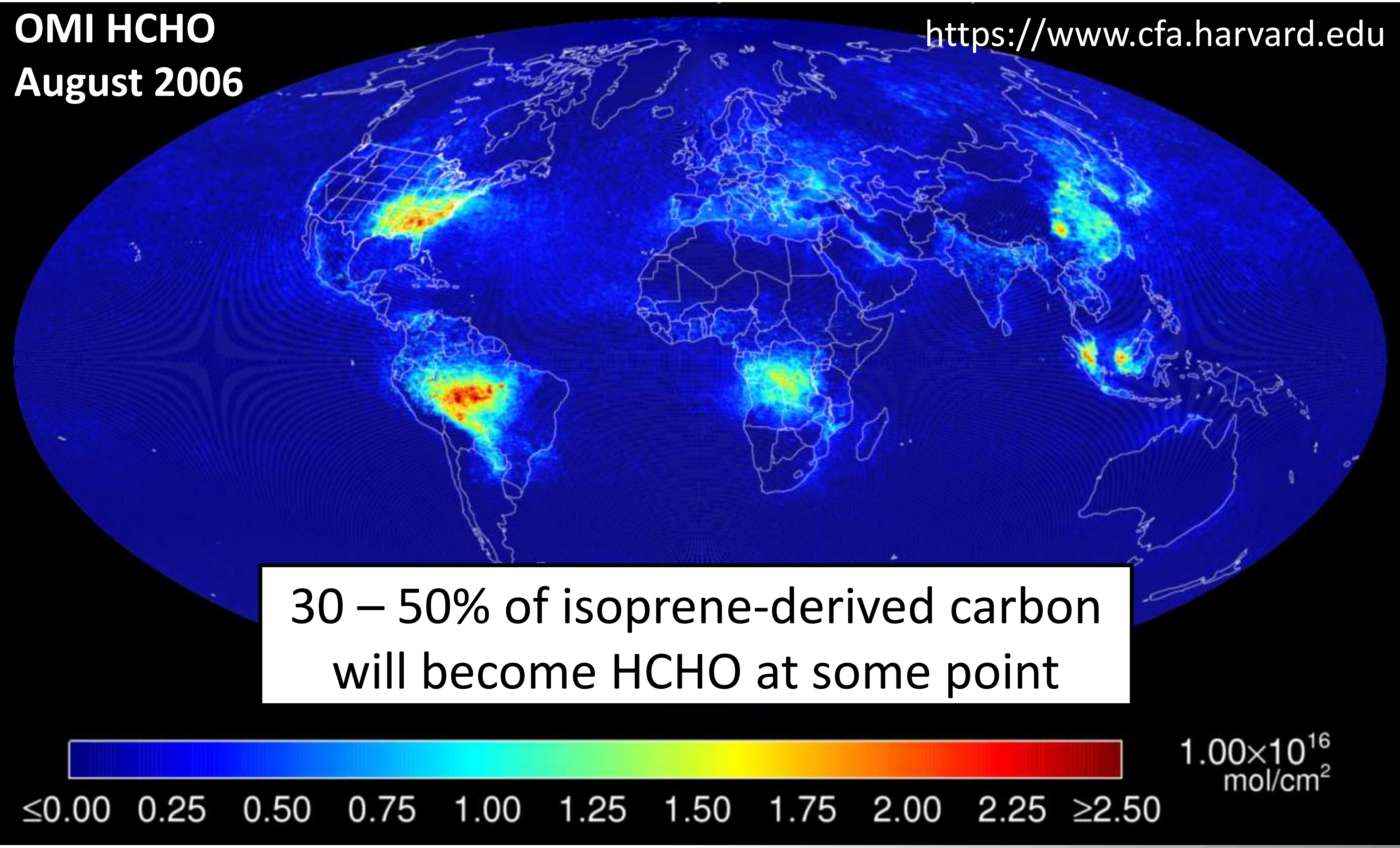
HCHO tracks photochemical evolution of VOCs.



1a) Yield related to VOC type
1b) Formation rate related to reactive carbon processing rate
2) HCHO is an important radical source

From Jen Kaiser

Formaldehyde (HCHO)



30 – 50% of isoprene-derived carbon will become HCHO at some point

Anthropogenic Influence

Many forms of anthropogenic influence:

- Land-use change (VOC, NH_3, N_2O emissions, …)
- Emissions: NH_3, SO_2, VOCs, NO_x, …

Identification of

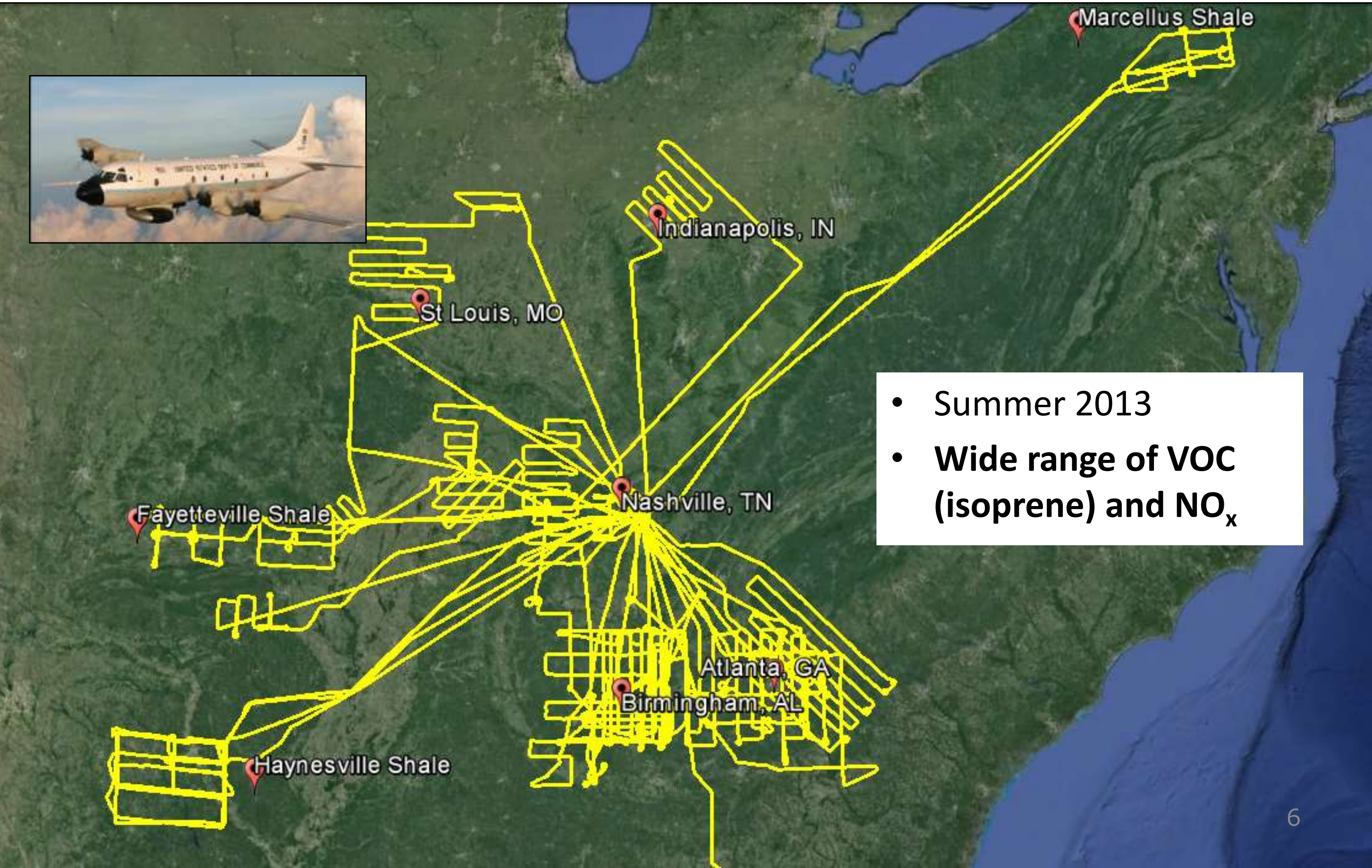
(a) Impact of NO_x emissions on VOC processing

(b) VOC emission type

(c) Investigation of aerosol glyoxal sink

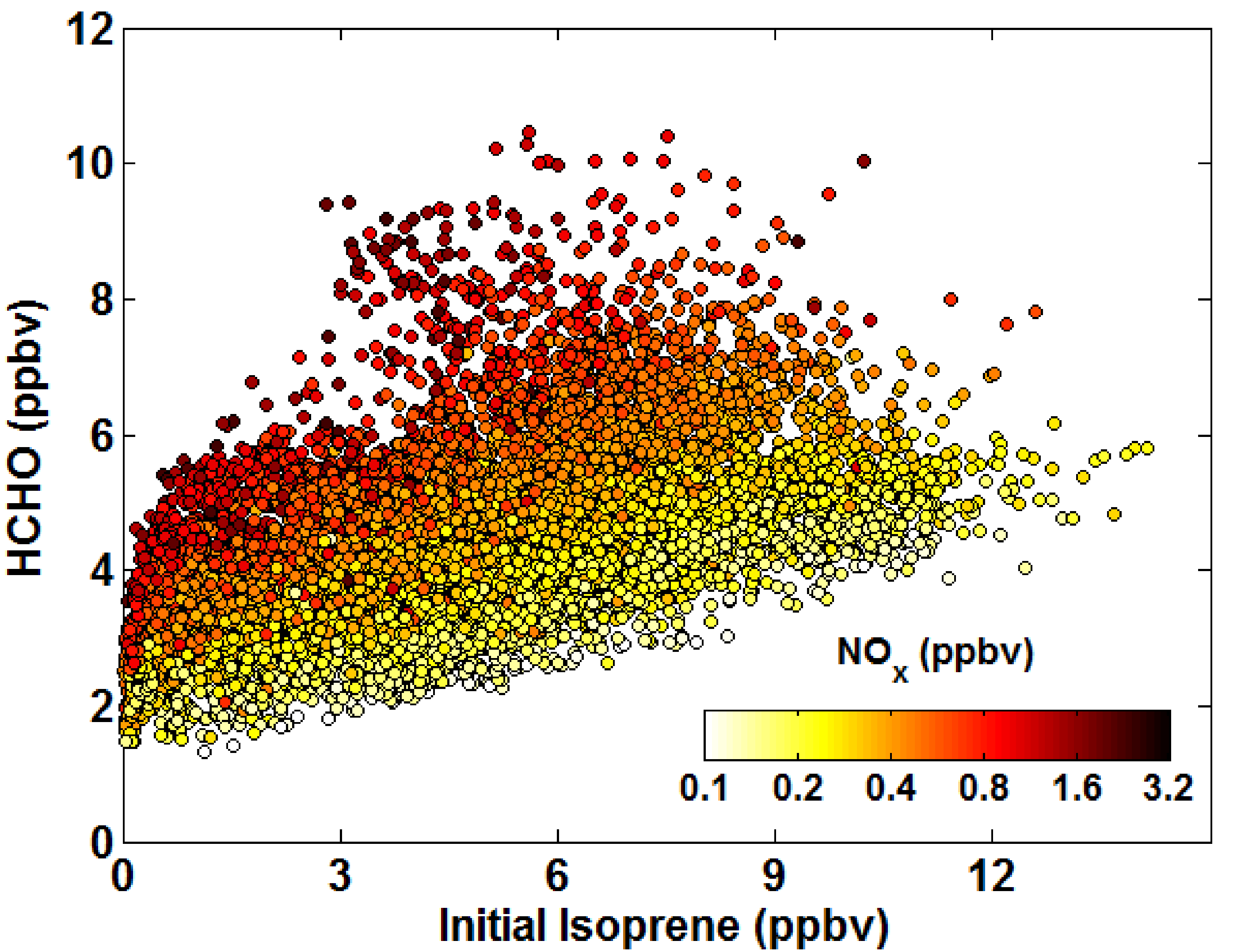
(Jingy Li, Jinqiu Mao)

SENEX (= SouthEast NEXus) Flights



- Summer 2013
- **Wide range of VOC (isoprene) and NO_x**

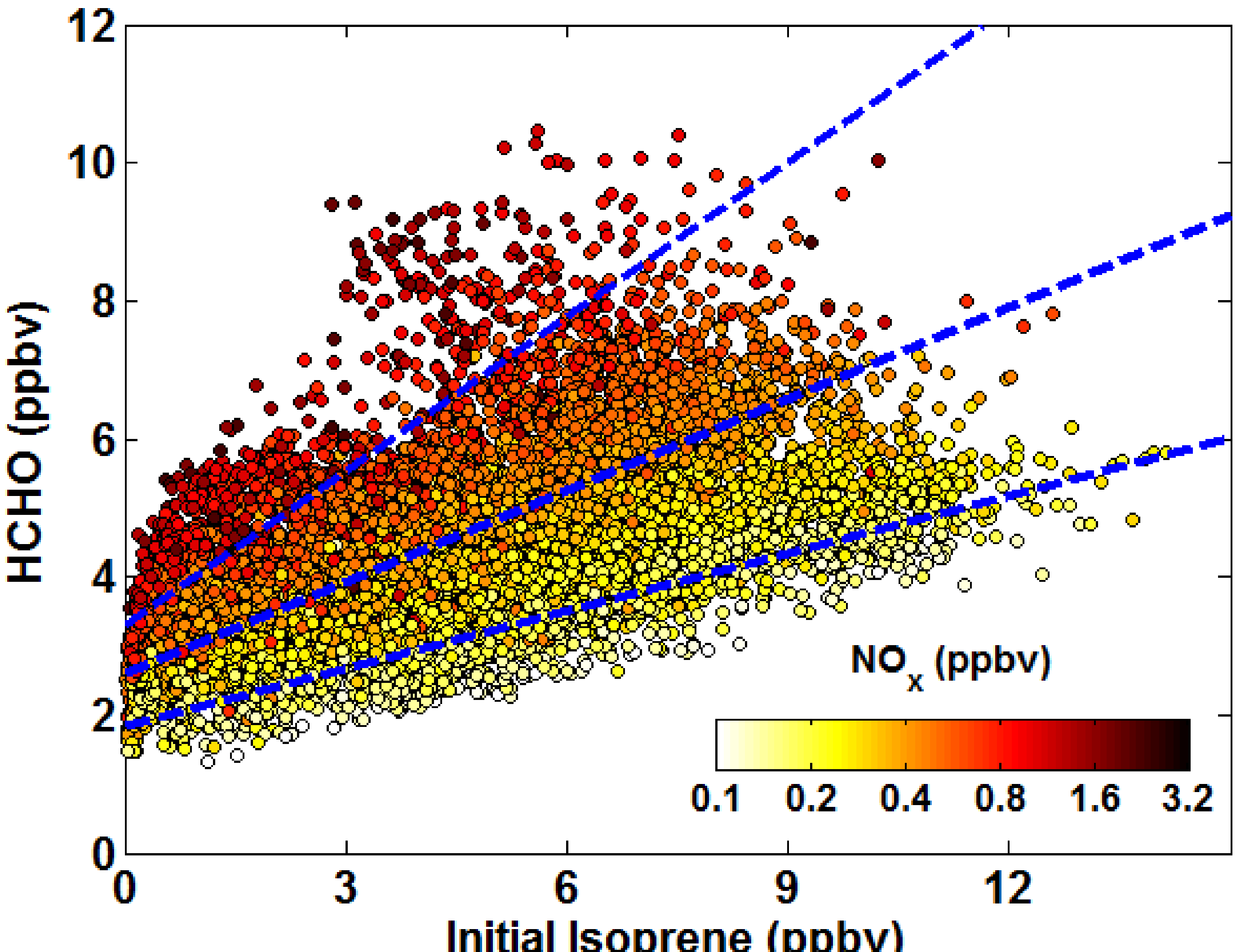
I. NO_x influence on HCHO



Margaret Marvin
AGU 2015

Glenn Wolfe ACP 2016

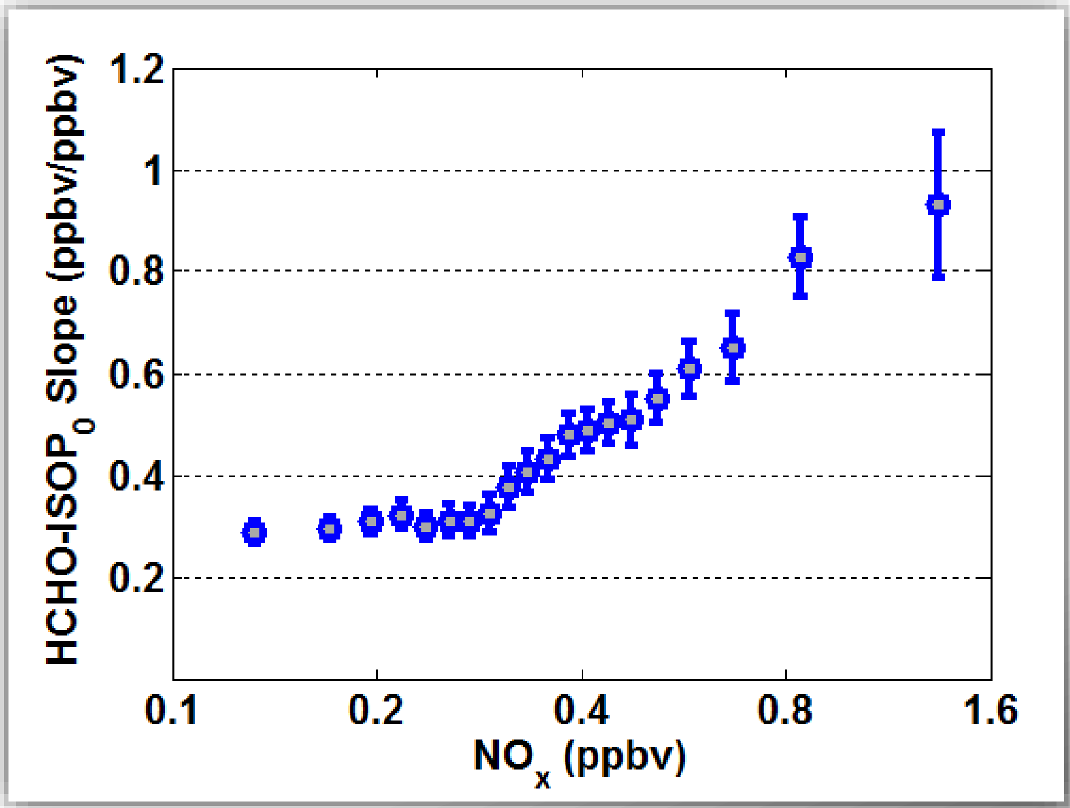
I. NO_x influence on HCHO



Group and fit by log(NO_x)

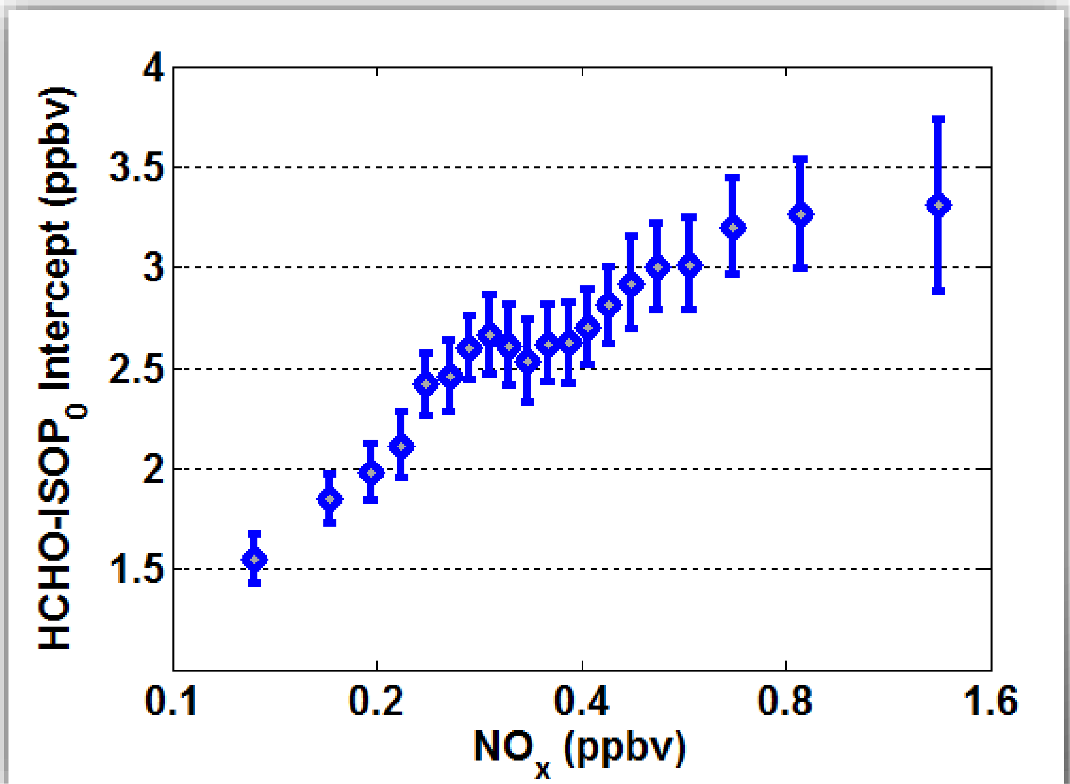
Slope: Isoprene Sensitivity of HCHO

"Isoprene Sensitivity" effectively represents the response of HCHO to a change in isoprene emissions



Intercept: Background HCHO

"Background" represents HCHO that cannot be directly linked to isoprene emissions (too aged or other precursors)



NO_x influence on HCHO: Comparison with Different Model Mechanisms

Mechanism	Species	Reactions	Reference
CB05	51	156	Yarwood et al. (2005)
CB6r2	56	216	Ruiz and Yarwood (2013)
MCMv3.2*	447	1428	Saunders et al. (2003)
MCMv3.3.1*	610	1974	Jenkin et al. (2015)

*Isoprene subset

CB: Carbon Bond Mechanism

- Condensed
- Commonly used for air quality simulations

MCM: Master Chemical Mechanism

- Explicit
- Benchmark mechanism

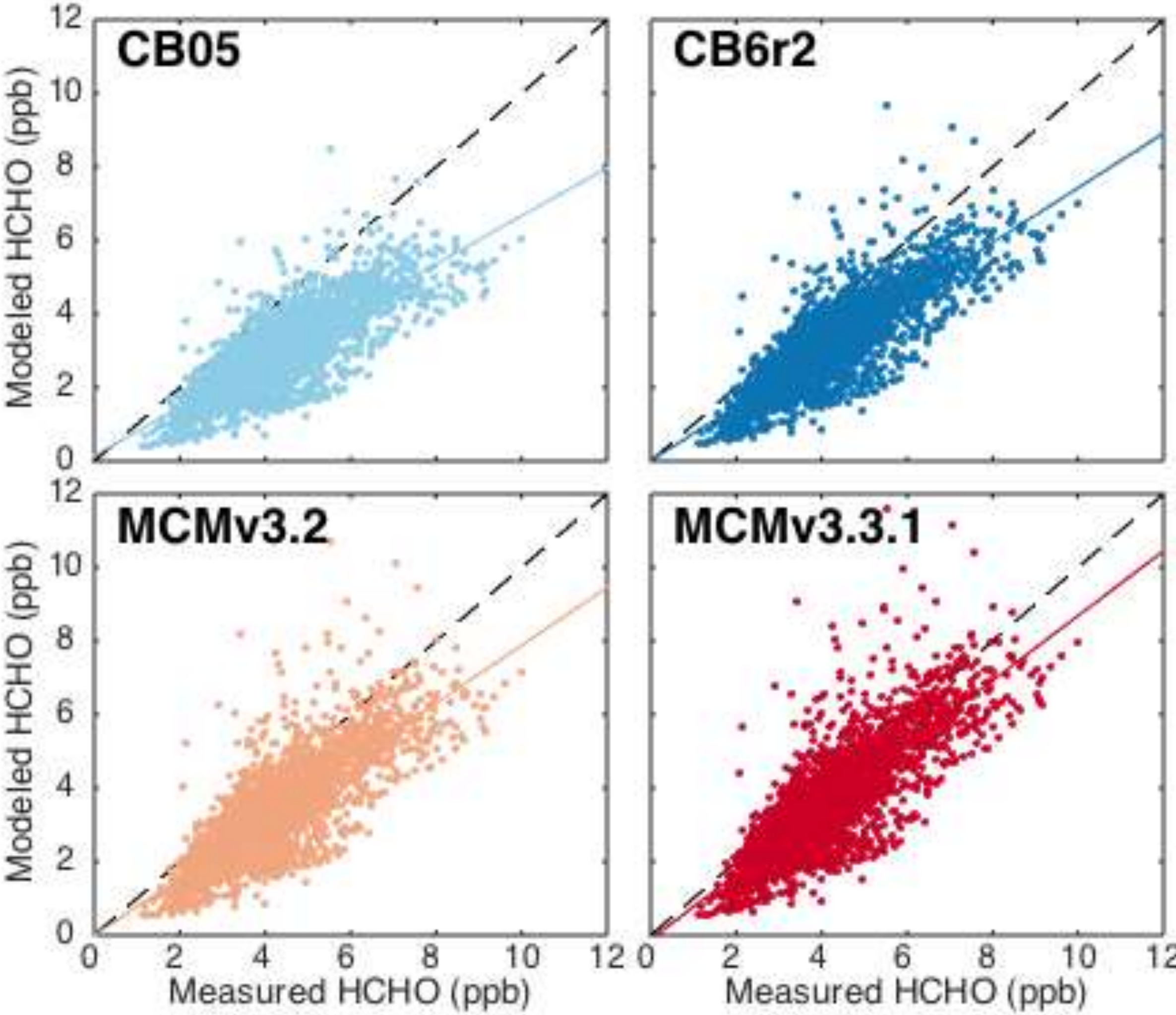
Box Model Simulations

University of Washington Chemical Model
(Wolfe and Thornton, 2011)

- Diel steady-state
- Constrained to aircraft observations of C_5H_8, NO, NO_2, CO, CH_4, O_3, PAN, CH_3OH
- Physical losses represented by a 24-hour lifetime
- Assumes clear sky conditions
- Four simulations
  - Differ only in choice of gas-phase mechanism

CB05
CB6r2
MCMv3.2
MCMv3.3.1

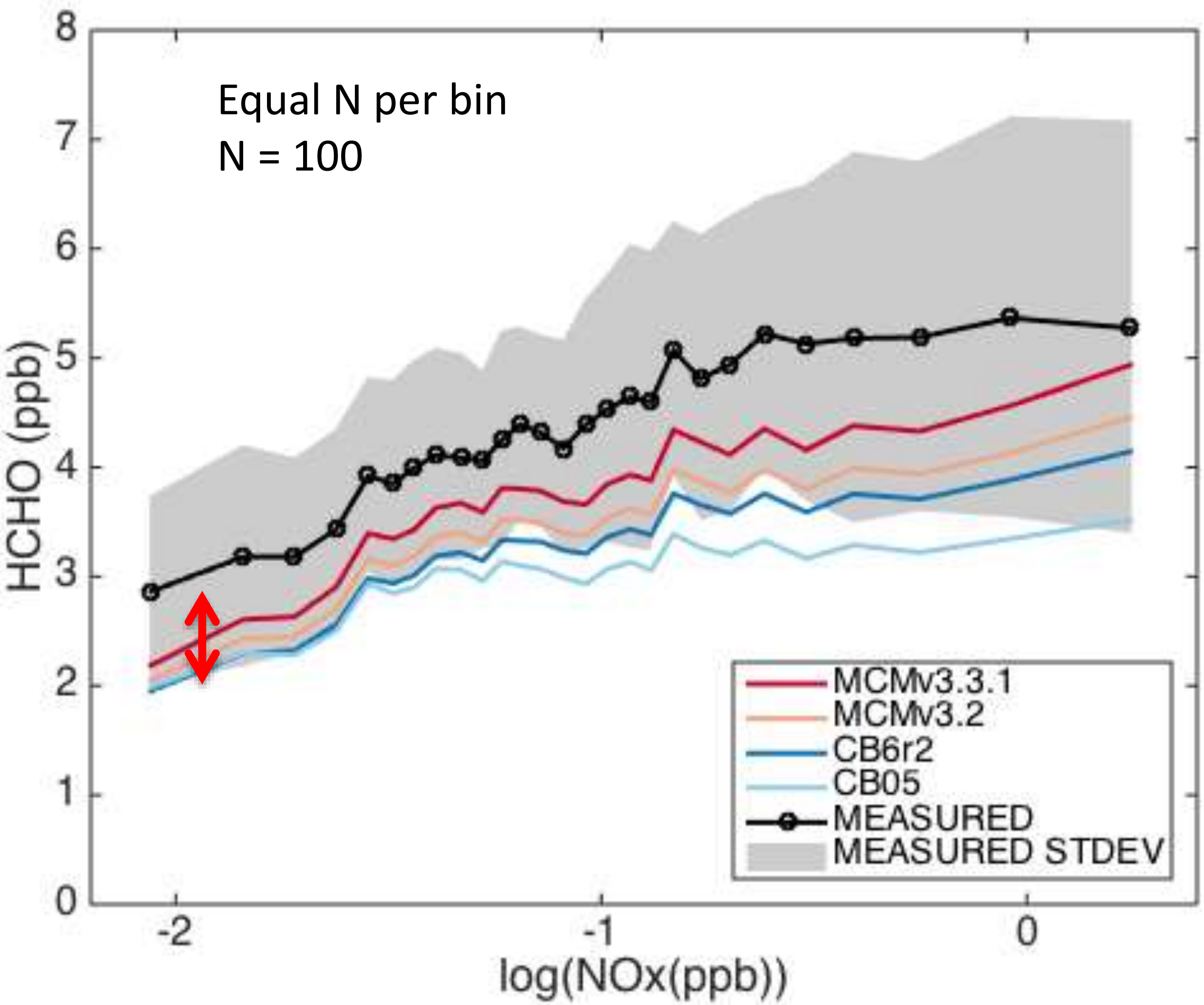
Model-Measurement Comparison



Linear regression analysis:

Mechanism	Slope	Int.	R^2
CB05	0.65	0.15	0.63
CB6r2	0.74	0.01	0.67
MCMv3.2	0.79	-0.01	0.64
MCMv3.3.1	0.88	-0.11	0.65

Chemical Dependence of HCHO Concentration on NO_x Conditions



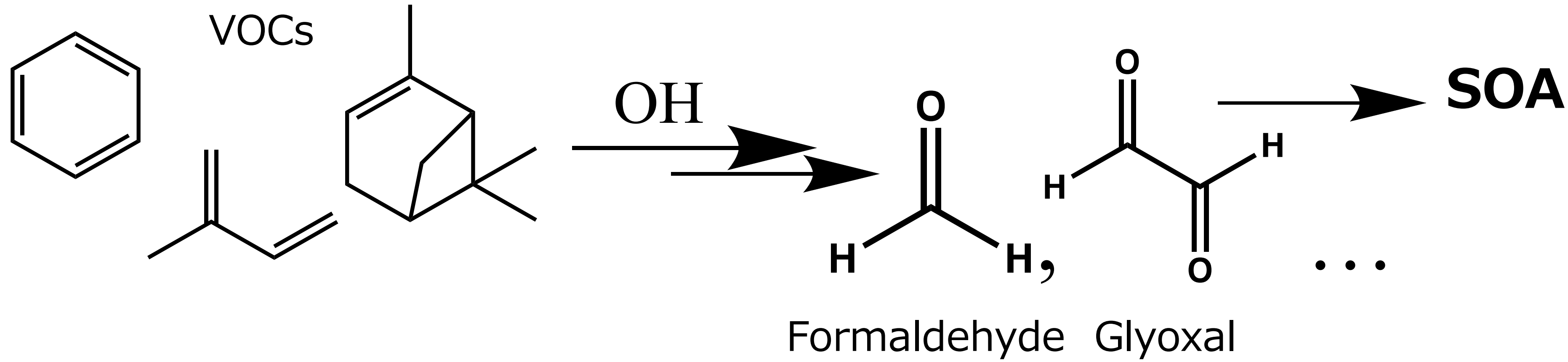
- Mechanisms maintain shape of dependence (slope)
- Mechanisms underestimate HCHO concentrations (intercept)

Take-Away Points

- HCHO variability driven by both emissions and chemistry
- Up-to-date mechanisms represent isoprene-HCHO relationship well but background HCHO not captured well
- Most of the NO_x-driven increase in HCHO reflects faster VOC oxidation

For more details: *Wolfe et al., ACP (2016)*

II. Formaldehyde and Glyoxal as Indicator of VOC Speciation



- Relative yields of glyoxal and HCHO differ between classes of VOC
- Similar atmospheric lifetimes
- Ratio related to local VOC species
- Measurable by satellite
- Aerosol important sink for glyoxal

Observations of R_{GF} have lead to conflicting conclusions.

Reference	Method	Biogenic R_{GF} (%)	Anthropogenic R_{GF} (%)
Vrekousiss et al. (2010)	Satellite	>4.5	<4.5
DiGangi et al. (2012)	LIF[a]/LIP[b]; review	<2	>2.5
MacDonald et al. (2012)	DOAS[c];	20-40	--
Li et al. (2014)	DOAS; model	0.2-17 (Depends on NO_x, OH, …)	
Miller et al. (2014)	Satellite	<4 (isoprene) >4 (terpenes)	~4

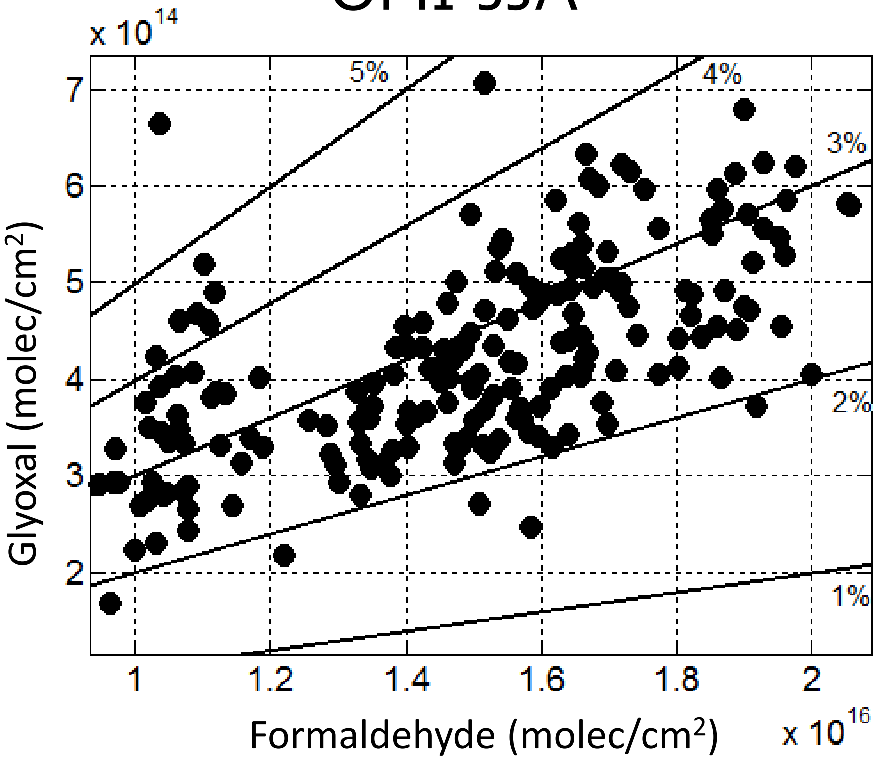
[a]Laser Induced Fluorescence (HCHO)

[b]Laser Induced Phosphorescence (CHOCHO)

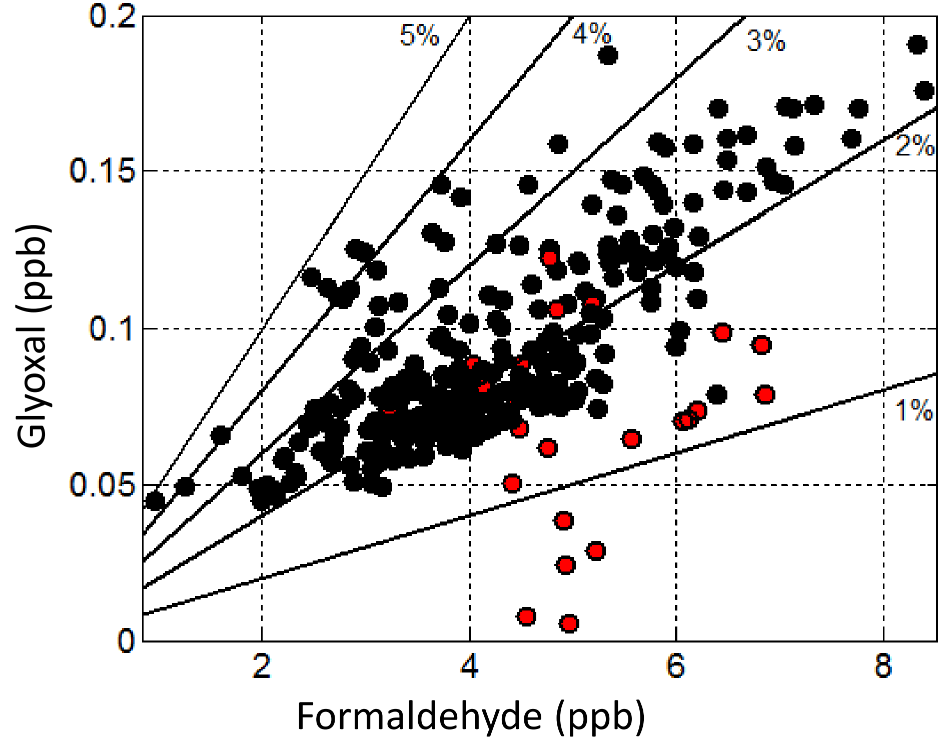
[c]Differential Optical Absorption Spectroscopy

Satellite and in situ R_{GF} in better agreement

OMI JJA



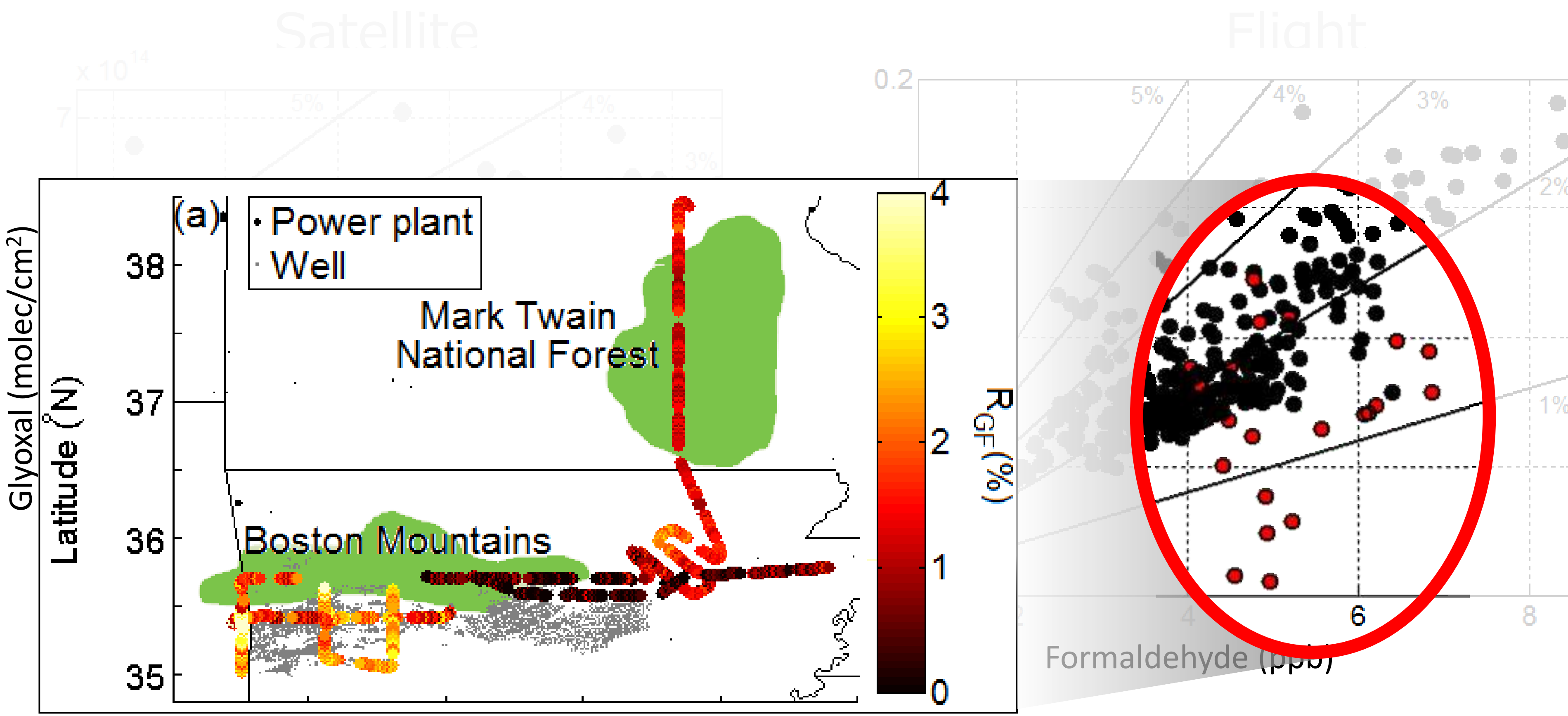
Flight

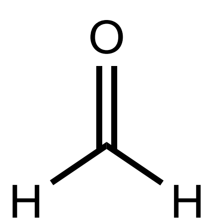


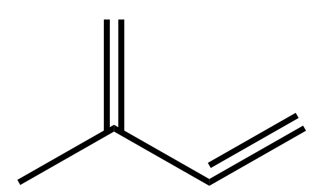
- Better agreement between platforms
- Outliers in flight based averaged out in satellite
- Flight-based provides VOC measurements

Kaiser, J. et al, *ACP*, **15**, 7571-7583, (2015).

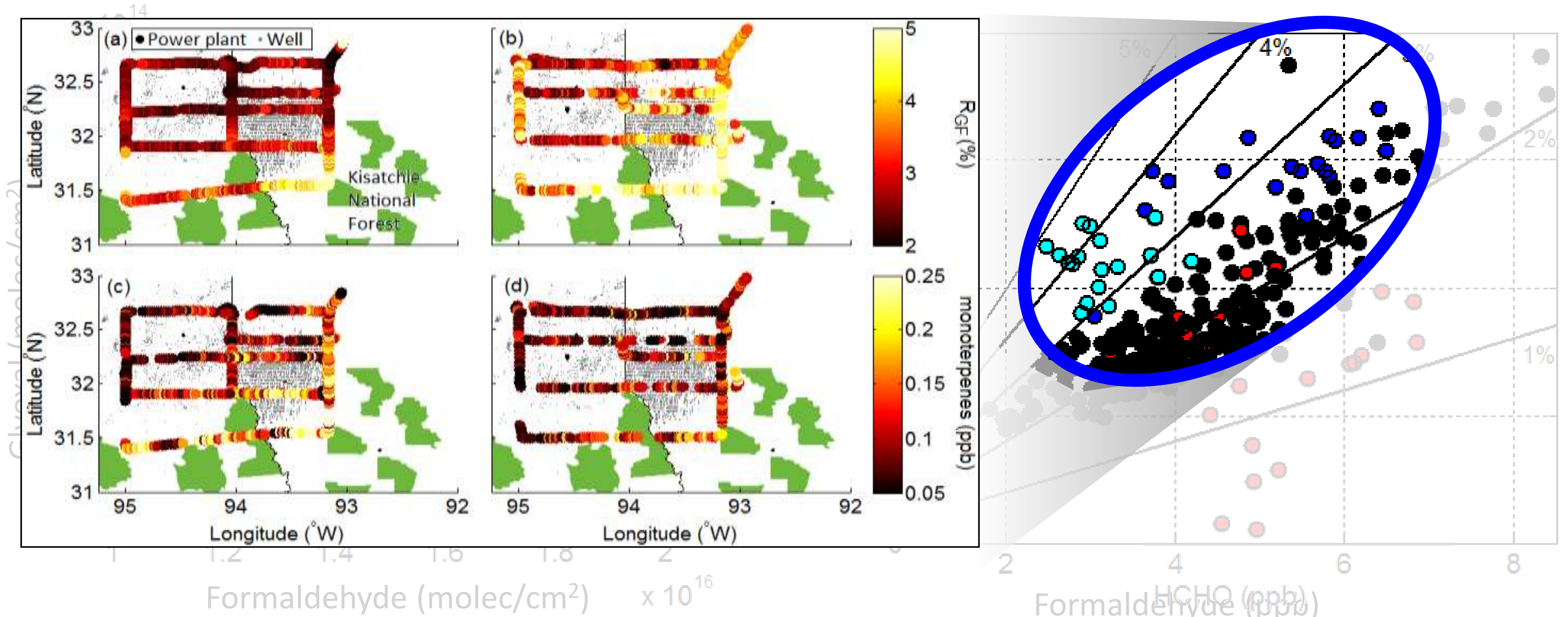
Low R_{GF} over the Ozarks and near gas flares.

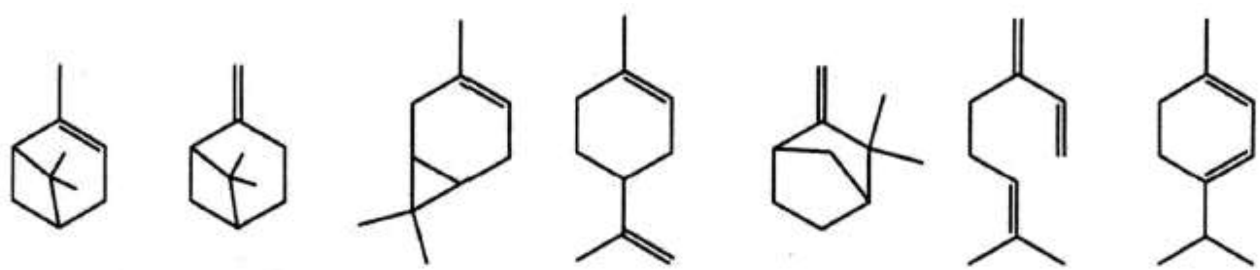




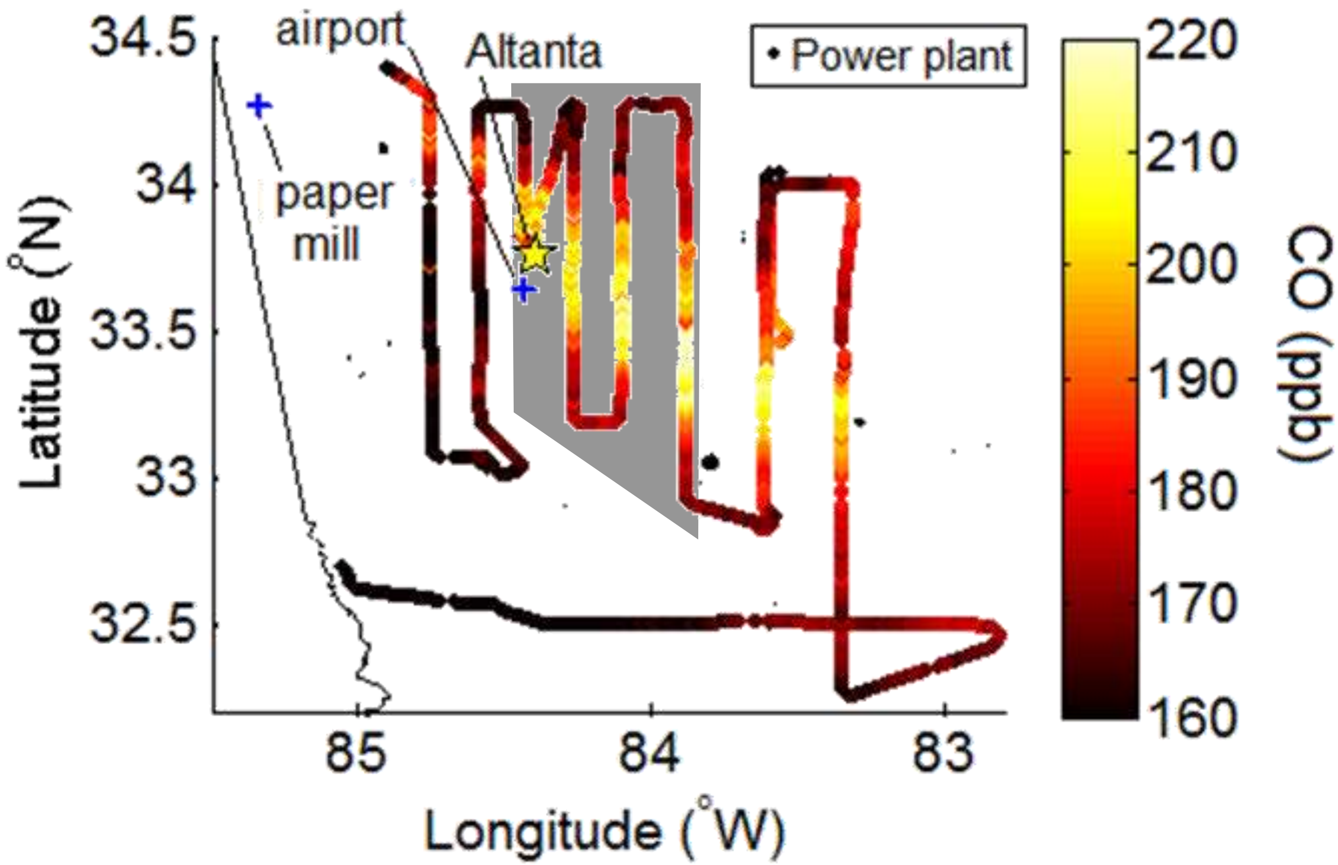


High R_{GF} is associated with monoterpenes.

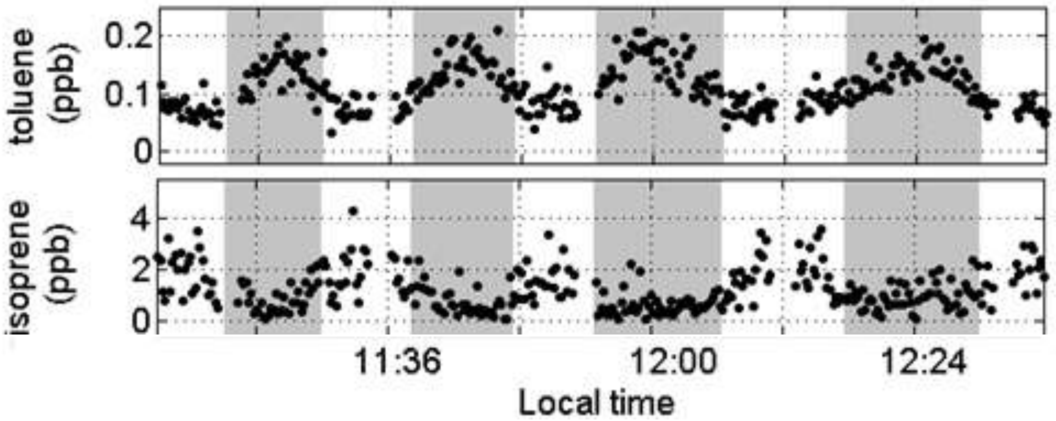




Urban plum: NO_x and Anthropogenic VOCs

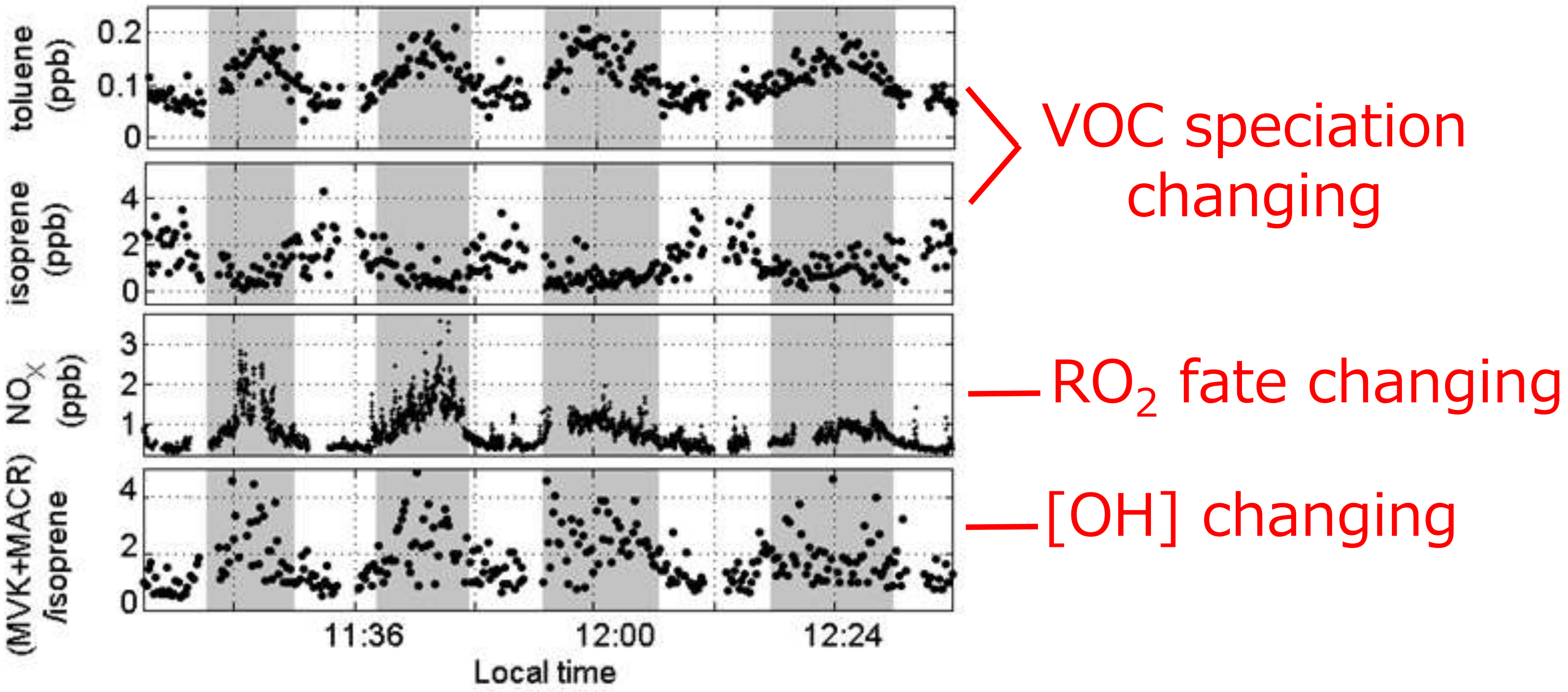


R_{GF} in a city outflow

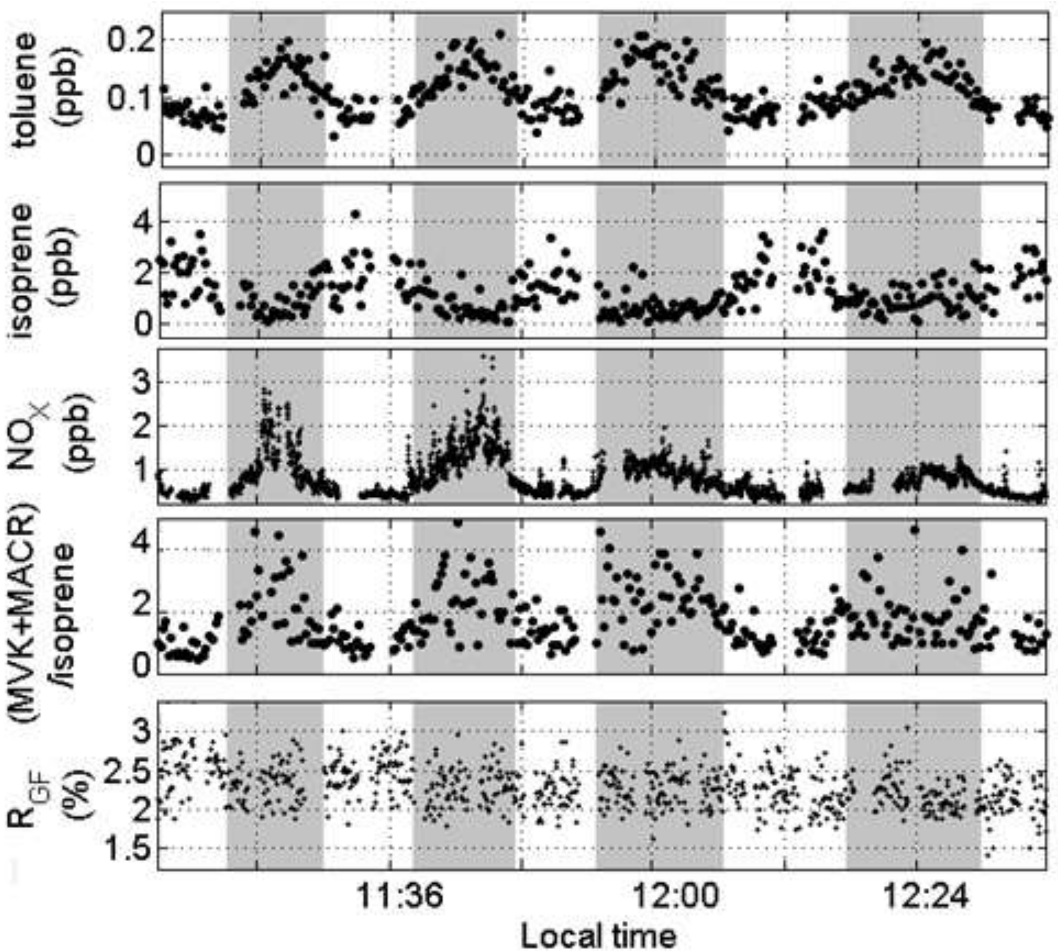


VOC speciation changing

R_{GF} in a city outflow



R_{GF} in a city outflow



VOC speciation changing

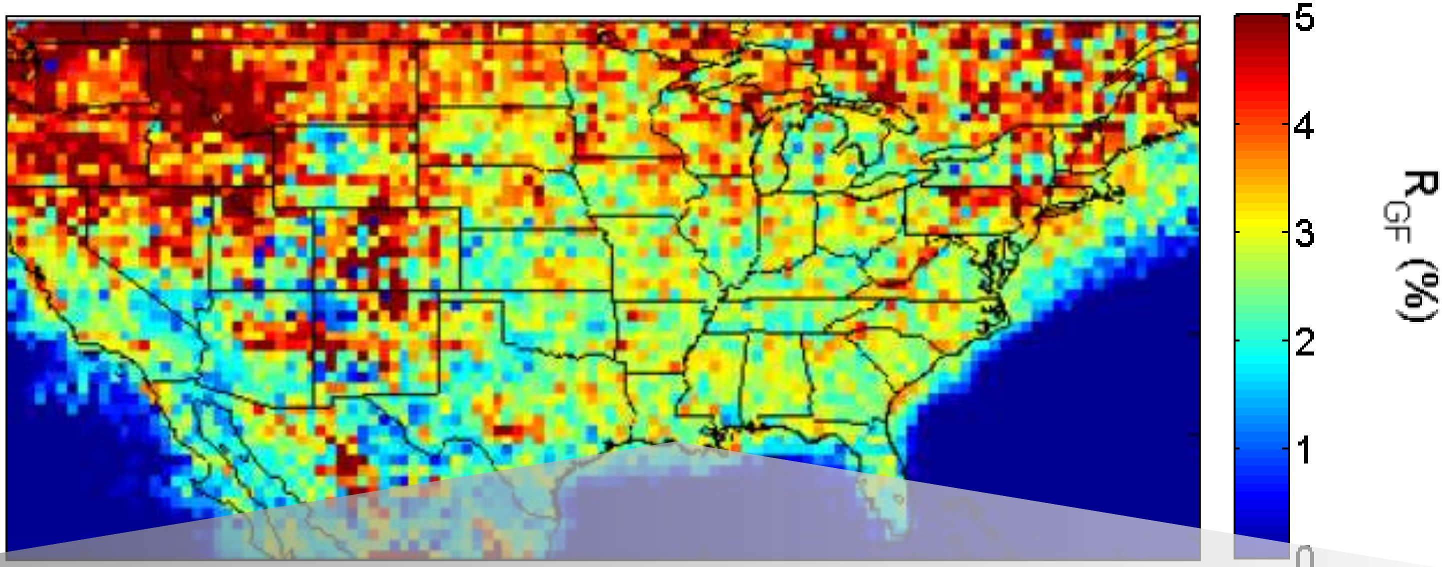
RO_2 fate changing

[OH] changing

R_{GF} consistent!

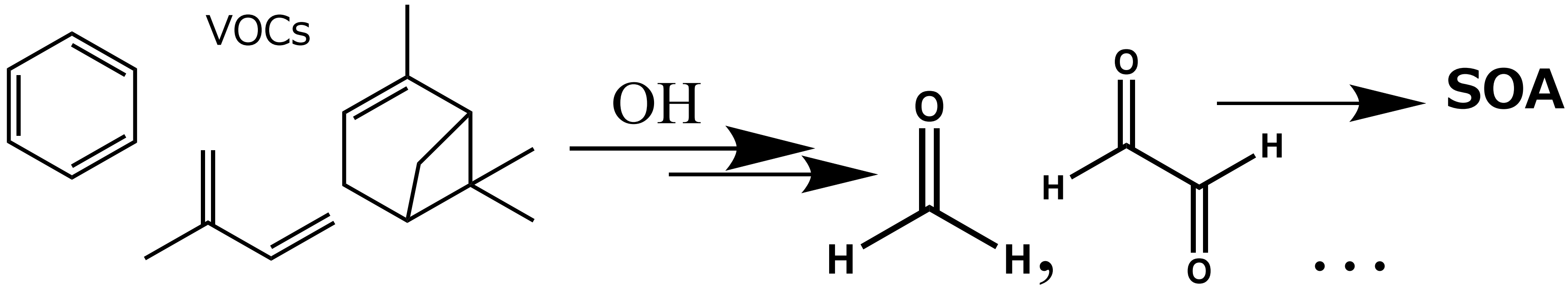
R_{GF} is only a tracer of dominant VOC species.

Trends are matched by satellite retrievals.



Quick, neighborhood-level R_{GF} in the near future!

Anthropogenic Influence on Glyoxal and Implications for SOA production



Formaldehyde Glyoxal

Overprediction of gas-phase glyoxal in model = SOA

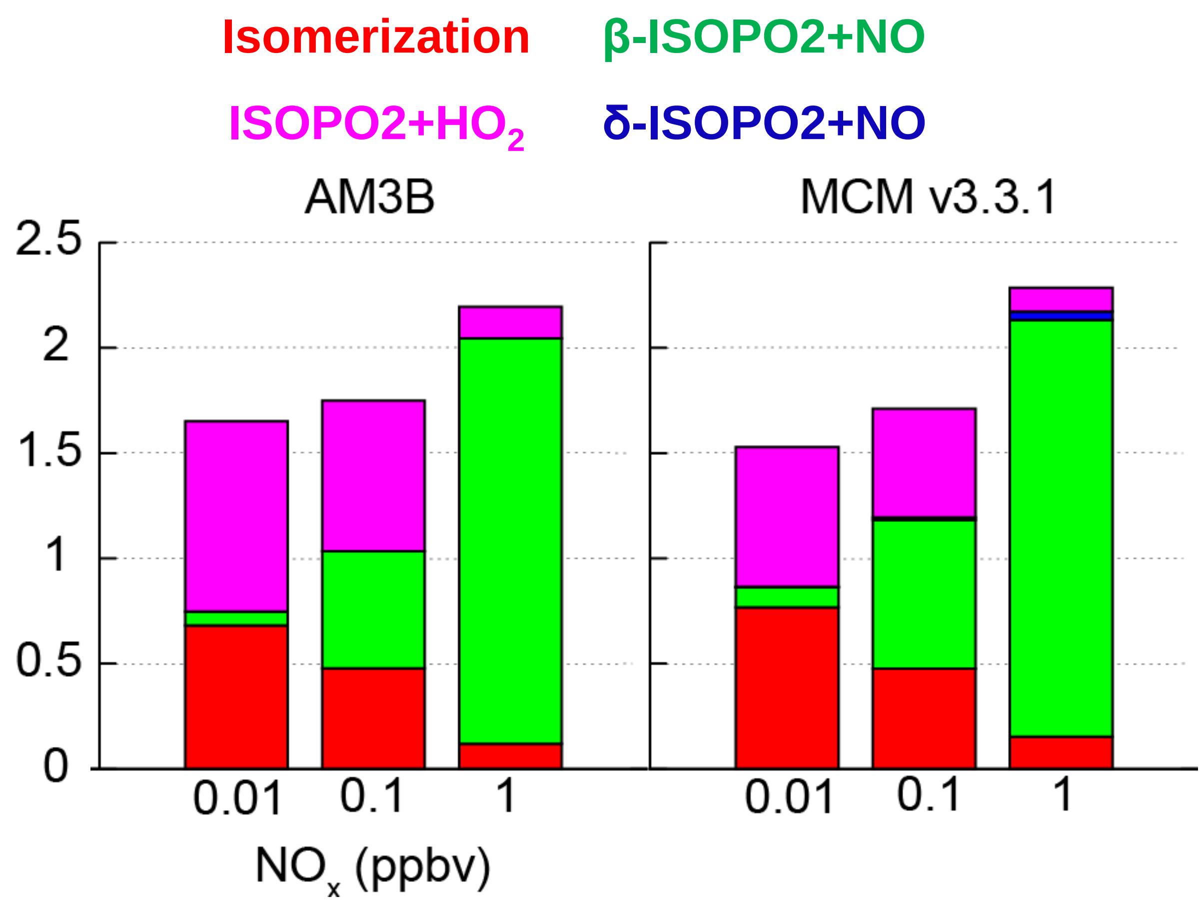
GFDL Atmospheric General Circulation Model AM3
Leeds Master Chemical Mechanism MCM v3.3.1

Jingqiu Mao, Jingyi Li

NO_x Influence on HCHO Production in Different Mechanisms

<u>HCHO yield</u> (ppbv) from isoprene

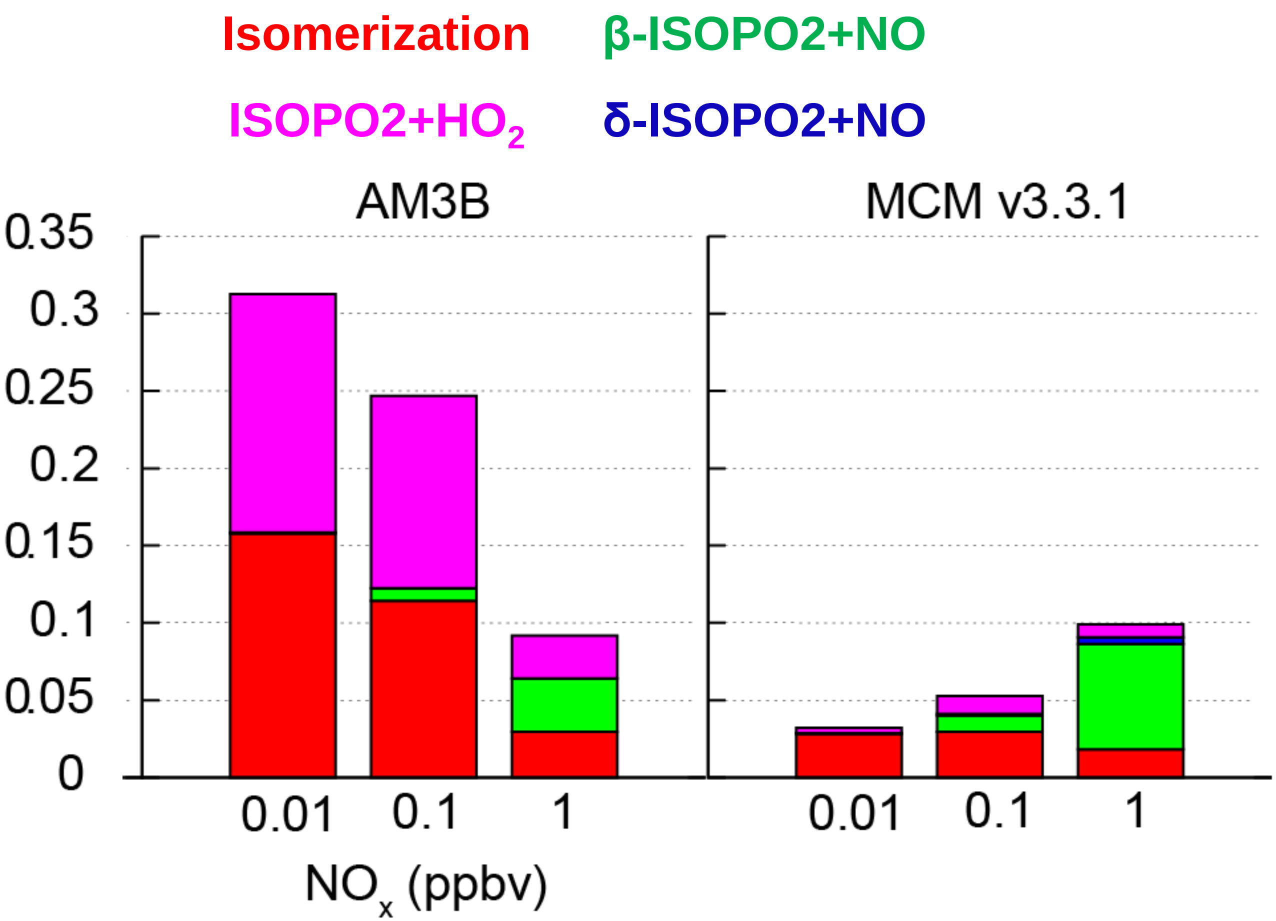
Box model:60 ppbv O_3
1 ppbv ISOP



Good agreement!

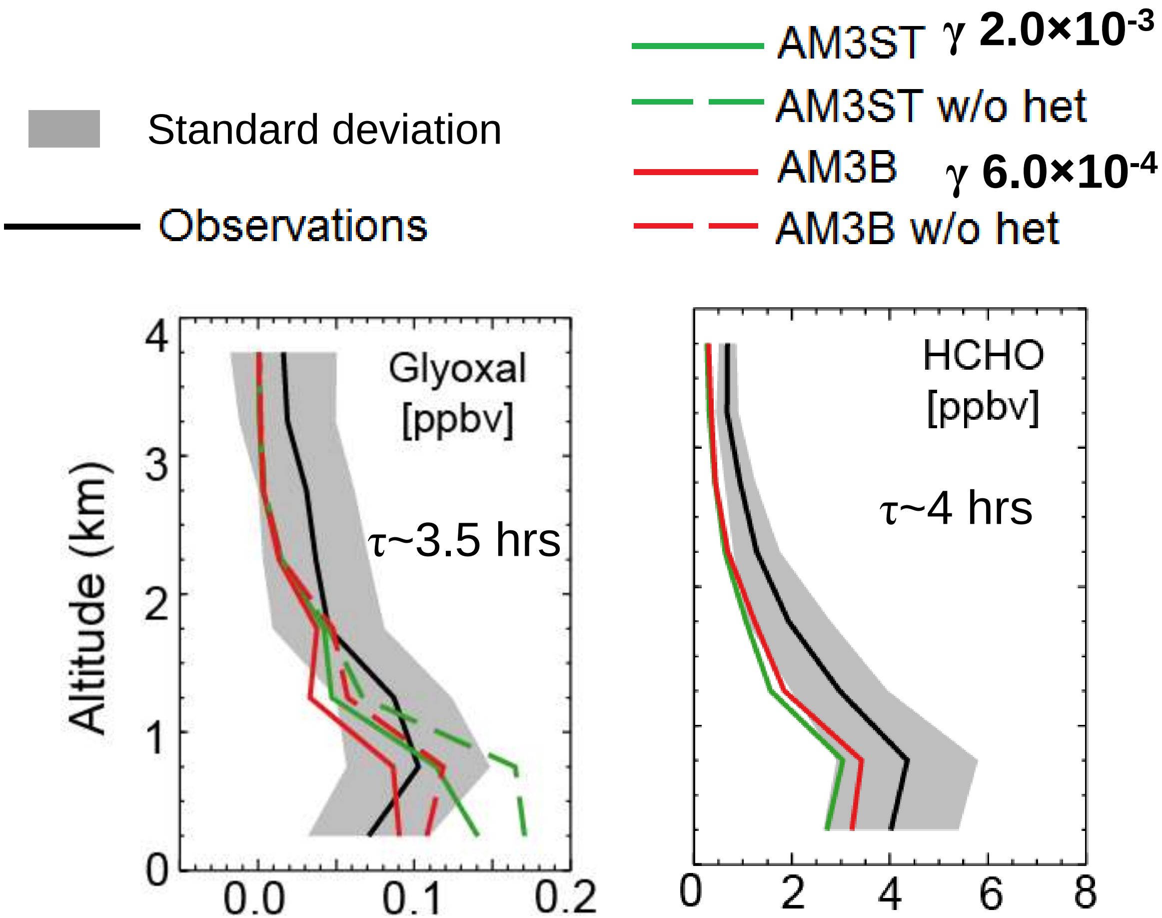
NO_x Influence on Glyoxal Production in Different Mechanisms

<u>Glyoxal yield</u> (ppbv) from isoprene



Significant discrepancy of yield and NO_x dependence

Mean Vertical Profiles During SENEX

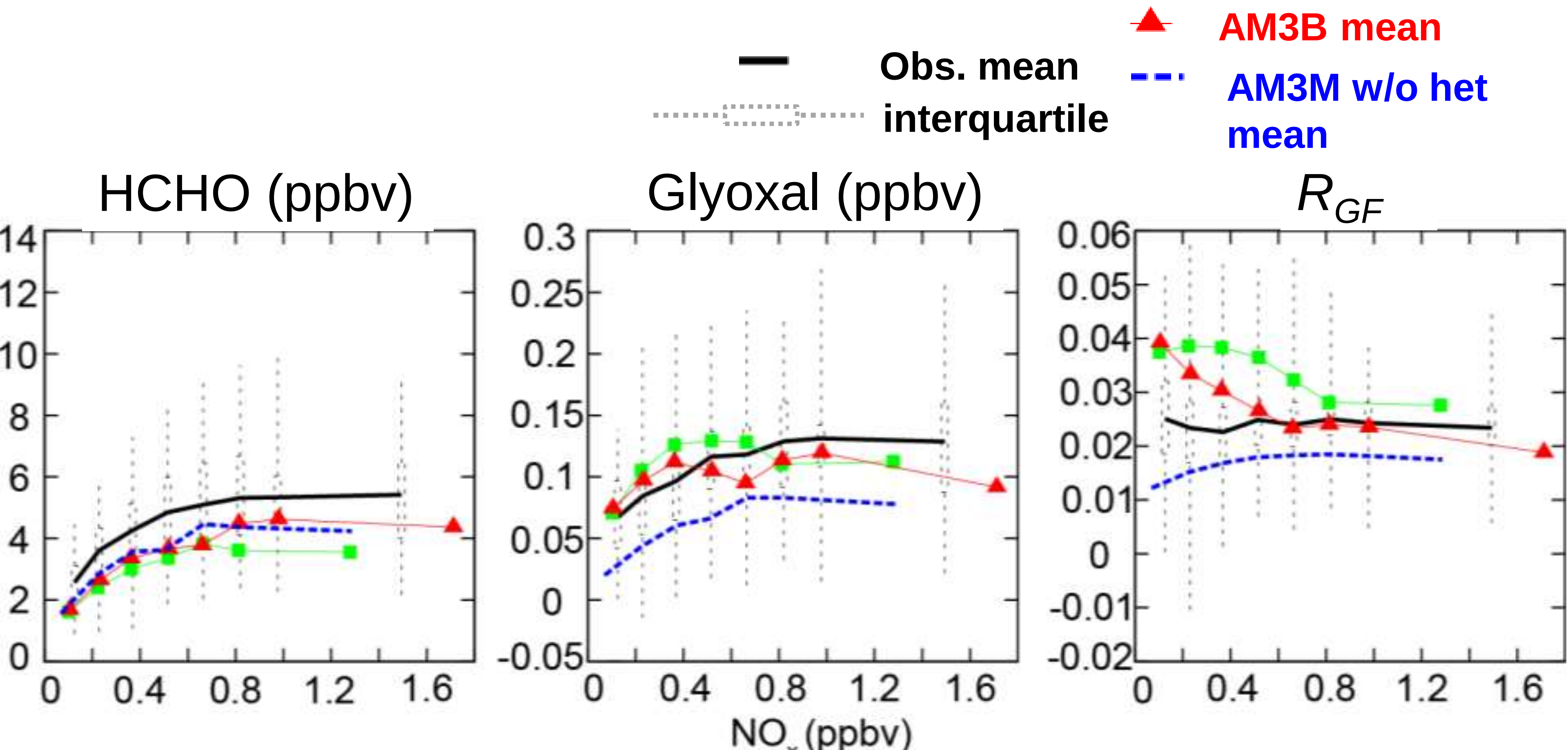


Heterogeneous loss of dicarbonyls **(irreversible) =>SOA**

γ_{glyx} ($\times 10^{-3}$)	**Reference**
0.8-7.3	Liggio et al. 2005
3.7	Volkamer et al., 2007
0-0.8(day)	Washenfelder et al., 2011
3.3	Waxman et al. 2013
~1.0 (OA)	V. Faye McNeill, 2015

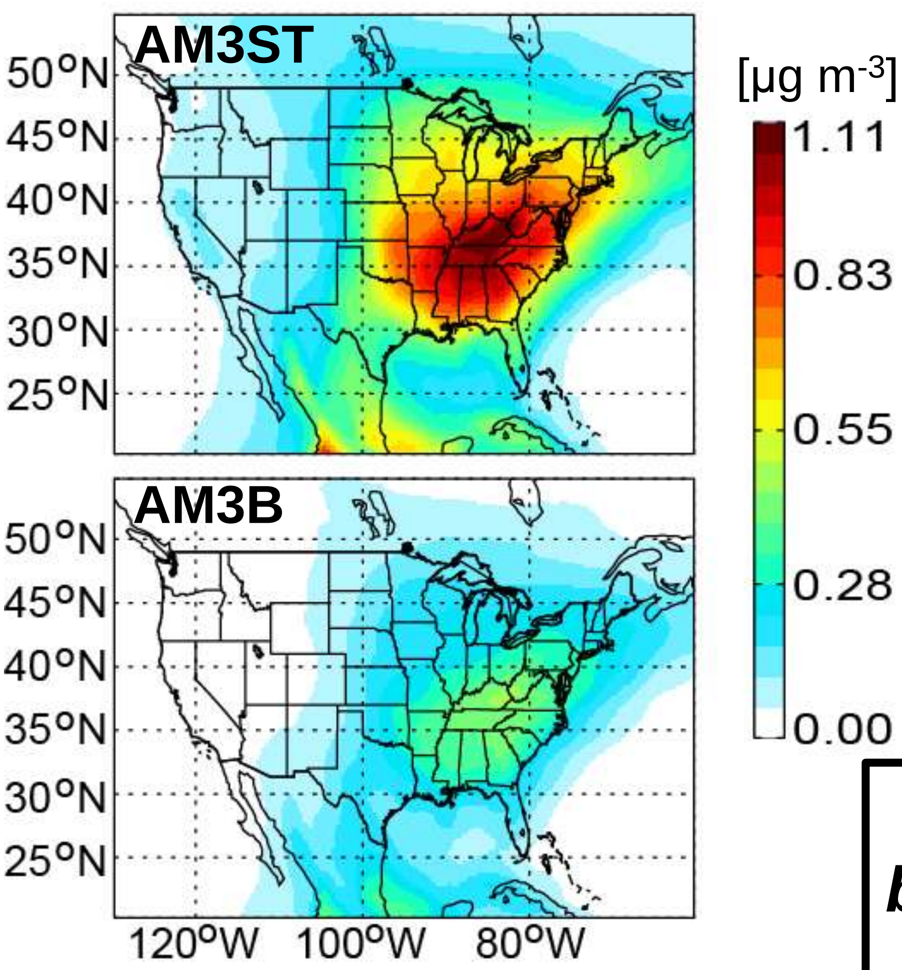
* From dry aerosols

Comparison with Observations



- NO_x dependence of HCHO and glyoxal are similar
  - ➢ HCHO is underestimated
  - ➢ AM3B could reproduce NO_x-glyoxal
- AM3B overestimate R_{GF} at NO_x < 0.5 ppbv
- AM3M (MCM v3.3.1) underestimates glyoxal and R_{GF} across NO_x levels

Glyoxal SOA



Boundary layer average during June-July of 2013

- Irreversible uptake by aerosols & clouds

0.5-1.0 μg m^{-3} (10-20% of total SOA)

Profound discrepancies between different mechanisms with this approach

Publications from Work Under This Grant

Published Manuscripts

- **Wolfe: Formaldehyde production from isoprene oxidation across NOx regimes ACP 2016**
- **Kaiser: Reassessing the ratio of glyoxal to formaldehyde as an indicator of hydrocarbon precursor speciation ACP 2015**
- De Gouw: Airborne Measurements of the Atmospheric Emissions from a Fuel Ethanol Refinery

Submitted Manuscripts

- **Li: Observational Constraints on Glyoxal Production from Isoprene Oxidation and Its Contribution to Organic Aerosol Over the Southeast United States GRL**

Manuscripts in Preparation

- DeGouw: Enhanced Removal of Biogenic Hydrocarbons in Power Plant Plumes Constrains the Dependence of Atmospheric Hydroxyl Concentrations on Nitrogen Oxides
- Marvin: Investigating Differences in Isoprene Oxidation Chemistry Between Gas-Phase Mechanisms Using a Constrained Chemical Box Model
- Yuan: Emissions and Chemistry of Volatile Organic Compounds in Early Spring of Western U.S.: Interactions between Oil/Gas Emissions and Biogenic Emissions
- Additional ones in early stages