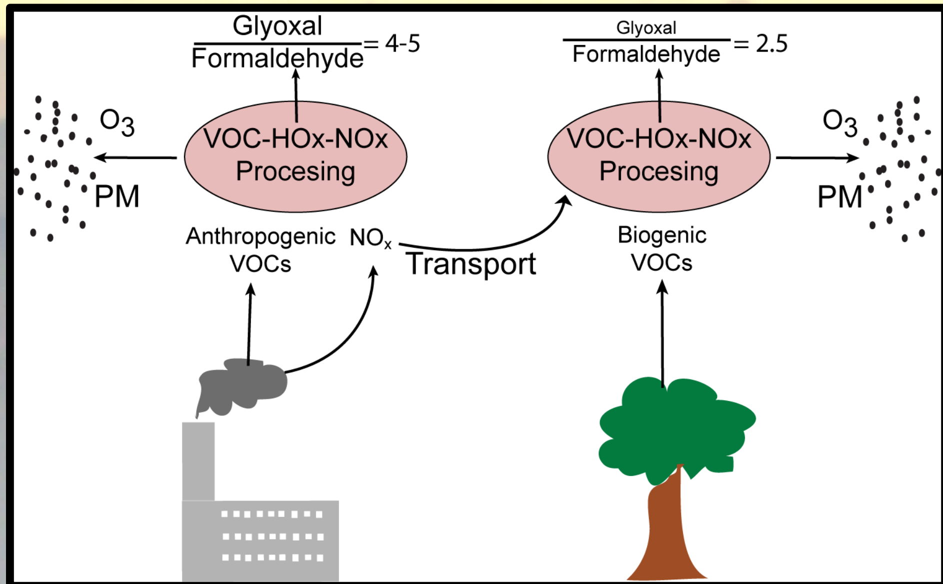
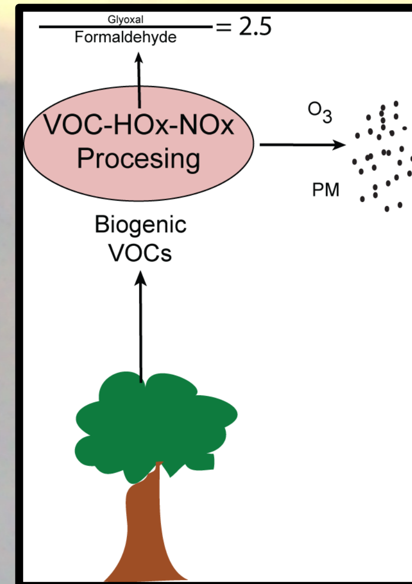
Assessing Synergistic Impact of Anthropogenic and Biogenic Emissions on Air Pollution Using Novel High-Sensitivity, Real-Time Monitors for Fundamental Carbonyls (*Formaldehyde, Glyoxal*)





Frank Keutsch
University of Wisconsin-Madison

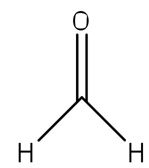
EPA Air Monitoring Kickoff Meeting, March 20, 2013, RTP, NC

This research is funded by
U.S. EPA - Science To Achieve Results (STAR) Program
Grant # R83513801

Formaldehyde and Glyoxal: Why Monitor Small Carbonyls?

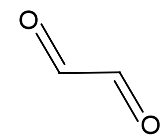
Formaldehyde

- Toxic air pollutant
- National cancer risk driver
- With benzene most significant estimated national cancer risk (air)



Glyoxal

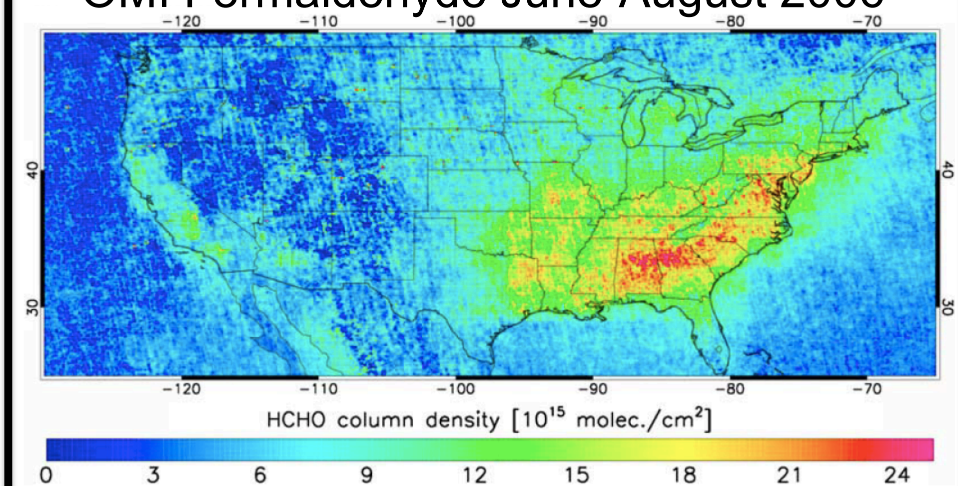
- Proposed important contributor to aerosol



Special role as satellite retrievals exist, providing important link to regional and global models

Tracers of oxidative chemistry that produces secondary pollutants

OMI Formaldehyde June-August 2006

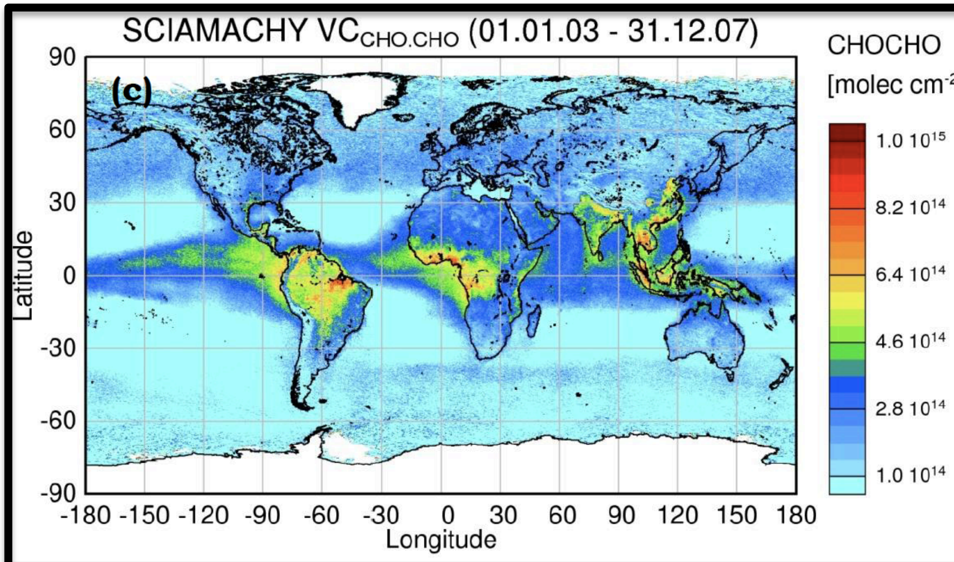


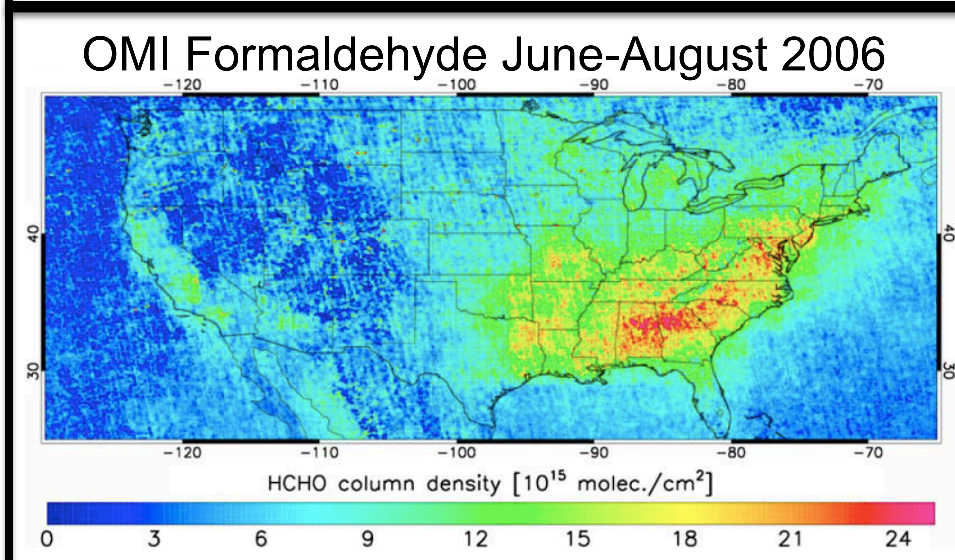
Millet, D.B. et al. J. Geophys. Res. 113, D02307, 2008

Formaldehyde and Glyoxal: Why Monitor Small Carbonyls?

Continuously monitor processes of *pollutant formation* not only pollutants

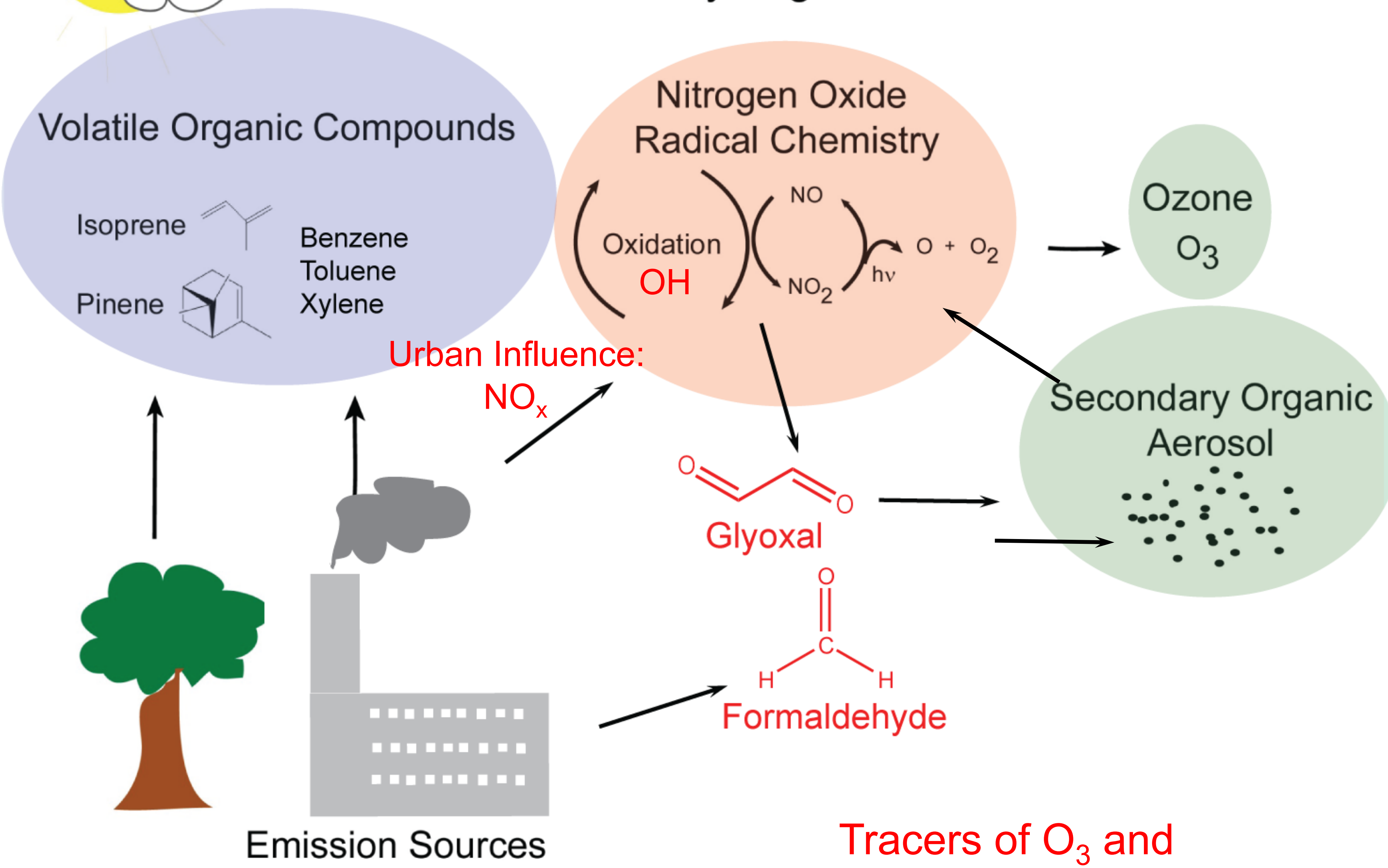
- Ozone and secondary aerosol formation
- Emissions
- Interaction of anthropogenic (controllable) and biogenic (difficult to control) emissions
- Fast, high accuracy/ precision robust instrumentation





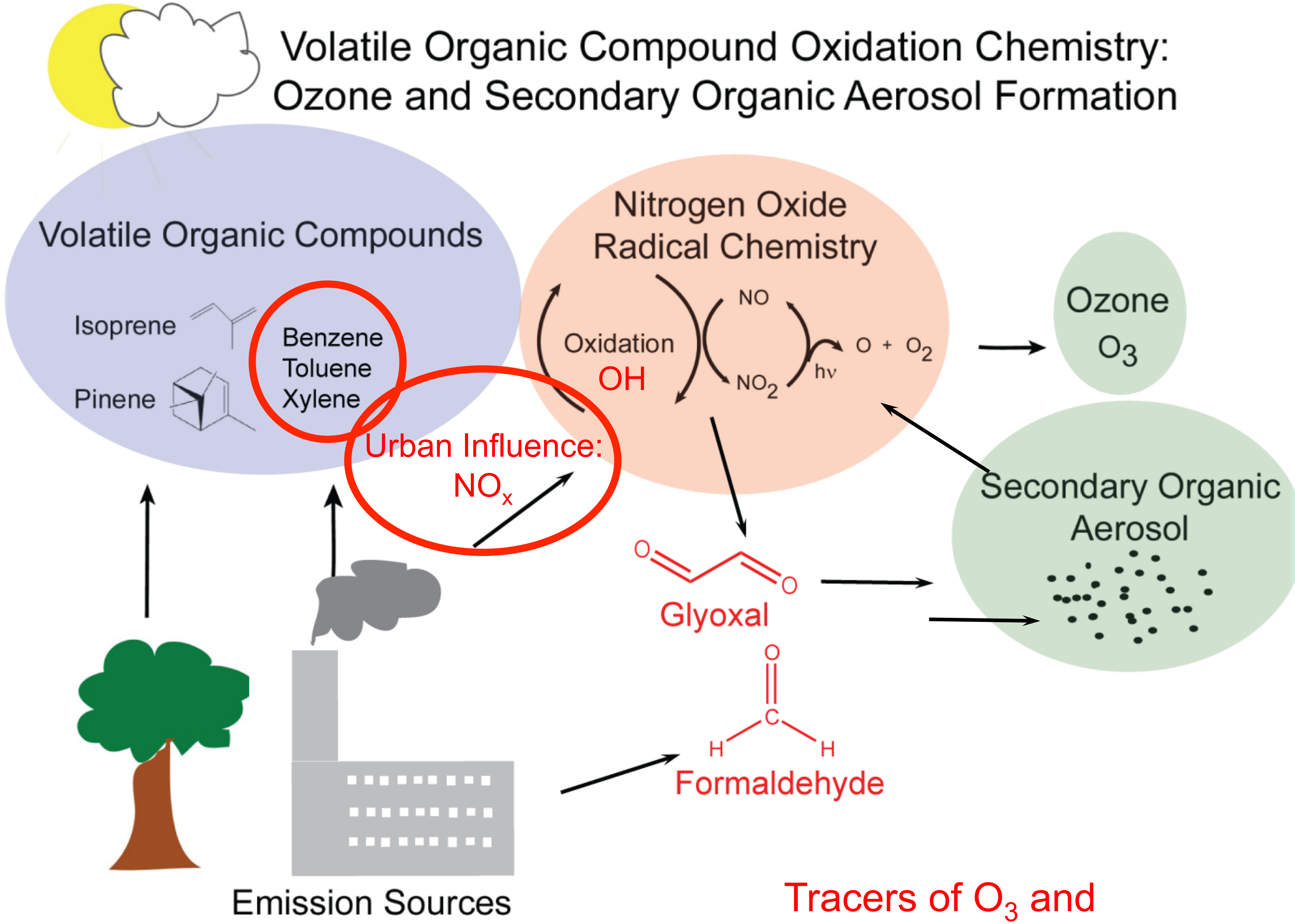
Vrekoussis, M. et al. , Atmos. Chem. Phys. 9, 4485 (2009).

Volatile Organic Compound Oxidation Chemistry: Ozone and Secondary Organic Aerosol Formation



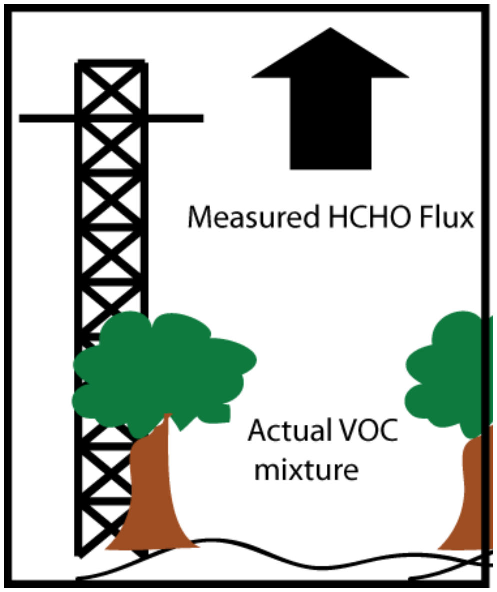
Tracers of O_3 and SOA Formation

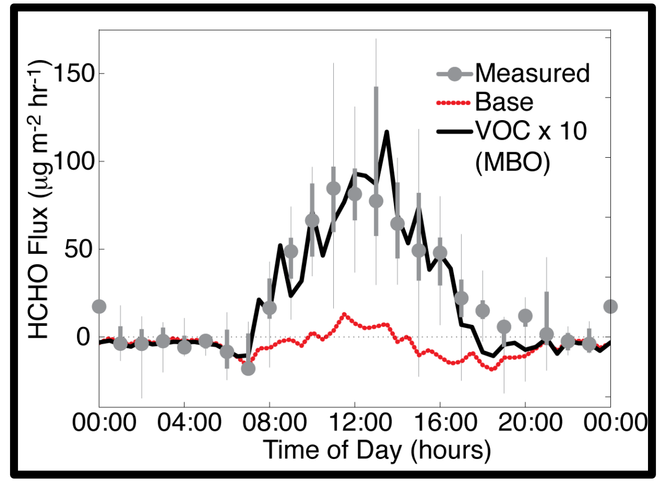
Volatile Organic Compound Oxidation Chemistry: Ozone and Secondary Organic Aerosol Formation



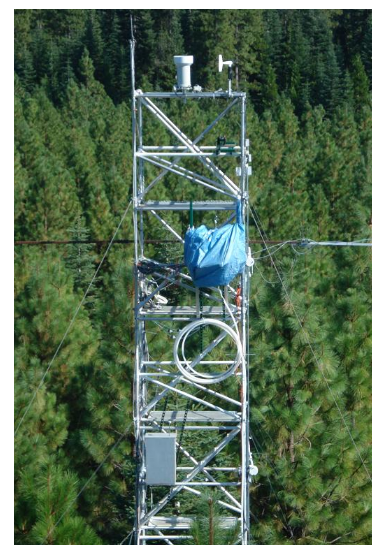
Tracers of O_3 and SOA Formation

Example: Formaldehyde as Tracer of Unaccounted Emissions





Fast formaldehyde flux measurements provide new insights into potentially missing emissions



J.P. DiGangi, ... FNK, Atmos. *Chem. Phys.*, 11, 10565 (2011).

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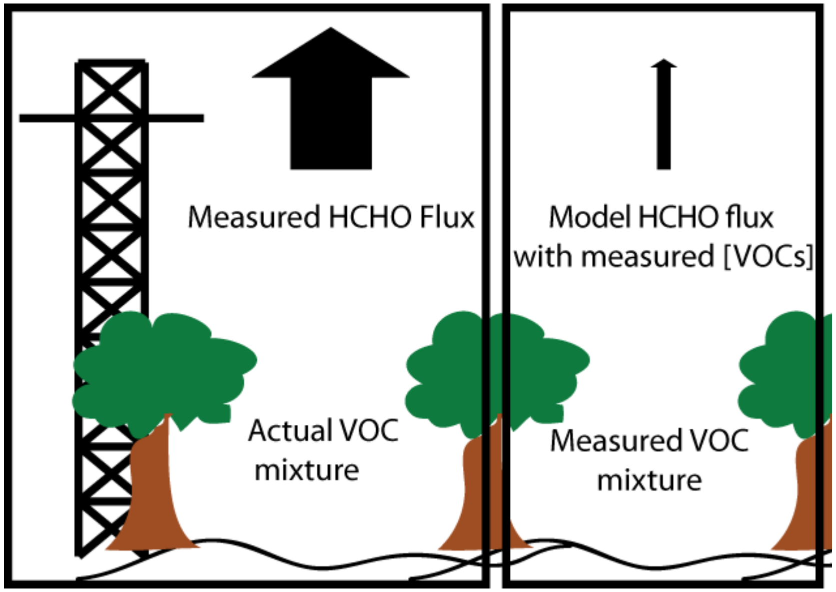

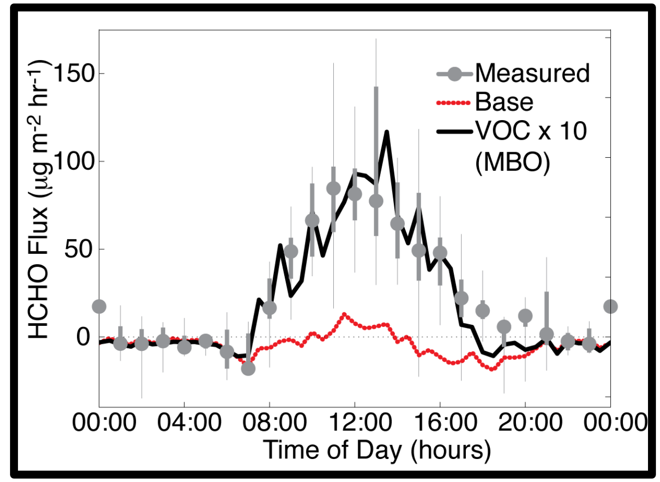

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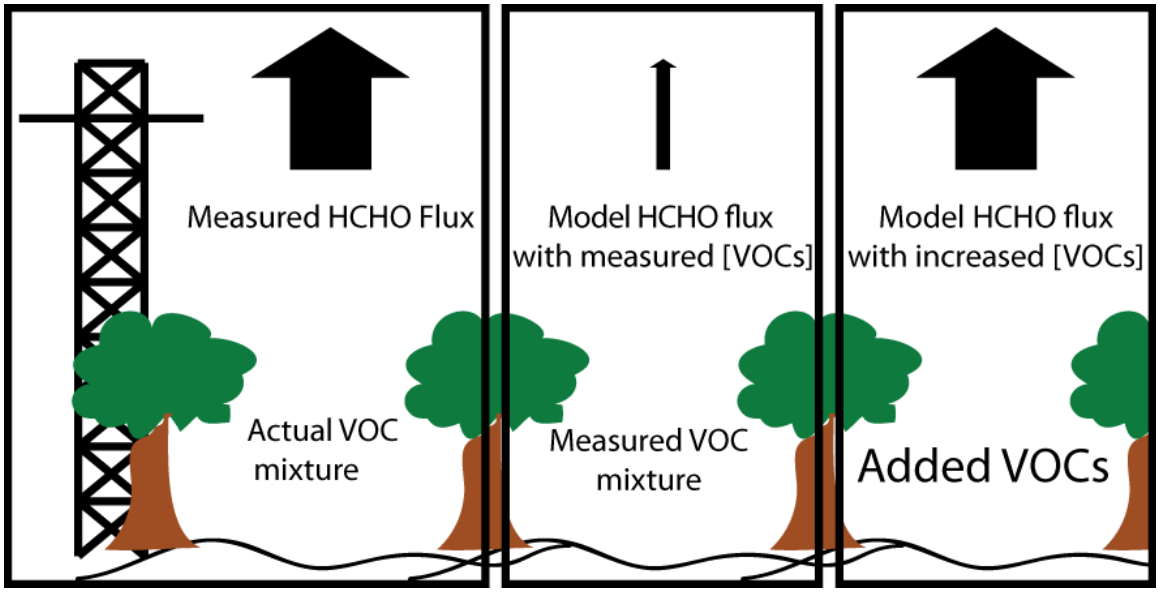

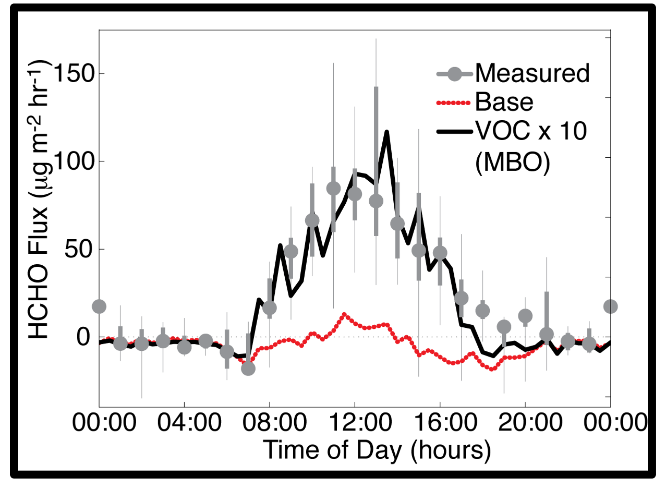

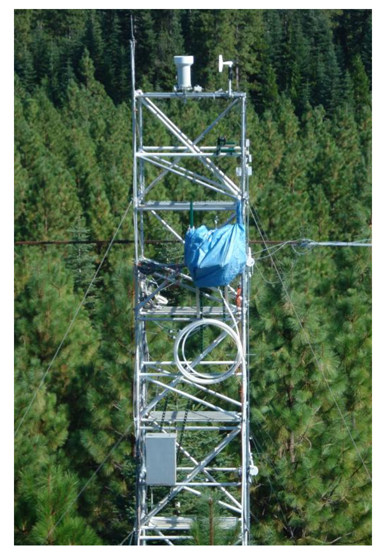

Fast formaldehyde flux measurements provide new insights into potentially missing emissions

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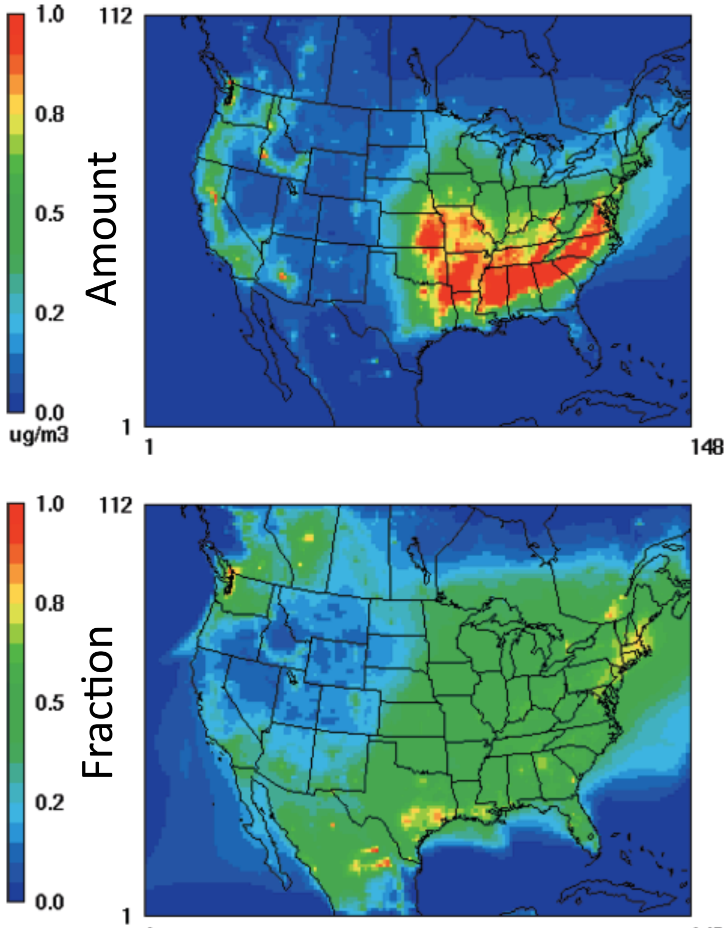
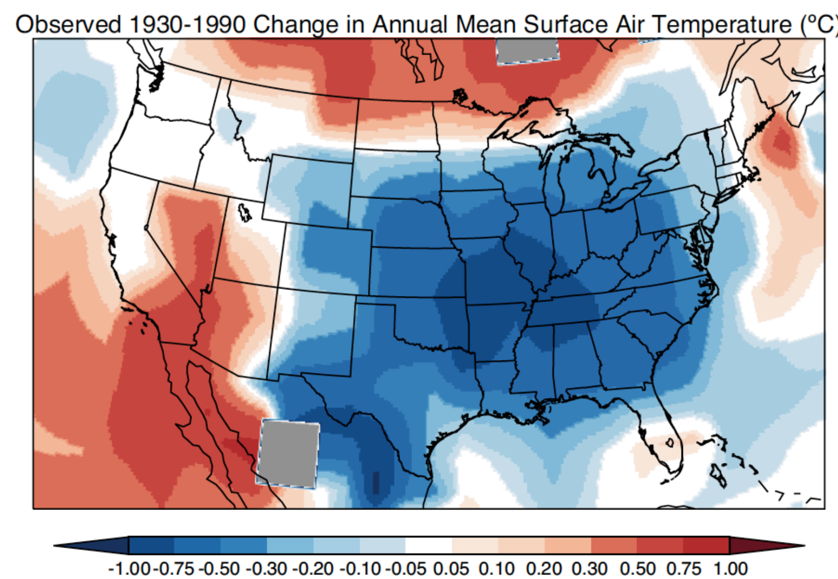
Goal: Formaldehyde and Glyoxal as Metrics of ***Anthropogenic Influence***



Controllable (from anthropogenic influence) biogenic SOA and 1930-90 temperature trend.



A.G. Carlton et al. *Environ. Sci. Technol.*, 44, 3376 (2010).
E.M. Leipensberger et al. *Atmos. Chem. Phys.* 12, 3333 (2012).

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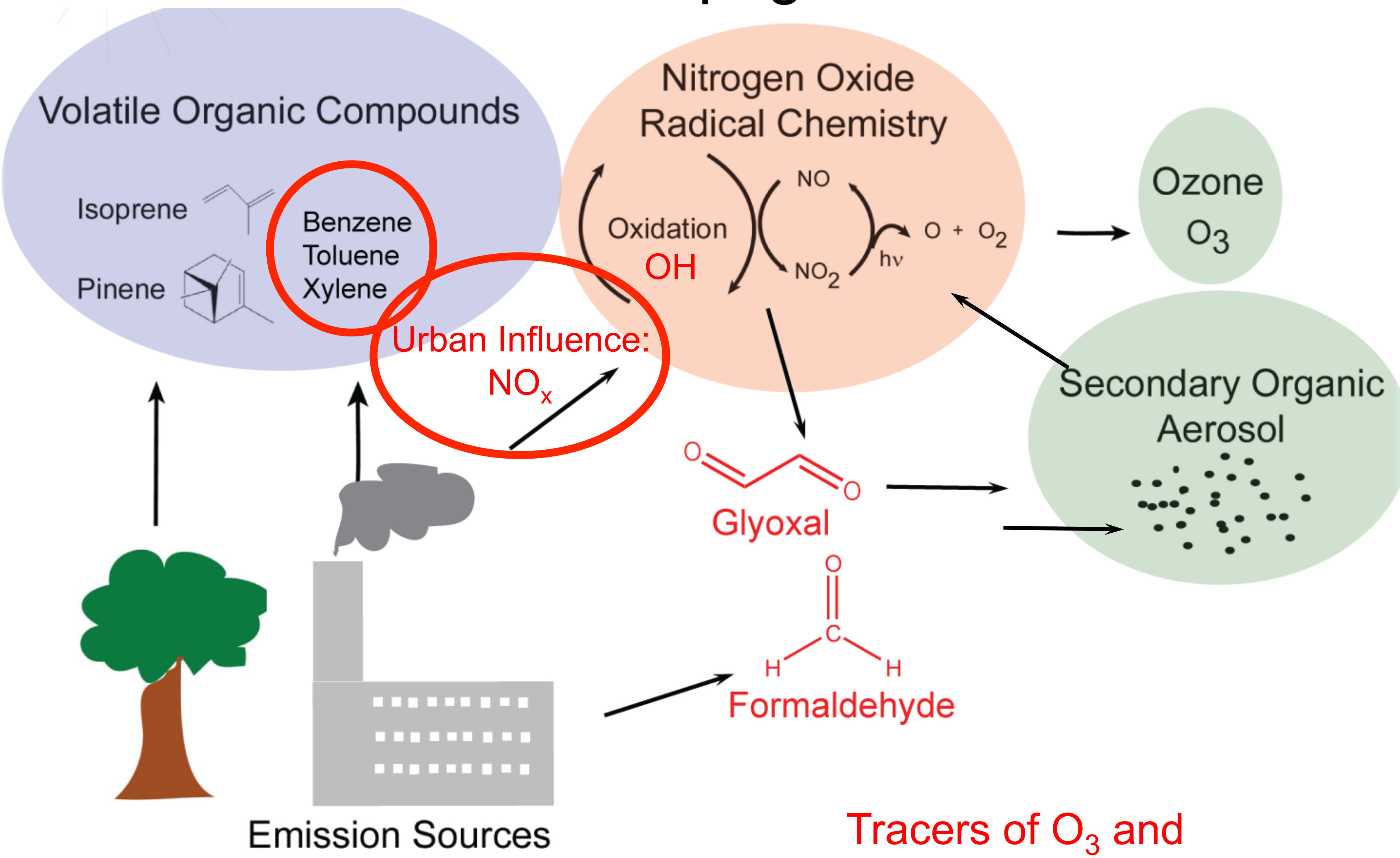

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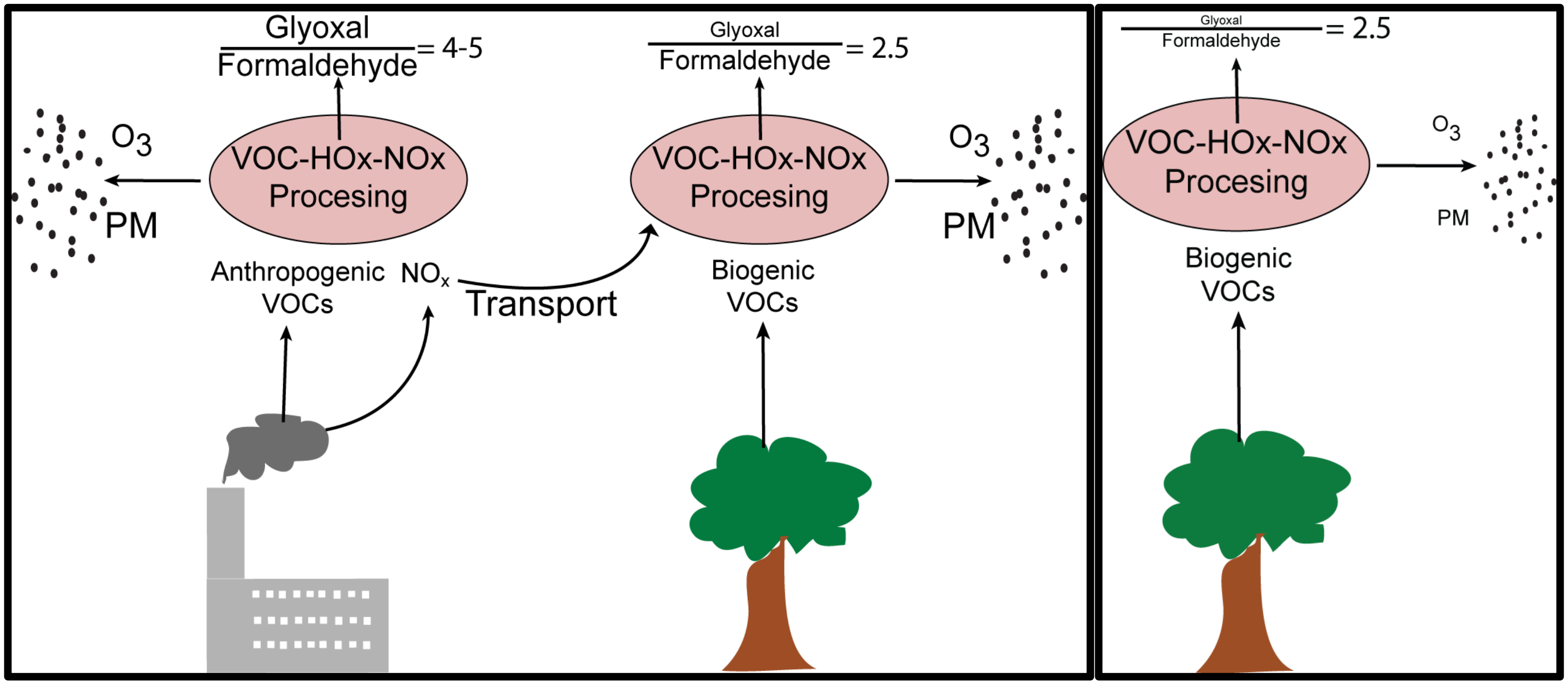
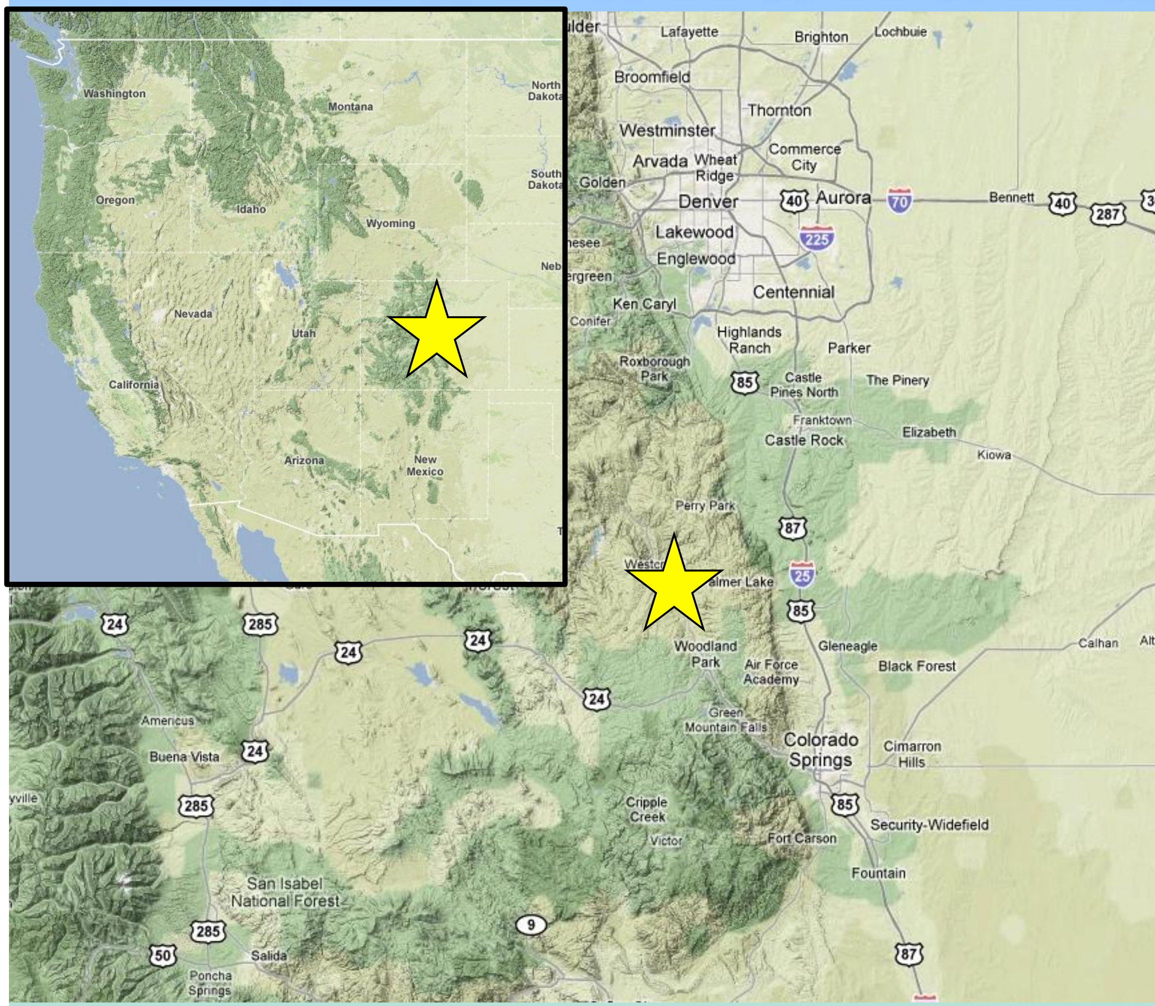
Goal: Formaldehyde and Glyoxal as Metrics of Anthropogenic Influence



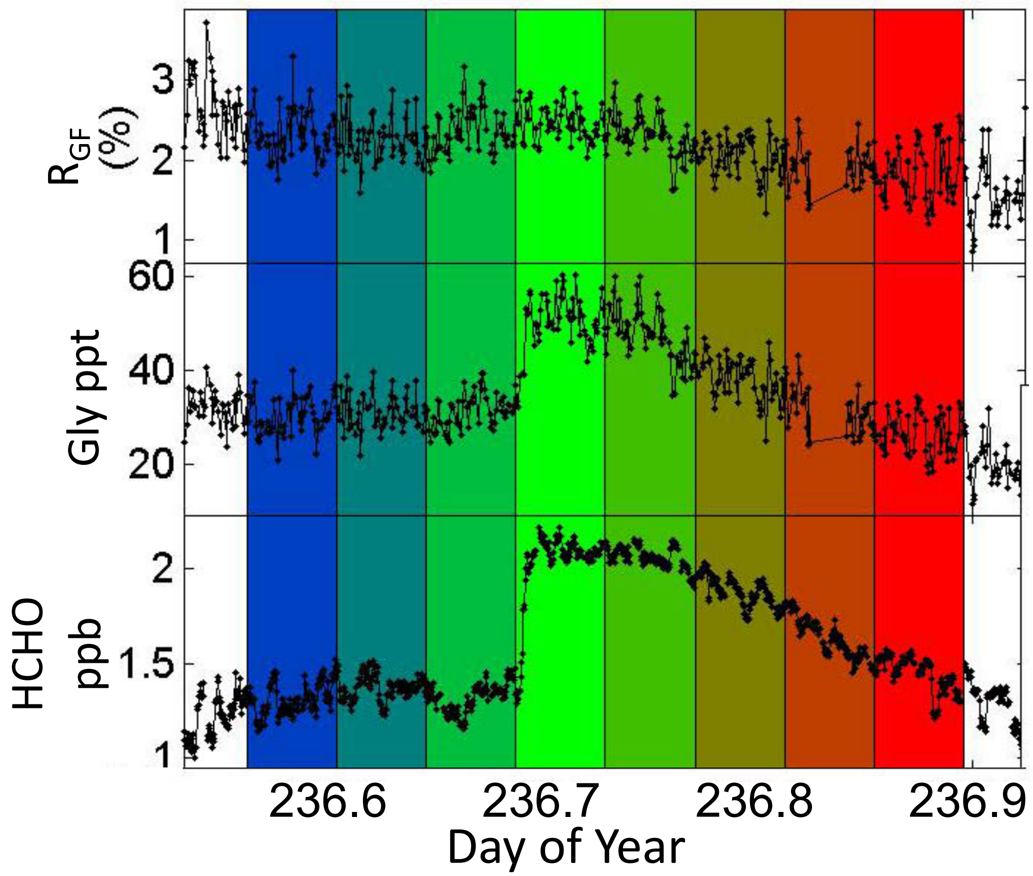
- Concentrations reflect anthropogenic influence via NOx
- Ratio reflects anthropogenic influence via VOC mixture
- In contrast to NOx and VOCs they capture degree of processing, reflecting the processes that drive secondary pollutant formation
- Other anthropogenic drivers exist (sulfate, primary aerosol, etc.)

Proof of Concept Test: BEACHON-ROCS



- Ponderosa pine forest, little undergrowth
- Major VOC emissions: MBO, monoterpenes
- Wide suite of instrumentation

Glyoxal, Formaldehyde and Their Ratio as Tracers of Anthropogenic Impact: NO_x during BEACHON-ROCS



- Shift in chemical regime from low to high NOx
- **Glyoxal and formaldehyde concentrations affected by NOx** but not R_{GF}
- Result of unchanged VOC mixture (and VOC concentration)
- ***Fast measurements key as chemistry is non-linear***

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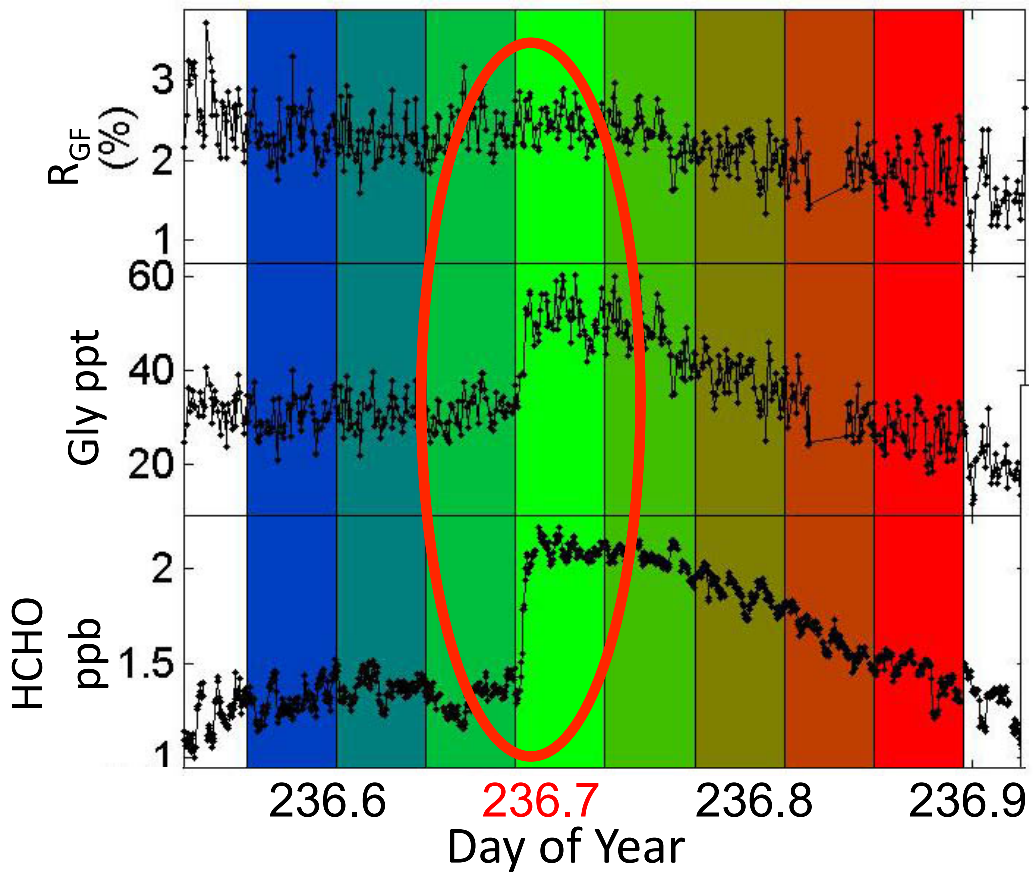

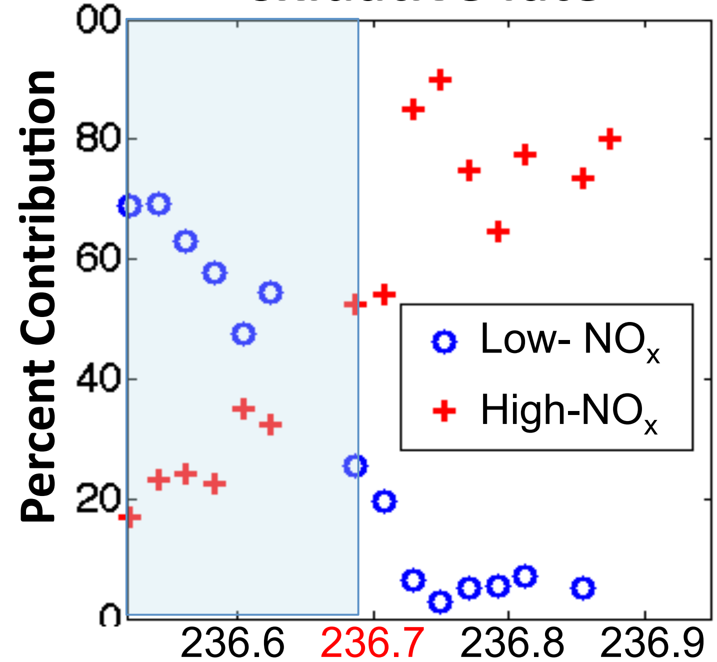

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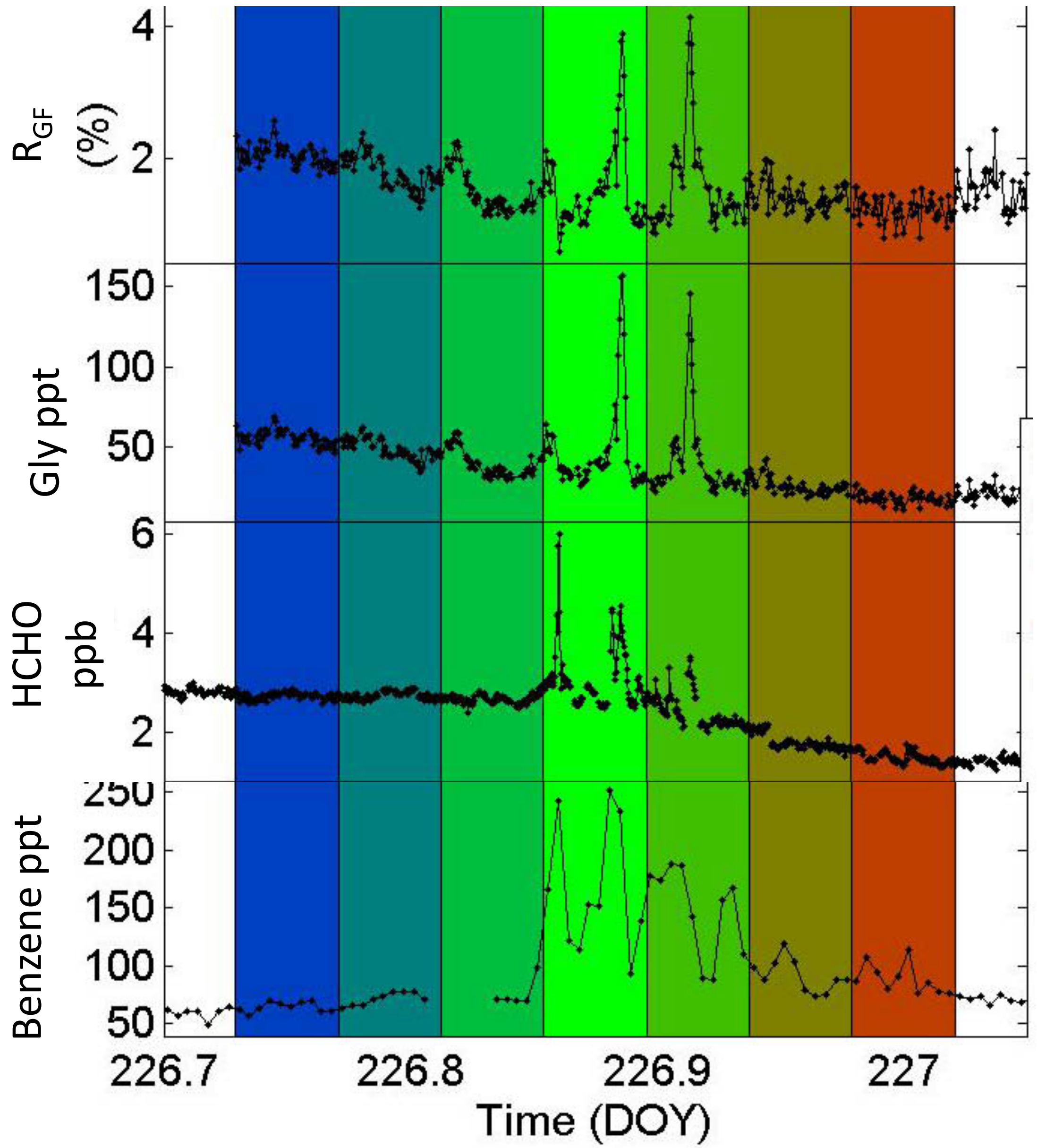
Glyoxal, Formaldehyde and Their Ratio as Tracers of Anthropogenic Impact: Anthropogenic VOCs

Anthropogenic VOCs (and biomass burning) increase R_{GF} significantly

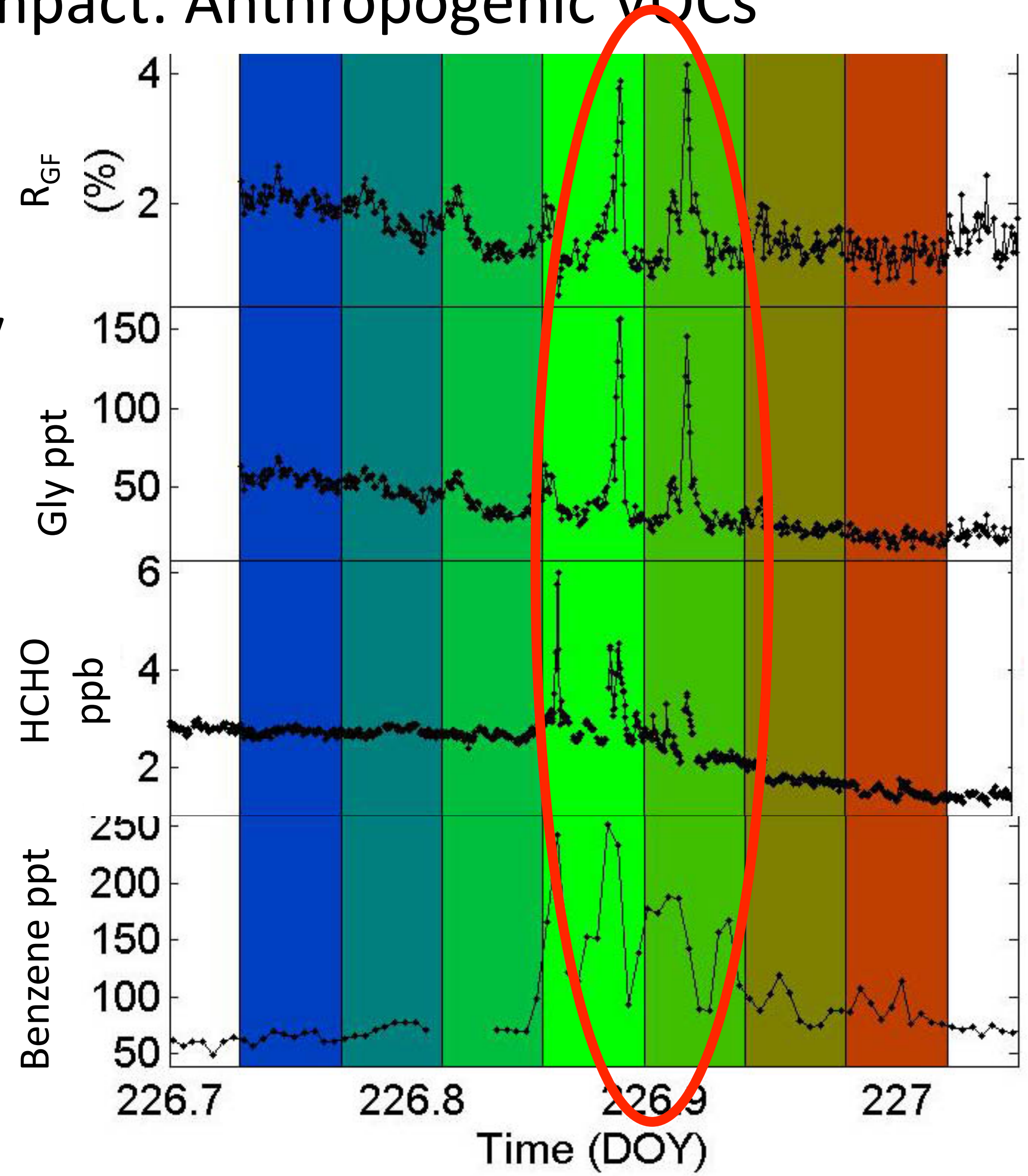


Glyoxal, Formaldehyde and Their Ratio as Tracers of Anthropogenic Impact: Anthropogenic VOCs

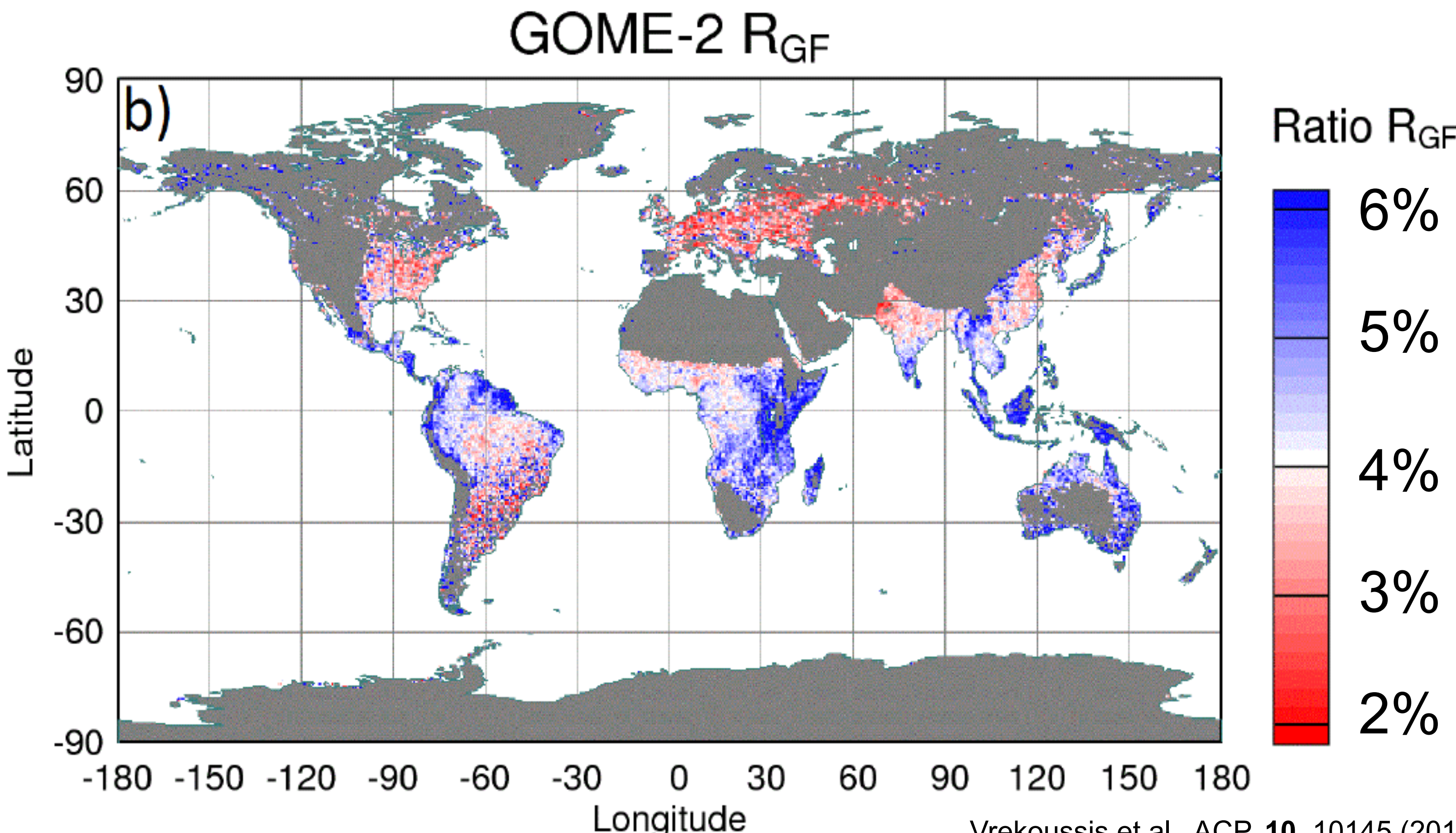
Anthropogenic VOCs (and biomass burning) increase R_{GF} significantly

Fast measurements critical as chemistry is non-linear

More and long-term measurements needed to further test this hypothesis



Satellite Glyoxal/Formaldehyde Ratios (R_{GF})



Vrekoussis et al., ACP, **10**, 10145 (2010).

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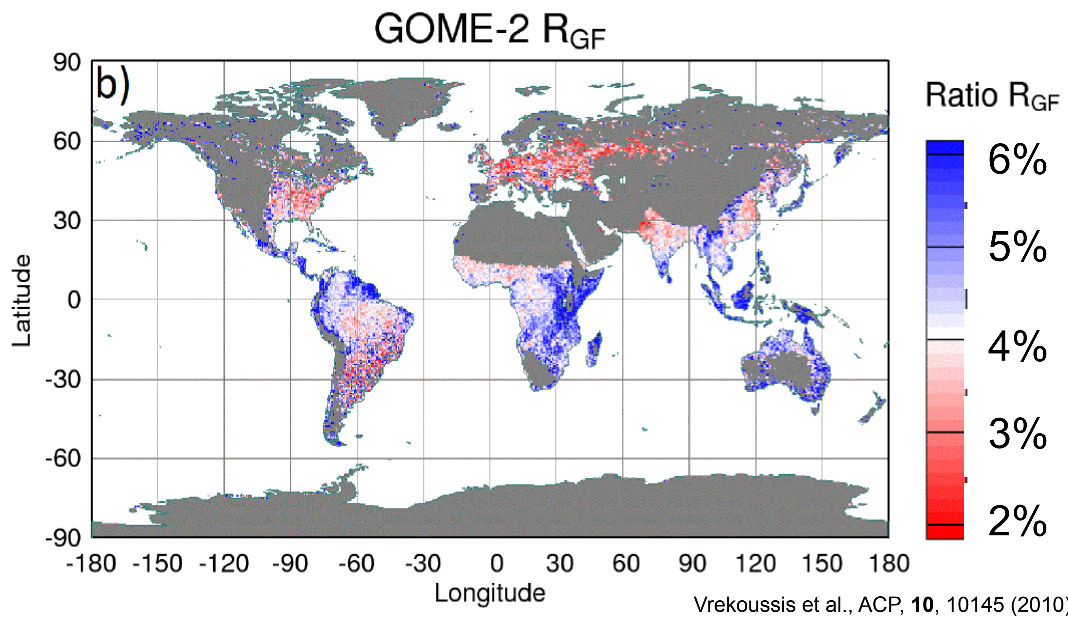
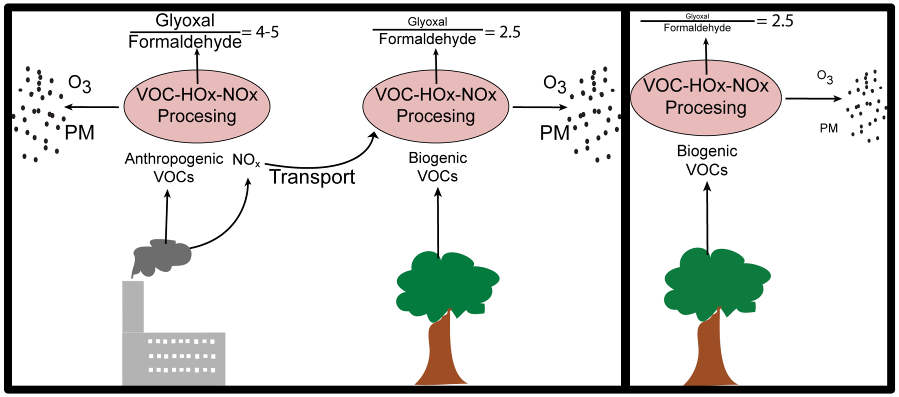


Vrekoussis et al., ACP, **10**, 10145 (2010).

- *Higher* R_{GF} over remote areas
- No diurnal information
- Column vs point measurements

- Global models use satellite R_{GF} for validation
  - Same models used to inform policy decisions
- Network of long-term, ground measurements for validation required

Milestones of Proposed Work

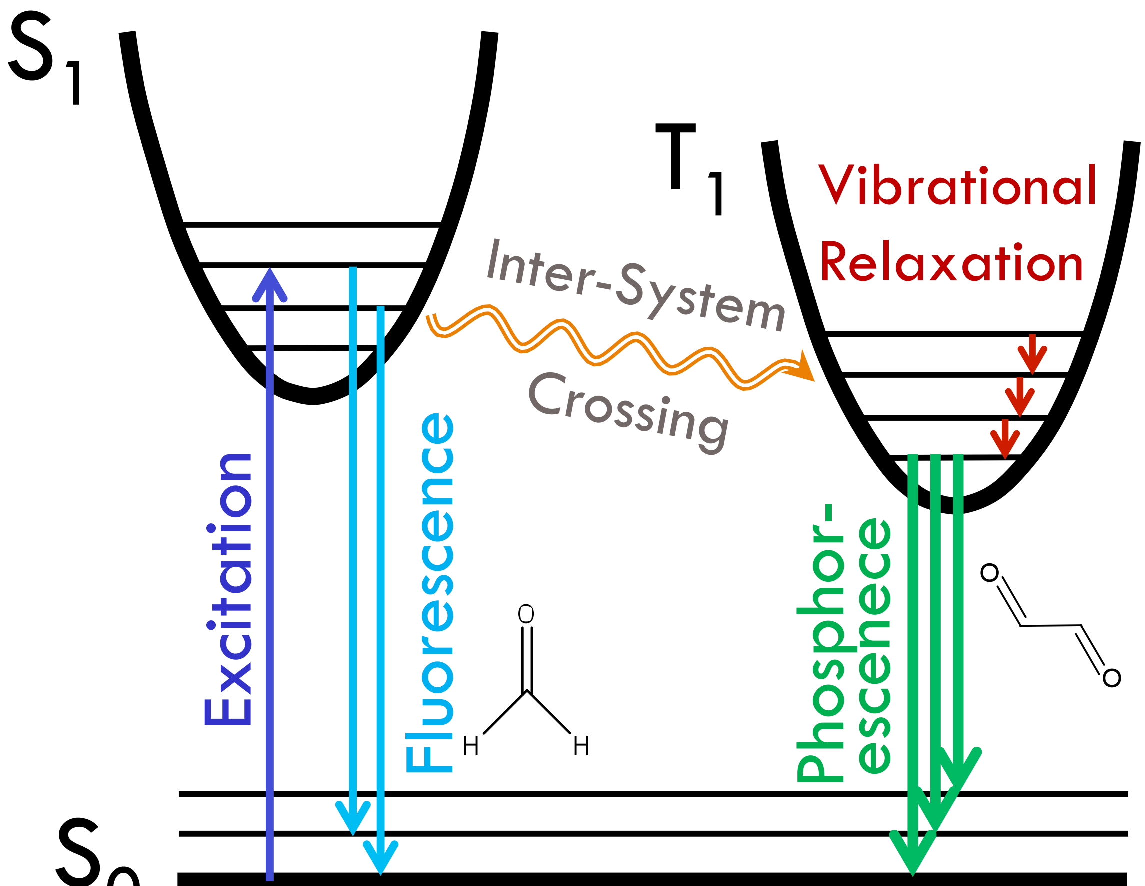


1. Long-term deployable, high accuracy/precision instruments *(completed for formaldehyde, near completion for glyoxal)*
2. Quality Control: Instrument intercomparison *(nearly completed)*
3. Year-long monitoring at Horicon, WI *(formaldehyde April, glyoxal August)*
4. Analysis of concentrations and ratio of glyoxal and formaldehyde as metric of anthropogenic influence
5. Comparison with regional models (CMAQ)

Instrument Methods and Development Goals

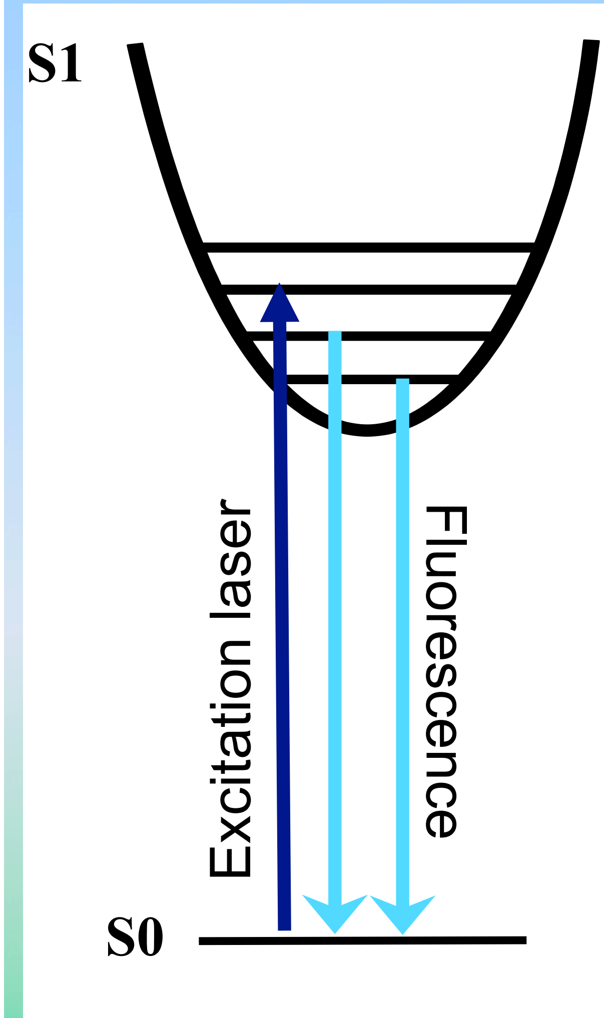
- Laser-induced emission spectroscopy coupled with laser advances enables:
- High sensitivity, turn-key, robust instrumentation for widespread, long-term datasets of key atmospheric species that provide metrics for important processes and comparison with models (and satellites):

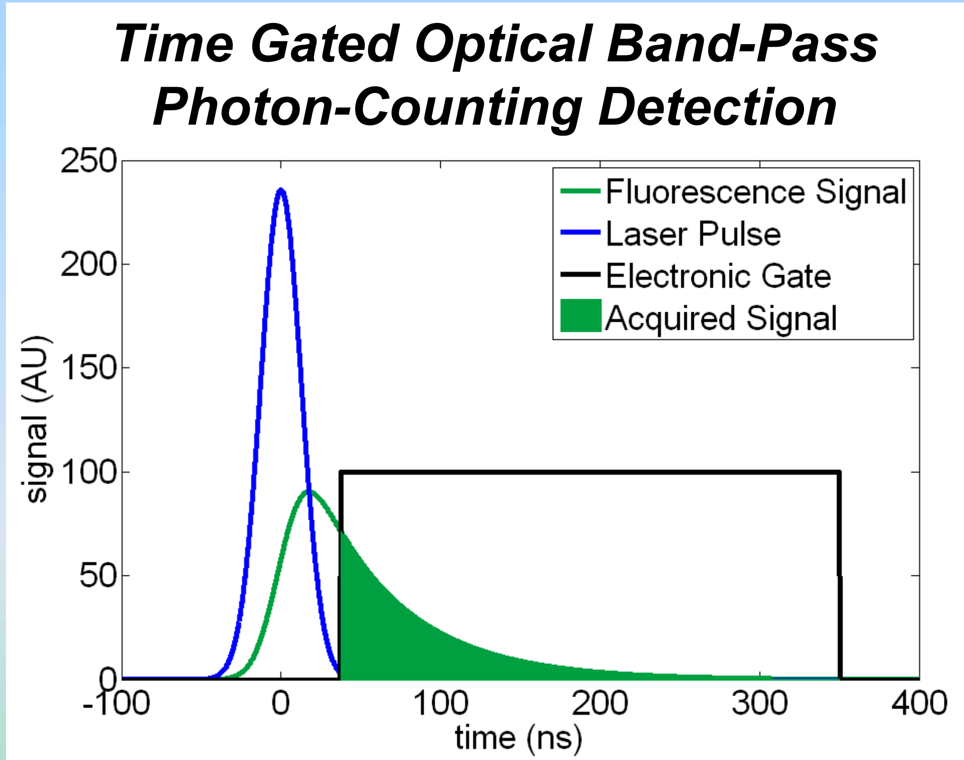
Laser Induced Emission Spectroscopy



- 440 nm excitation for glyoxal
- 353 nm excitation for formaldehyde
- Fluorescence occurs in ns
- Phosphorescence occurs in µs
- Band-pass filter for detection

Laser-Induced Formaldehyde Fluorescence and Glyoxal Laser-Induced Phosphorescence





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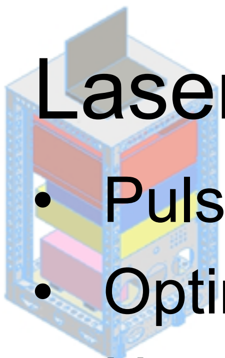
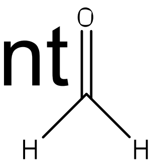
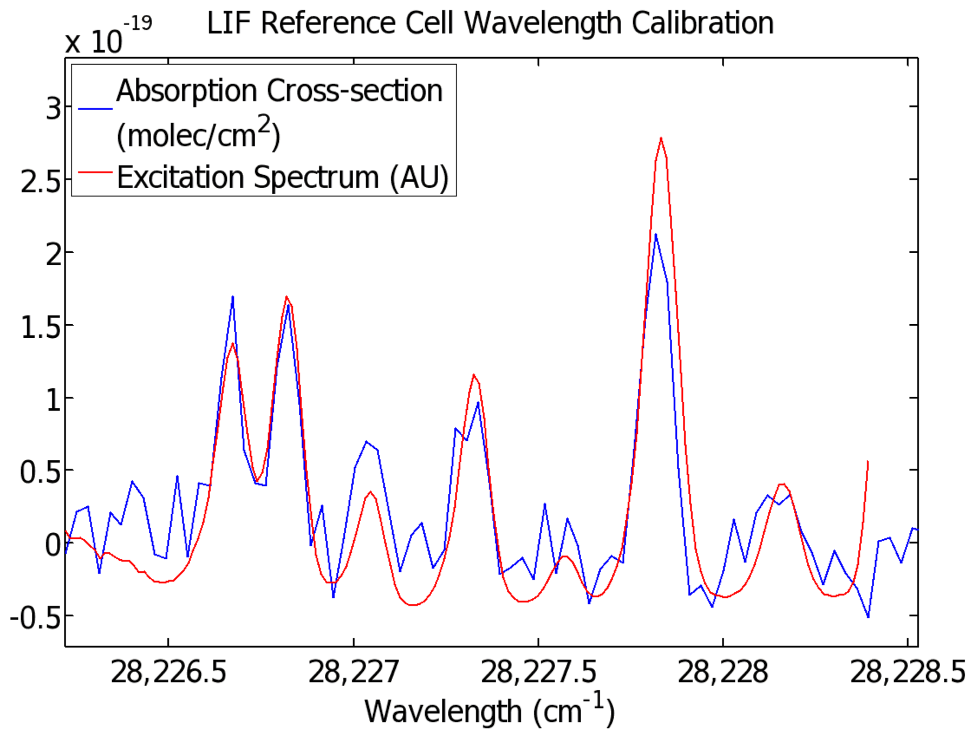


Laser Requirements for HCHO LIF Instrument



- Pulsed laser
- Optimal excitation region ~ 353 nm
- Narrow spectral linewidths (0.07 cm^{-1})
- Tunable at 10 Hz
- Low power consumption, small size, robust



Structured Spectrum

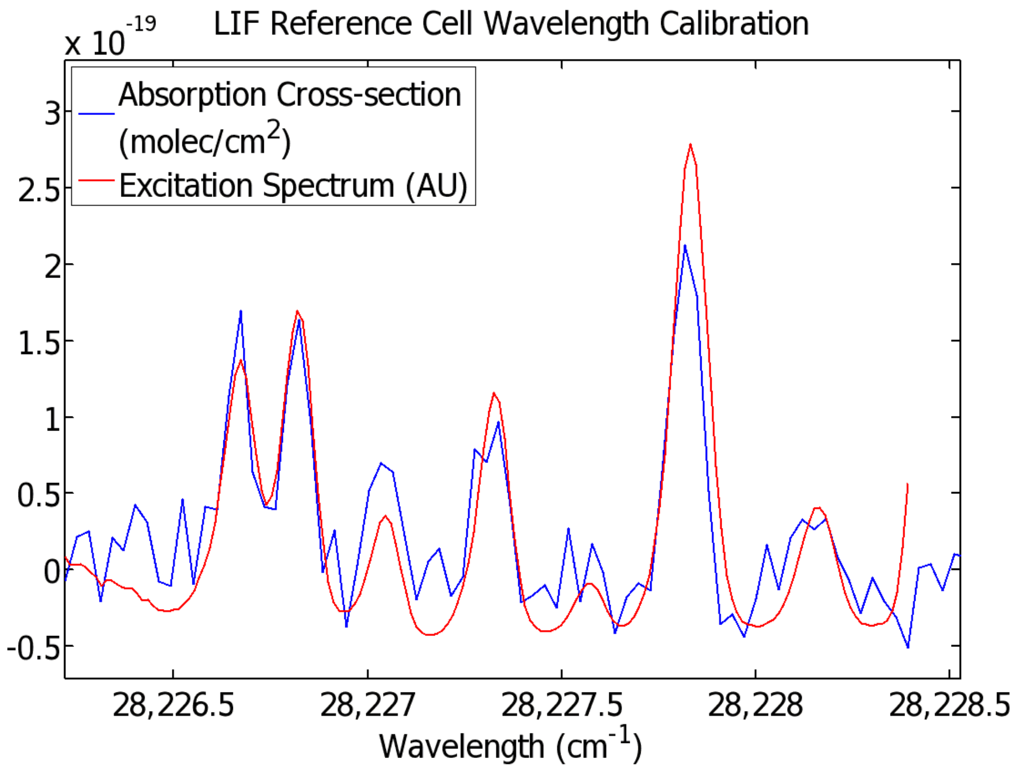
↓

Selectivity

* Co *et al.* J. Phys. Chem. A, **109**, 10675 (2005).

Key Technology: First Narrow Bandwidth UV Pulsed Fiber Laser

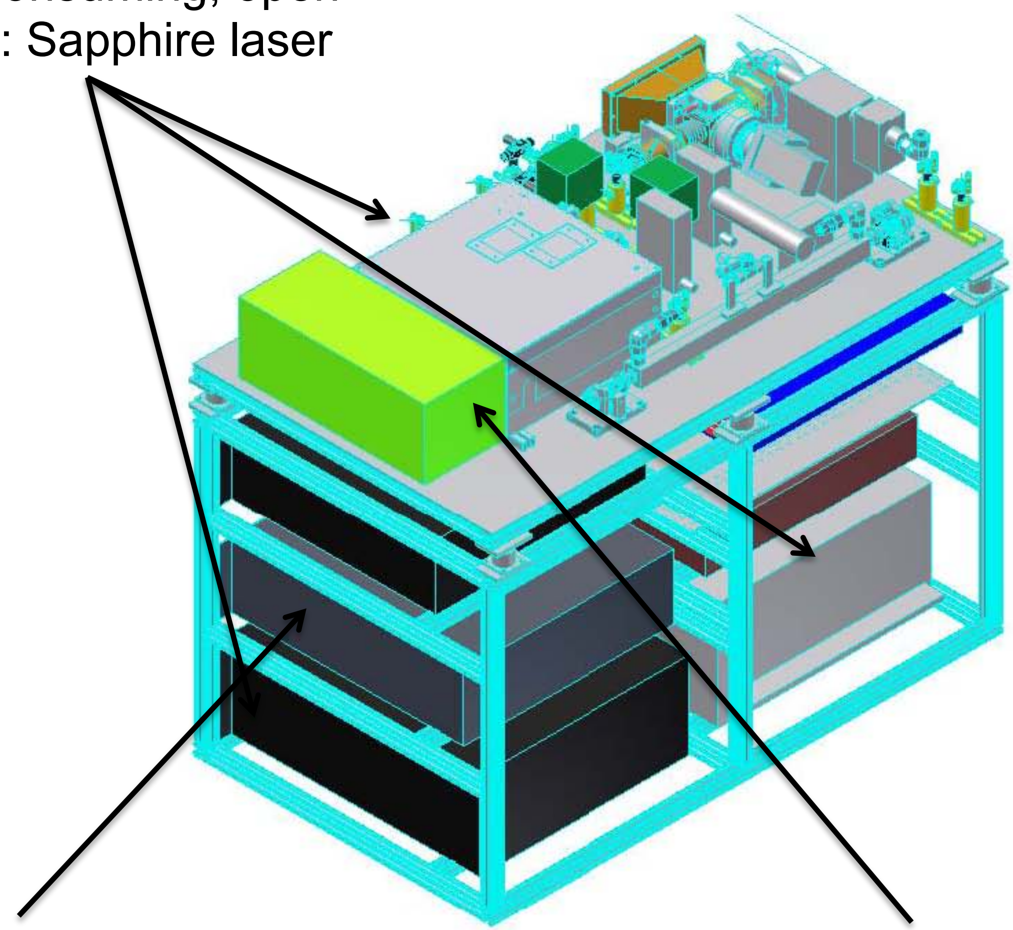
- Laser Power: <40 mW
- Size/Weight: <1 ft^3, <10 lbs
- Electrical Power: <100 W
- Laser Bandwidth: <0.01 cm^{-1}
- Rugged and turnkey operation
- No aligning or cleaning optics



Comparison With Other Methods

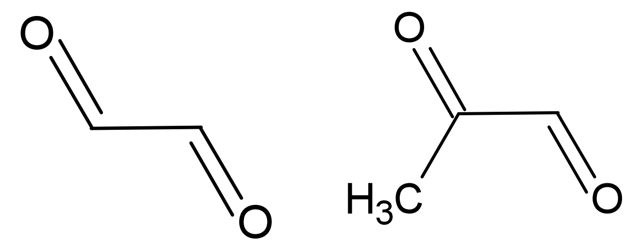
Technique	3σ Detection Limit (sampling time)	Reference
Quantum Cascade Laser Spectroscopy	~96 ppt_v (1 s)	(McManus et al., 2010)
Tunable Diode Laser Spectroscopy	~180 ppt_v (1 s)	(Weibring et al., 2007)
Proton Transfer Reaction Mass Spectrometry	300 ppt_v (2 s)	(Wisthaler et al., 2008)
Hantzsch Derivatization	50 ppt_v (1 min)	(Wisthaler et al., 2008)
Madison FILIF (field)	~300 ppt_v (1 s)	(DiGangi et al., 2011)
Madison FILIF (laboratory)	~25 ppt_v (1 s)	(DiGangi et al., 2011)
STAR formaldehyde sensor (field)	_< 30 ppt_v (1s)	not published

Development of a Glyoxal Monitoring Instrument

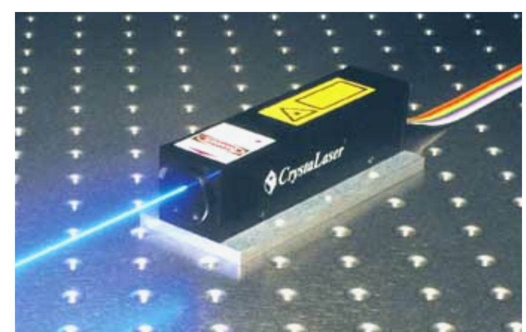


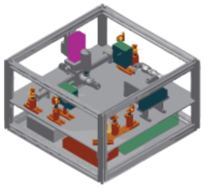
Upgrades:

- Compact computer
- Catalytic reference cell
- Q-switched compact laser
- Methylglyoxal

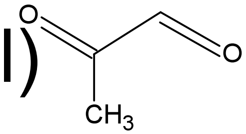


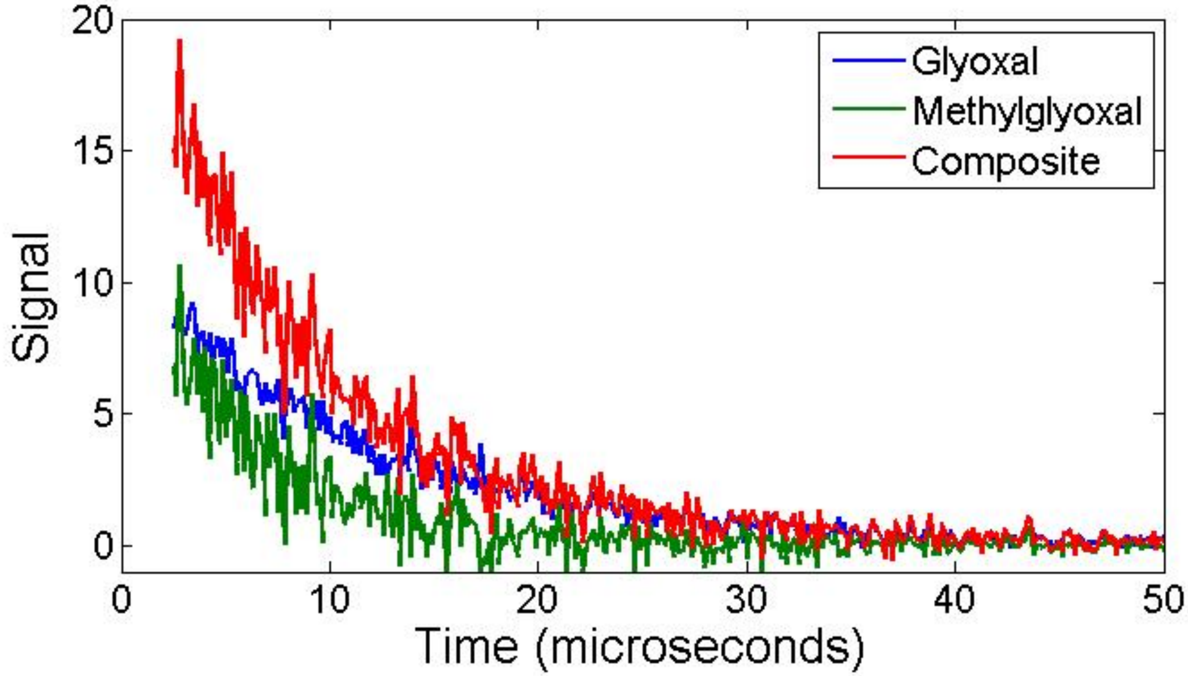
Glyoxal Methylglyoxal





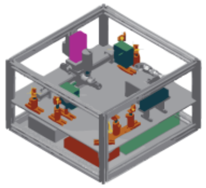
Laser-Induced Phosphorescence of (methyl) GLyOxal Spectrometer (LIPGLOS)



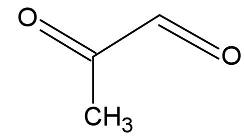


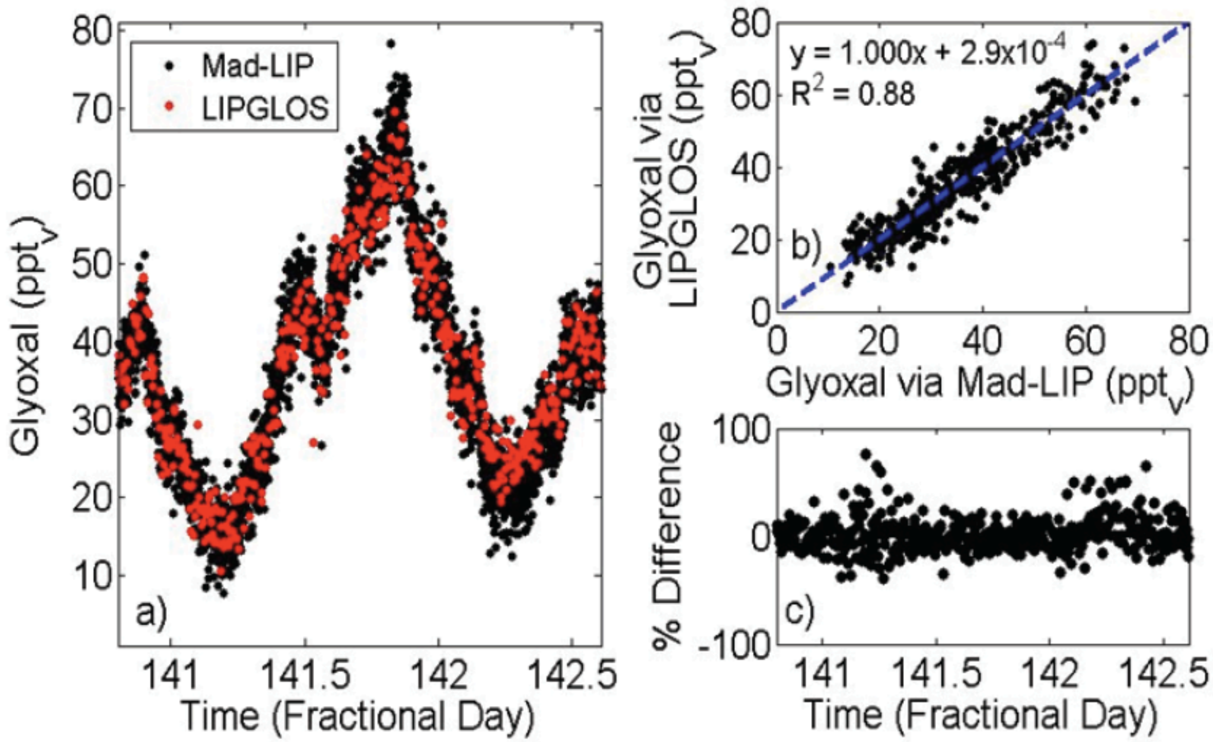
$$S(t) = A \cdot e^{-t/\tau_{gly}} + B \cdot e^{-t/\tau_{mgly}} + C$$

First instrument to use deconvolution of phosphorescence lifetime (of glyoxal and methylglyoxal) to determine concentrations



Quality Control: LIPGLOS vs. MAD-LIP Ambient Glyoxal





- MAD-LIP precision at 141.25 days: 2.9 ppt in 40 sec.
- LIP-GLOS precision at 141.25 days: 2.9 ppt in 80 sec.
- Methylglyoxal precision ~80 ppt$_v$ in 5 min.
- Simplicity allows long term measurements

Henry, Kammrath, FNK, *Atmos. Meas. Tech.* 5, 181-192 (2012).

Deployment at Horicon, WI

- Year-long monitoring of glyoxal and formaldehyde starting mid-April
- Horicon site is well instrumented
- Will provide much more extensive dataset for analysis of R_{GF} as a metric for anthropogenic influence
- Comparison with models

Monitor	Monitor Equipment	Designation	Analysis Method	Sampling Frequency
Ozone	API Ozone	SLAMS /NCore	UV Photometry	Continuous
PM2.5	R&P FRM 2025	SLAMS /NCore	Gravimetric	1/6
PM2.5 FEM	Met-One BAM-dual	Urban Transport/ /Ncore	Beta Attenuation	Continuous
Fine Particle Species	Met-One Speciation	Regional	Gravimetric	1/3
Meteorology	Met One Meteorological	Other	Mechanical	Continuous
Sulfur dioxide	SO2, High Sensitivity	NCore level 2 site	UV fluorescence	Continuous
NOy	NOY High Sensitivity	NCore level 2 site	UV fluorescence	Continuous
Carbon Monoxide	CO High Sensitivity	NCore level 2 site	UV fluorescence	Continuous
Volatile organics and carbonyls	Canister and Cartridge	NATTS	GC-MS	1/6

Table 3: Selected monitored species, instrumentation, methods and sampling frequency

Deployment at Horicon, WI

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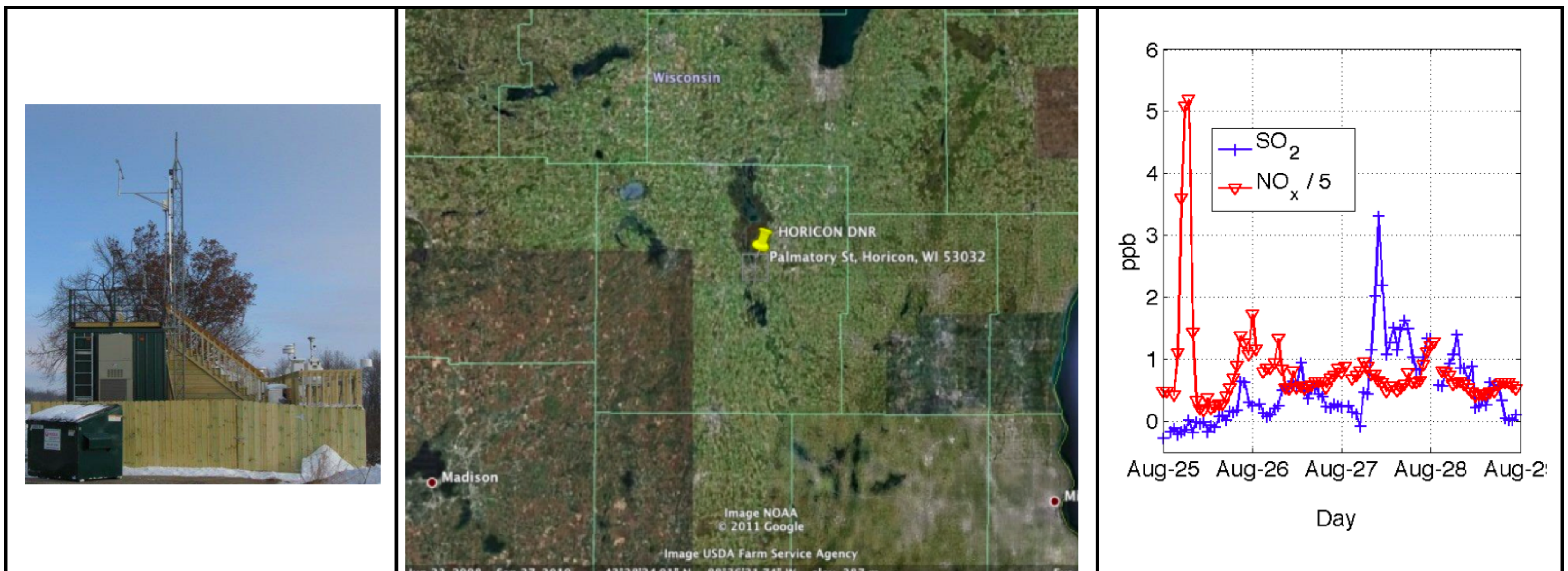
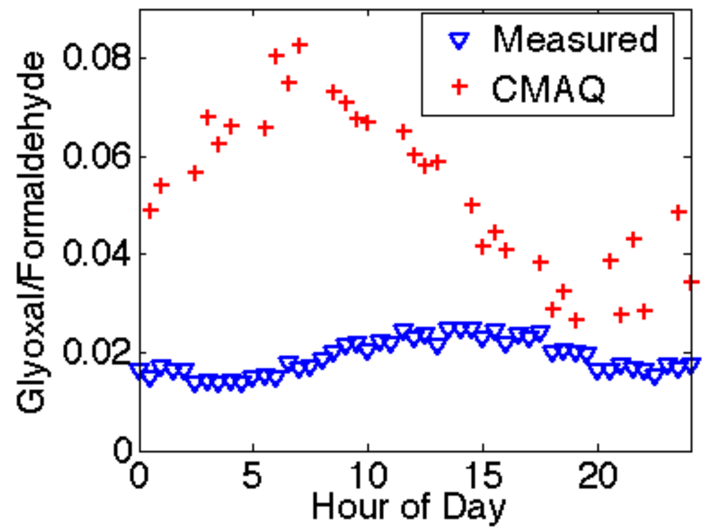


Figure 7 shows the location of the HORICON site and the structures housing instrumentation, and a data from August 2010 that shows different pollution events indicated by high SO_2 and NO_x concentrations.

Overall Goals: Proven Instruments and Comparison with Models of Anthropogenic/Biogenic Interactions

Goal 1: Robust, fast, high precision/accuracy monitors of formaldehyde and glyoxal as metrics of anthropogenic biogenic interactions and processes of secondary pollutant formation.

Goal 2: Comparison with models of secondary pollutant formation, especially representation of processes of anthropogenic/ biogenic interactions.



Acknowledgments:

Annmarie Carlton (CMAQ modeling)

David Grande DNR, Wisconsin (Horicon site)

BEACHON-ROCS Science Team

EPA for funding

Courtesy Annmarie Carlton, Rutgers