VARIABLE EMISSIONS FROM POINT SOURCES AND THEIR IMPACTS ON OZONE FORMATION

A CASE STUDY OF THE HOUSTON AREA

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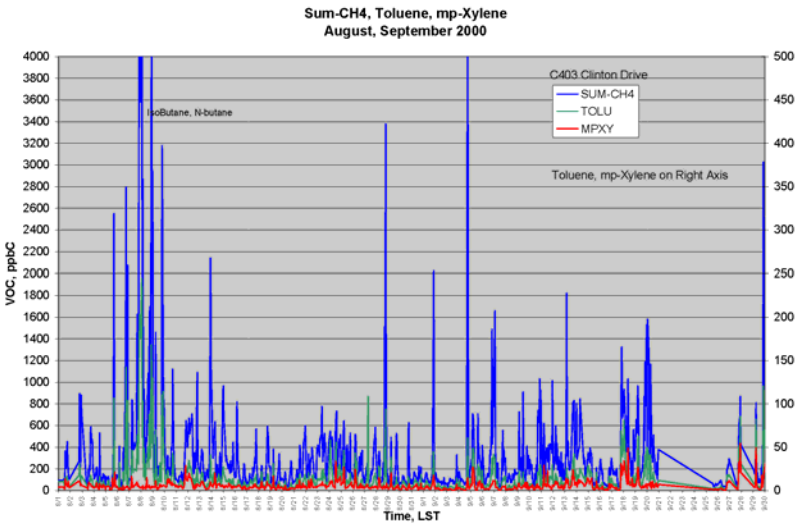
Variable Point Source VOC Emissions

- Observational evidence indicating variability in point source VOC emissions
- Process data indicating variability in point source VOC emissions
- Modeling variability in point source VOC emissions
- Implications for ozone formation and air quality modeling

What observations do we have, indicating that point source VOC emissions are highly variable?

(Episodic high VOC concentrations)



	Sum-CH4 ppbC	Alkanes ppbC	Alkenes ppbC	Aromatics ppbC	Ethene ppbC	Propene ppbC
All Sites						
max	16703.4	16443.6	2357.7	1157.3	536.0	2195.9
99.5th percentile	3242.9	2944.4	420.2	201.4	149.4	264.6
99th percentile	1845.0	1547.3	316.9	168.8	109.0	168.2
95th percentile	763.9	529.8	126.2	96.2	41.9	46.9
90th percentile	523.6	362.4	78.7	68.4	25.6	25.6
50th percentile	131.2	88.0	16.2	17.8	4.8	3.5
average	256.4	187.8	36.0	29.6	11.5	13.3
stddev	571.4	532.5	73.8	36.4	23.2	53.2

- Ground based monitors show significant variability in hydrocarbon concentrations, much larger variations than can be explained by meteorology

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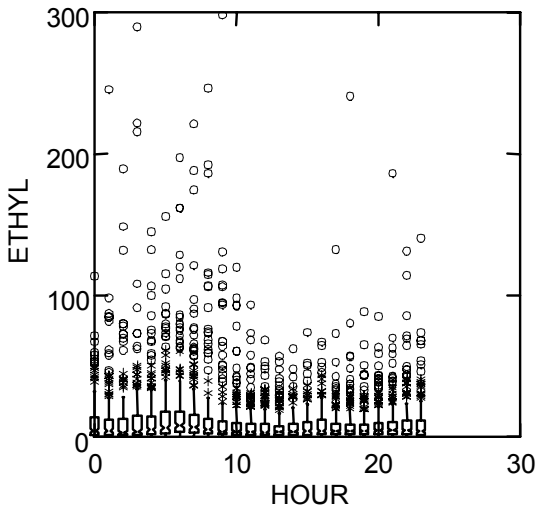
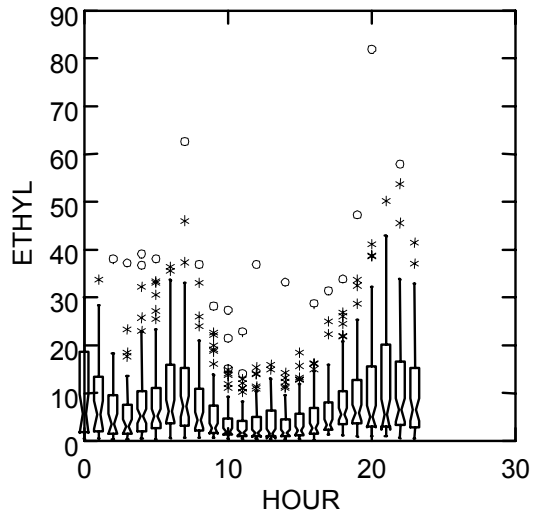
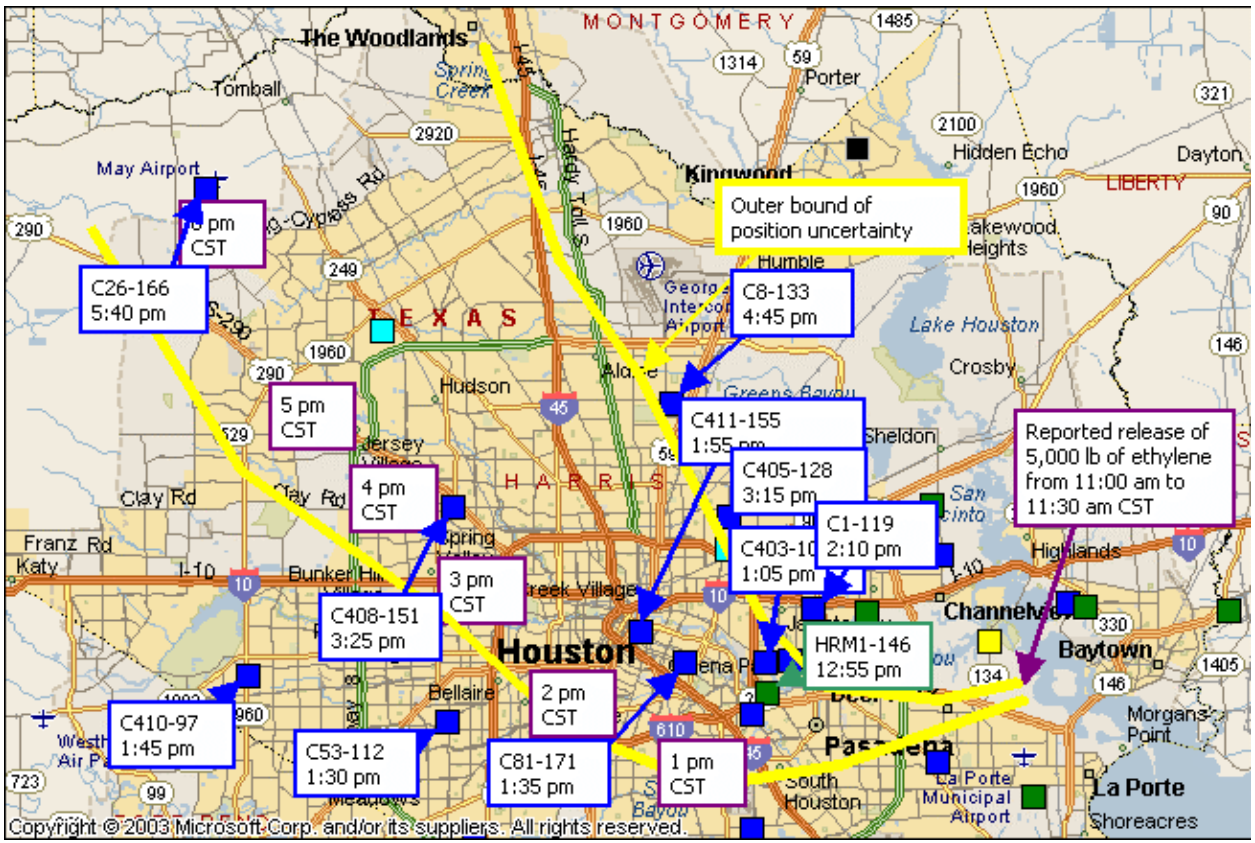




- Variability in hydrocarbon concentrations is much greater in industrial source regions than in residential regions
- Concentrations of highly reactive VOCs in industrial source regions frequently (once per week per compound per site) exceed 100 ppbC

What observations do we have, indicating that point source VOC emissions are highly variable?

(Episodic high ozone concentrations)



What observations do we have, indicating that point source VOC emissions are highly variable?

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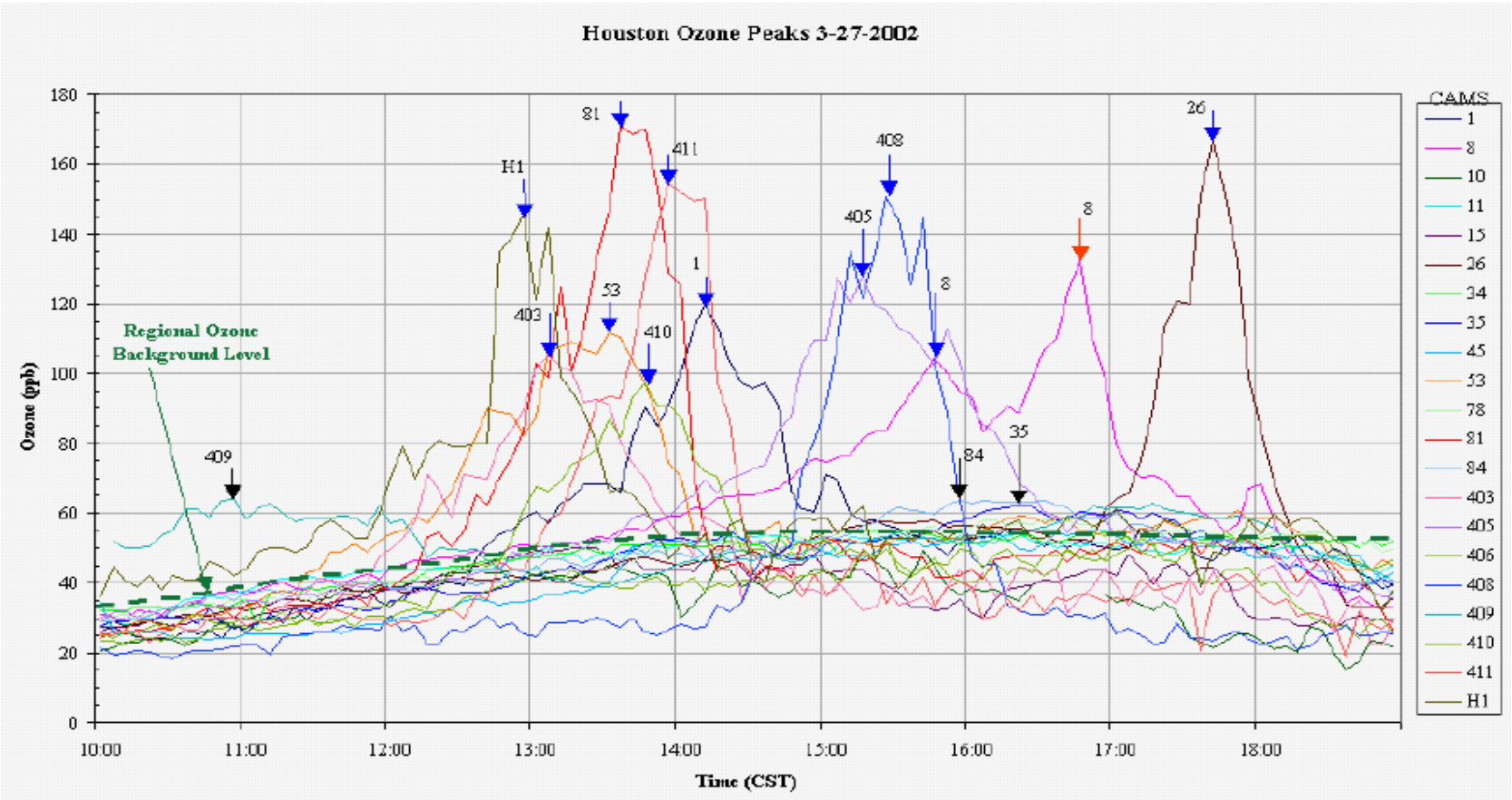

Conceptual Model for Point Source VOC Emissions

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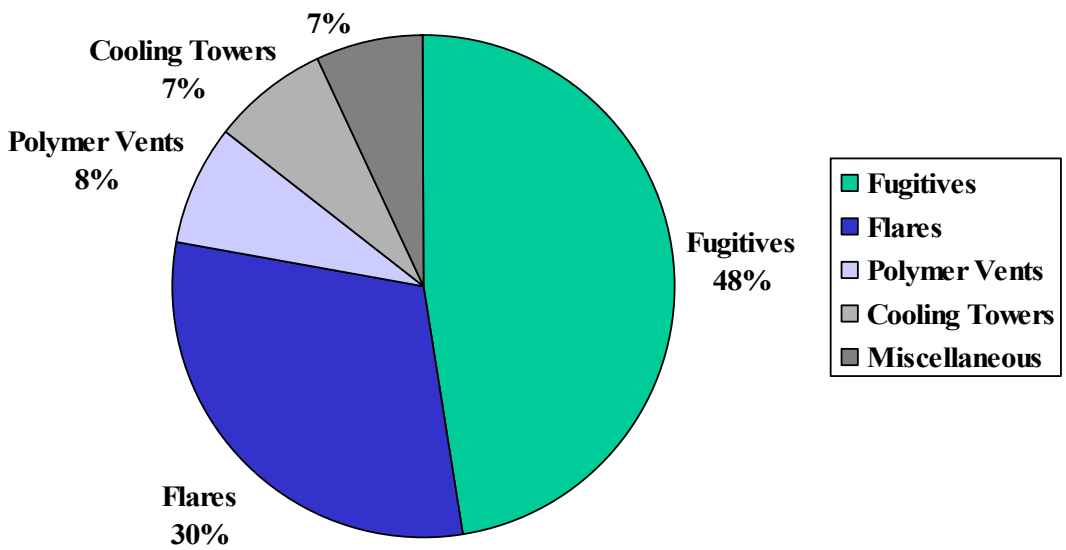
Sources of variable industrial emissions: what we know

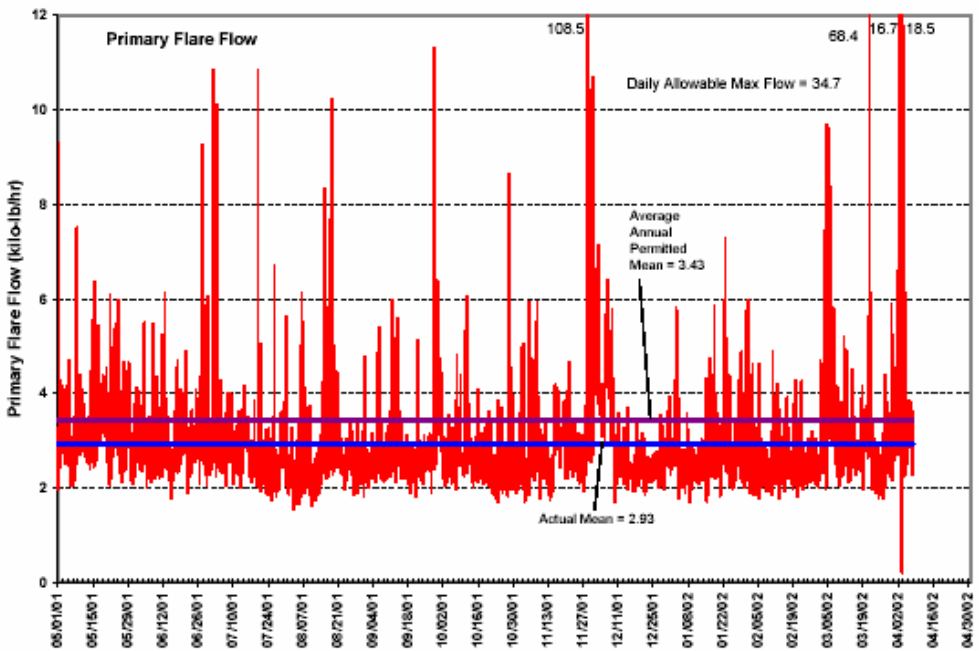
- Sources are ubiquitous (all volatile compounds, all locations, all times of day)
- Sources are intermittent
- Ozone concentrations “only” reach 250 ppb
- Concentrate on HRVOCs – these represent a set of compounds that must be addressed, and a relatively small number of major sources are involved

Sources of HRVOCs in annual inventory



- Major sources include olefin manufacturing, olefin polymerization and refining

Emissions are variable



- Nearly Constant emissions
- Routinely Variable emissions
- Authorized Highly Variable emissions
- Unauthorized Variable emissions*

* Emissions events and scheduled maintenance, startup, and shutdown activities

Finding:

The overall magnitude and the variability in emissions of highly reactive volatile organic compounds (HRVOCs) from point sources are dominated by contributions from flares, cooling towers, various vents and sources of fugitive emissions.

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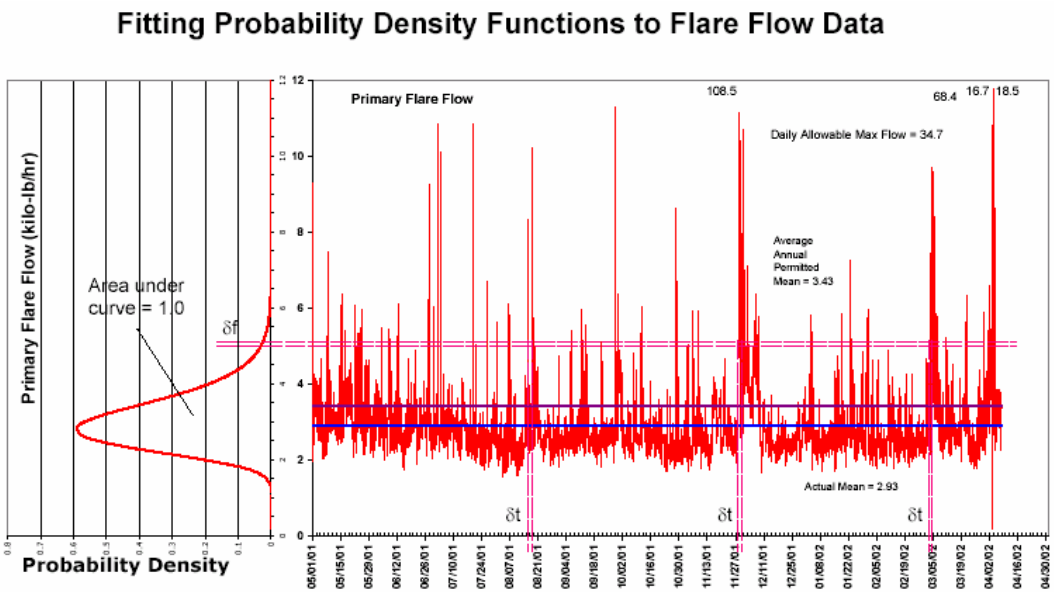
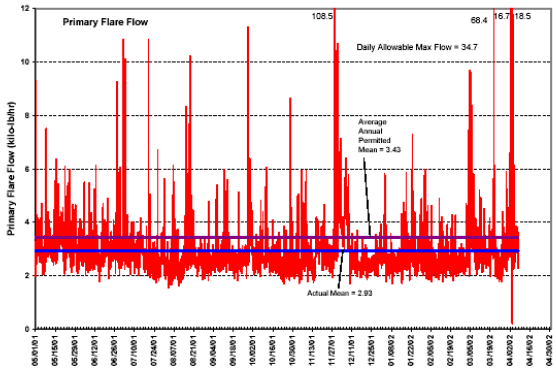
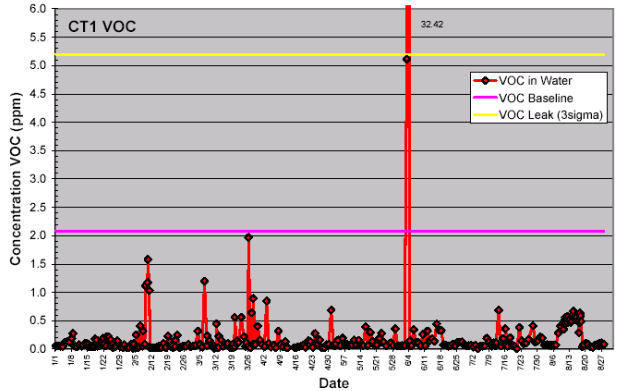
Modeling variability in point source VOC emissions

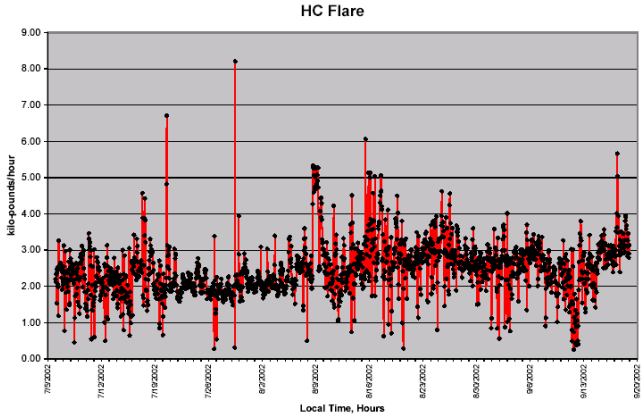


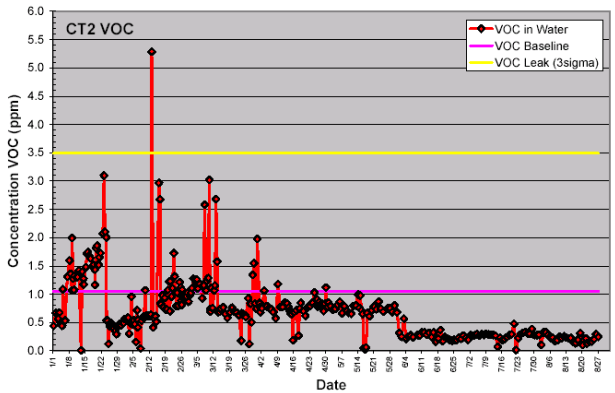
- Use a probability distribution function (PDF) to record a series of snapshots of emissions

Different process units have different variability









Finding:

The magnitude and variability in HRVOC emissions from point sources can be effectively characterized using probability distribution functions.

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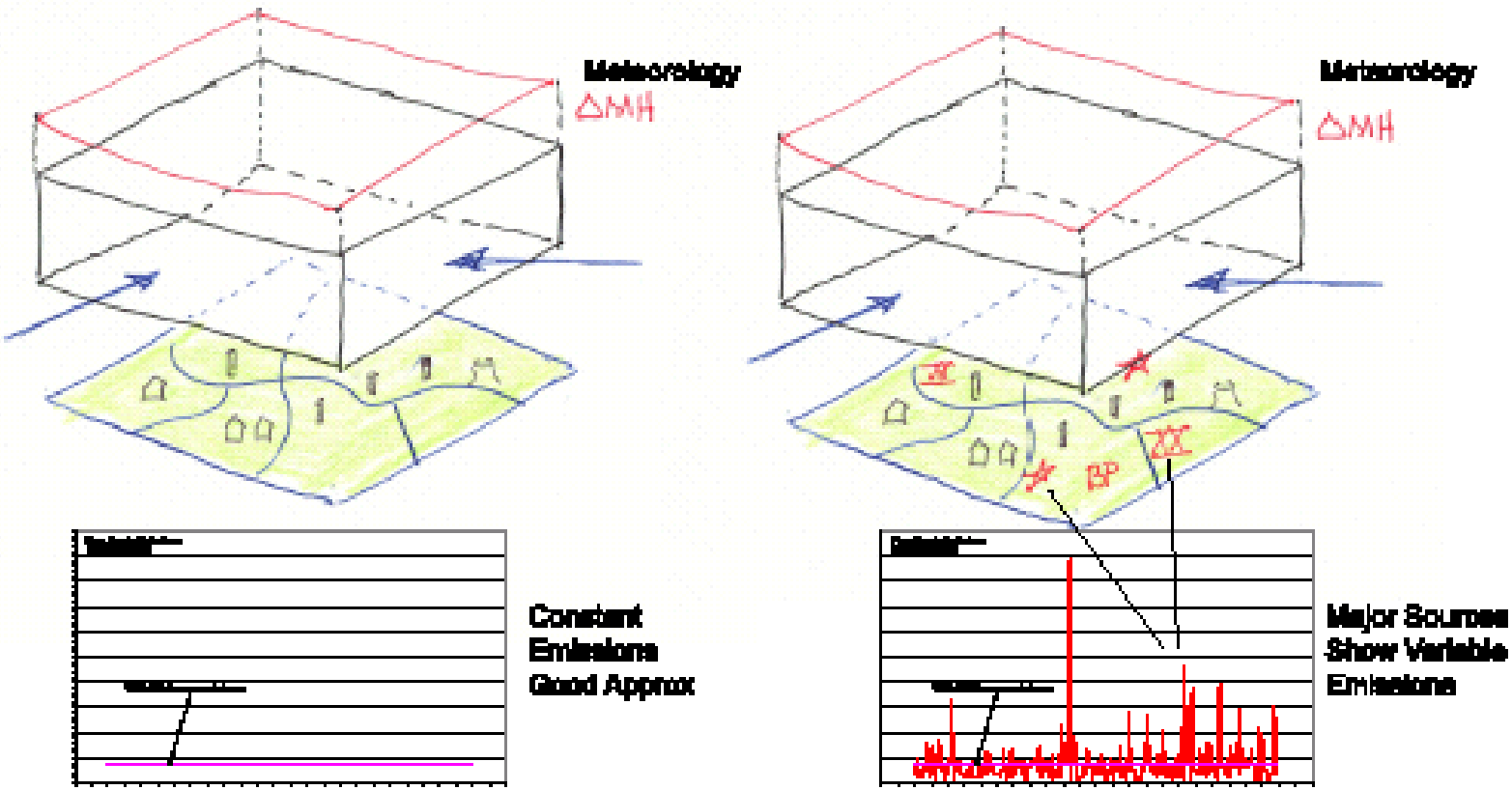
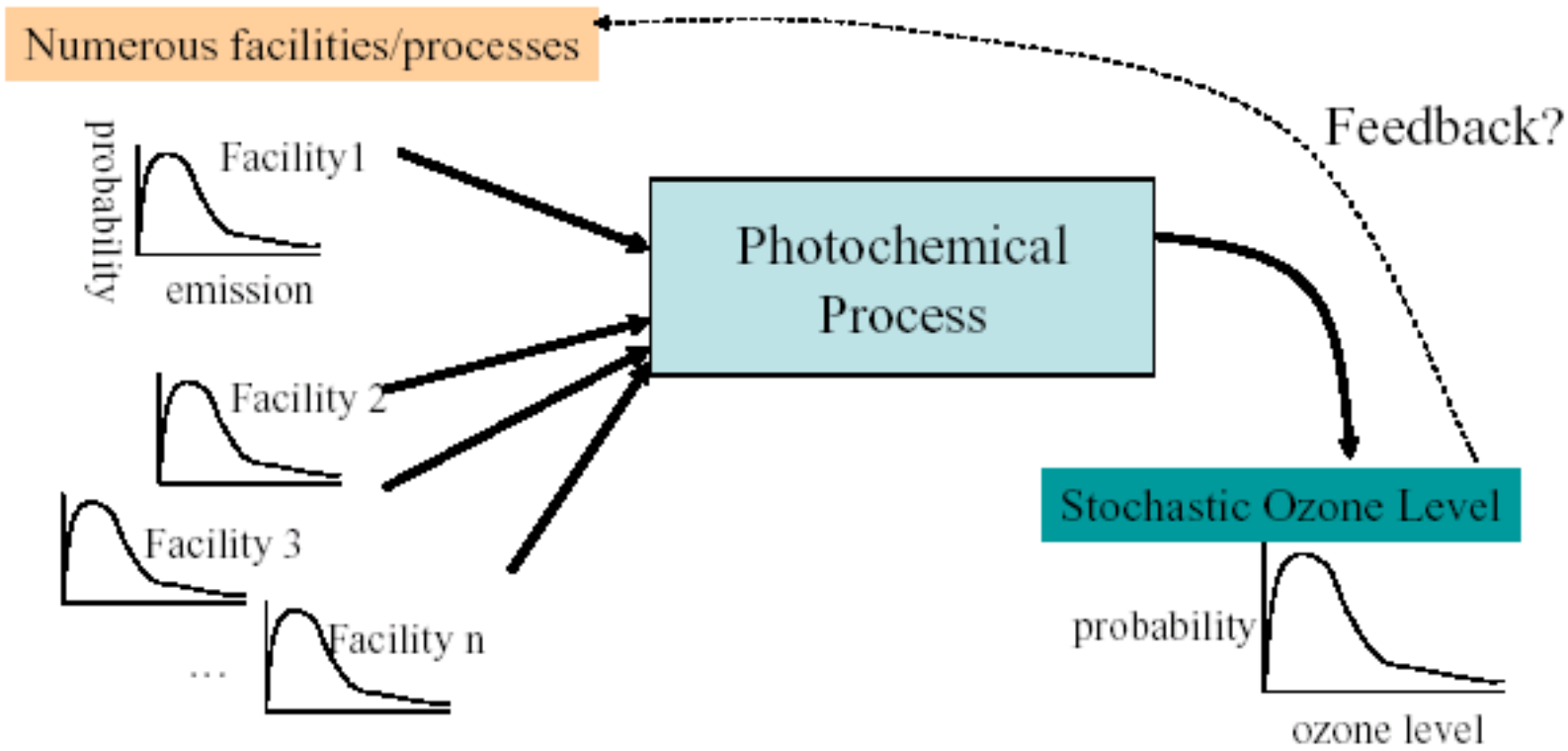
Conceptual issue



Air quality models for SIP development

- Historical episodes are emission snapshots
- Need to separate emissions that change from episode to episode from those that remain nearly constant
- In evaluating SIP effectiveness, need to consider an album of many emission snapshots

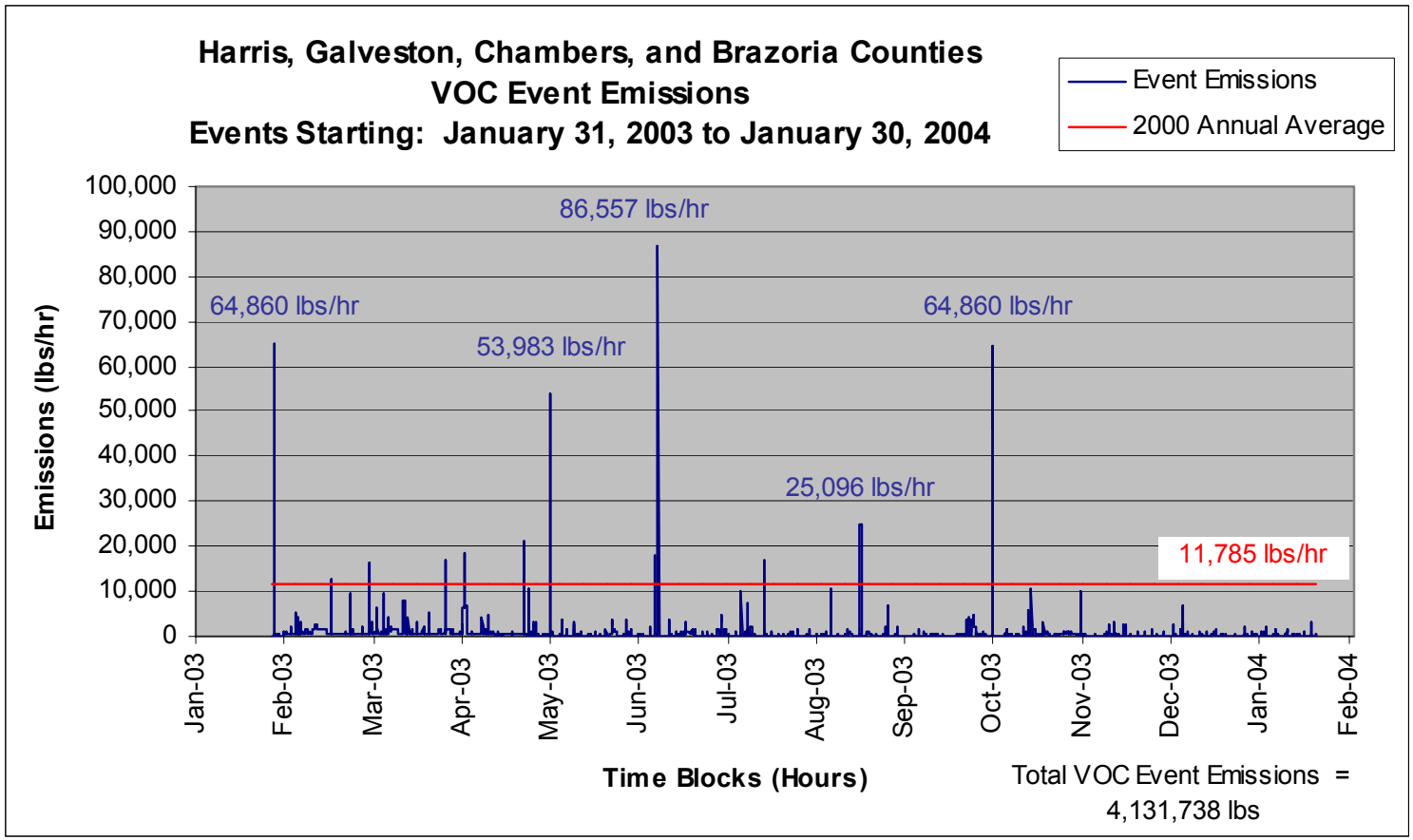
An album of emission snapshots



What photochemical modeling tools do we use?

- Currently impossible (due to resource and computational constraints) to consider enough emission snapshots with the full regional photochemical model
- Episodic emissions are most important in industrial source region
- Consider many emission snapshots using a version of the full regional model that focuses on a smaller spatial area (industrial source regions)
- Examine most important snapshots with the full model

An emission snapshot for a sub-region



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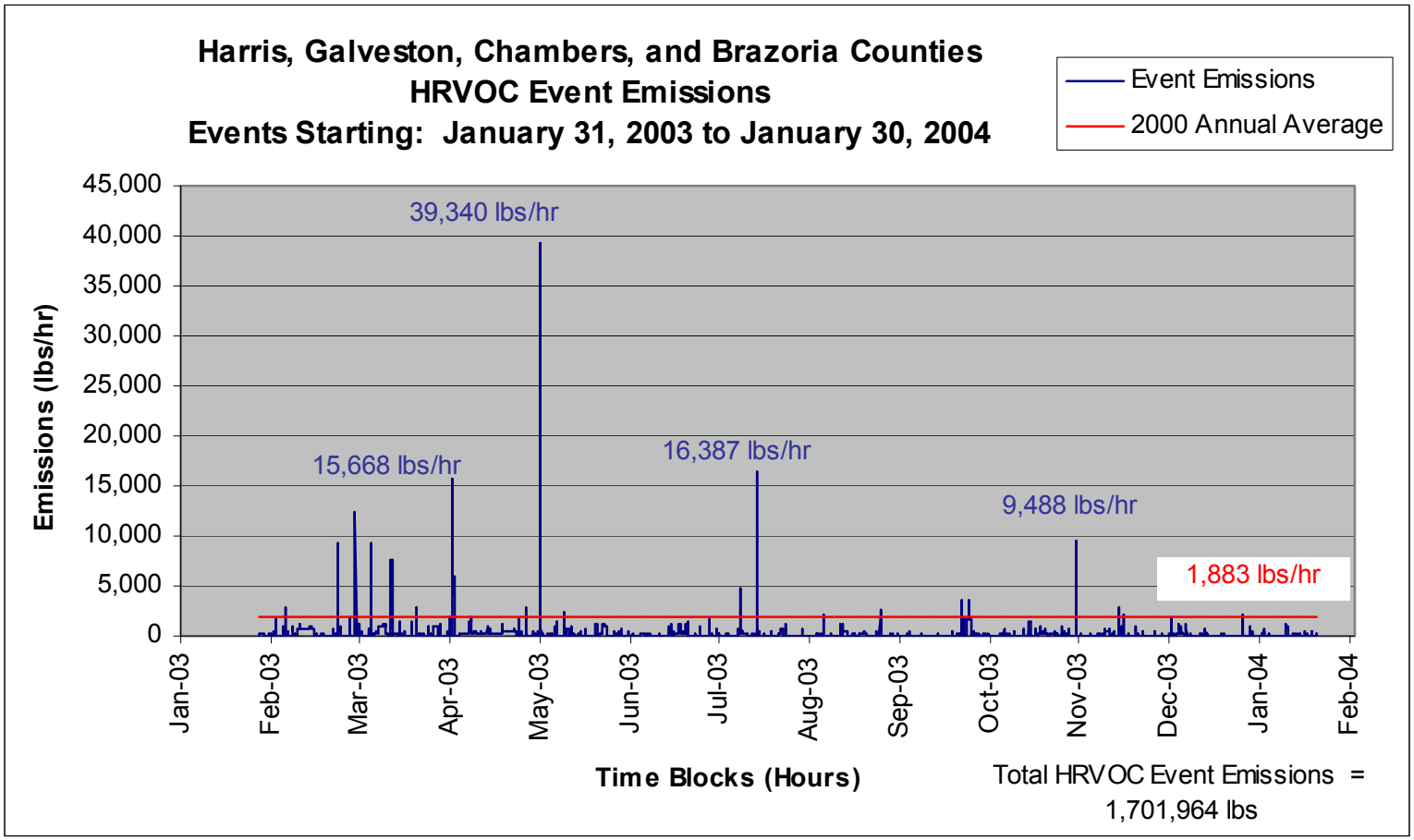

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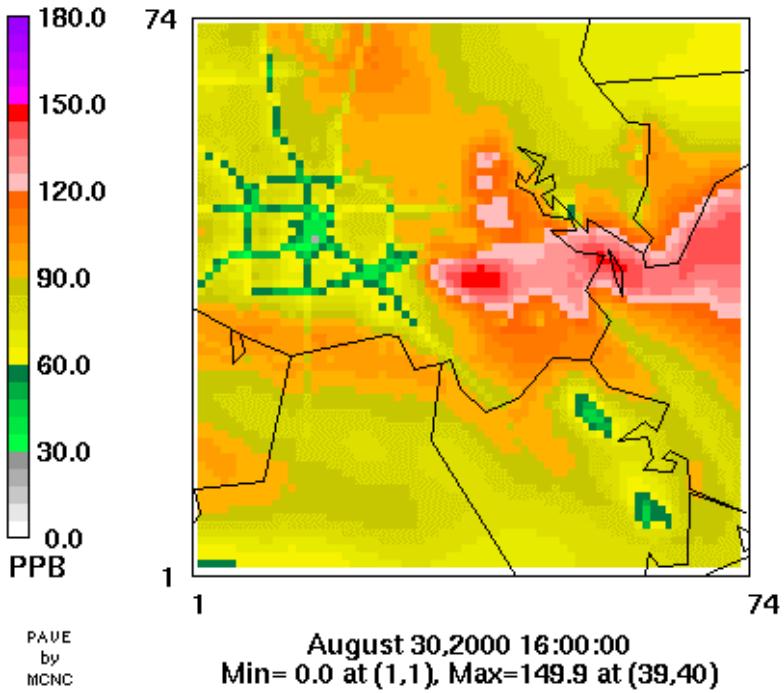

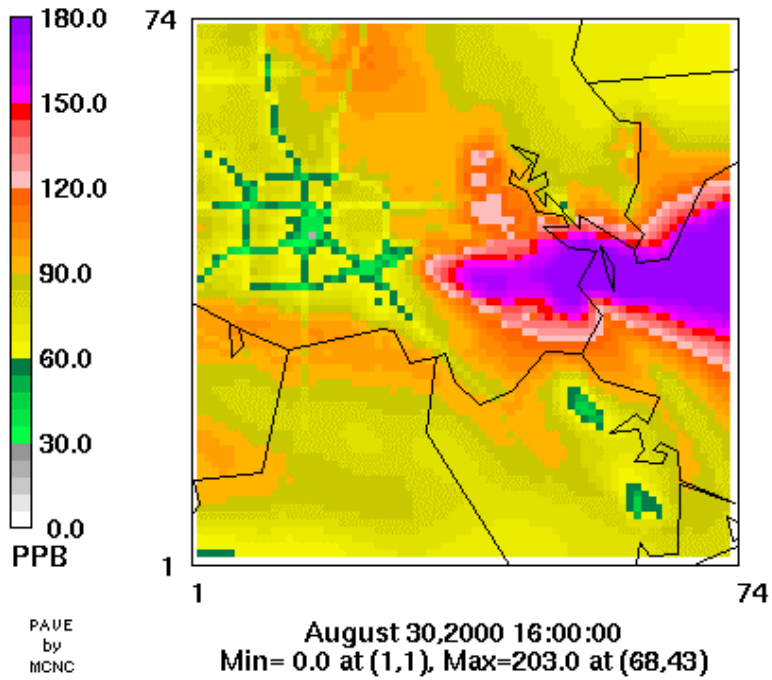

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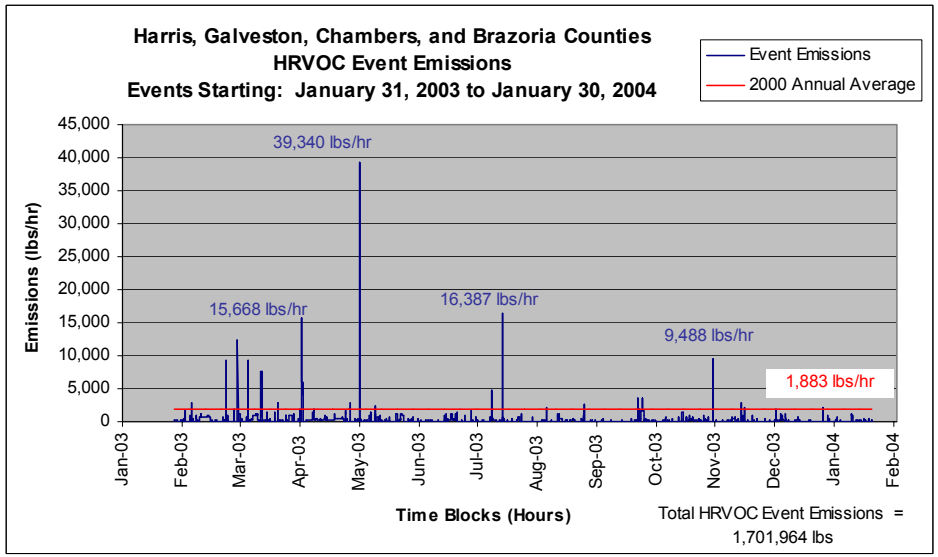

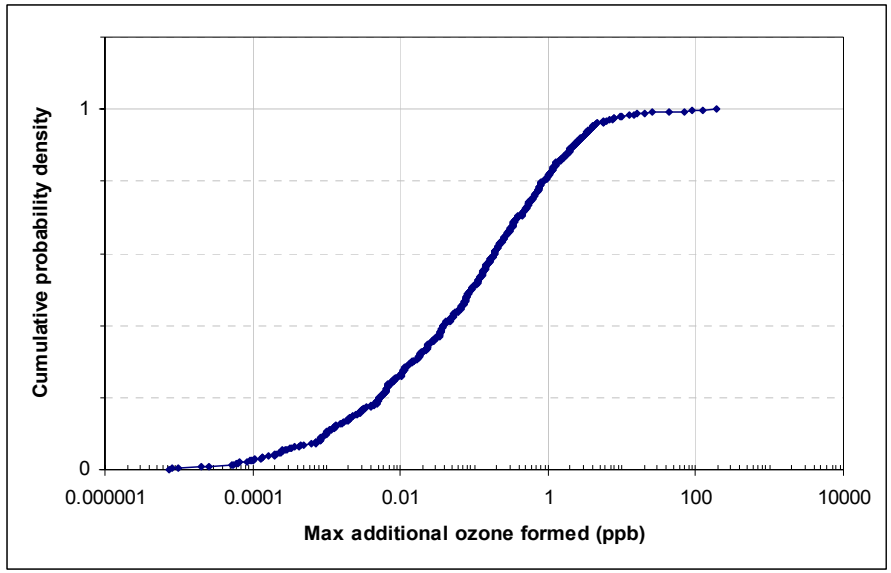

Finding:

Only about 1% of emission events lead to >10 ppb increases in ozone concentrations. Variability in impact is due to time of day, magnitude and duration of releases; meteorology is also significant

Routine process variability leads to smaller changes in predicted absolute ozone concentrations, but the effect of variability on the response to control strategies is larger than the response of absolute ozone concentrations

Summary

- Point source VOC emissions are variable
- Variability is due to a ubiquitous group of source types – probably flares, fugitives, process vents and cooling towers
- Variability (not nearly constant emissions) leads to observations of HRVOC concentrations in excess of 100 ppbC on a weekly basis
- HRVOC concentrations in excess of 100 ppbC can, under commonly observed conditions, lead to extensive ozone formation
- Need to model an album of emission snapshots to adequately describe ozone formation

Citations

- Murphy, C. F. and D. T. Allen "Hydrocarbon Emissions from Industrial Release Events in the Houston-Galveston Area and their Impact on Ozone Formation," *Atmospheric Environment*, 39, 3785 – 3798 (2005).
- Nam, J., Y. Kimura, W. Vizuete, C. Murphy, and D. T. Allen, "Modeling the Impacts of Emission Events on Ozone Formation in Houston, Texas," *Atmospheric Environment,* in press.

Emission variability not confined to VOCs or petrochemical facilities