

Formaldehyde and VOC Tracer Relationships by PTR-MS

**Tom Jobson
Washington State University**

Motivation

- SRP has identified production of new radicals from formaldehyde (HCHO) as a fundamental research issue (section 4.3)
- SRP notes in the conclusion that there is a pressing need to incorporate “ ... enhanced sources of new radicals into air quality models...”

Impact of HCHO on HO_x radical budget:



radical production rate key to modeling ozone production rates

- Key issue: What are the sources of formaldehyde (HCHO)?
Can these be controlled?

HCHO Sources

Formaldehyde Sources

(1) **Primary** – direct emissions

Industrial Emissions

Vehicle Exhaust (gasoline, diesel)

(2) **Secondary** - produced in the oxidation of many organics

ethene, propene : **Industrial Emissions**

isoprene : **Natural VOC emissions**

alkenes, alkanes, aromatics : **Vehicle Emissions**

- Source attribution must be variable due to variability in both source types.
- **Identify and measure tracers to attribute HCHO to various sources:**
 - Primary and secondary**
 - Natural and anthropogenic**
 - Vehicle emissions and HSC emissions**

Friedfeld et al., (2002) related HCHO in Houston (Deer Park site) to CO (primary) and O₃ (secondary) concentrations in a source attribution study : 66% = secondary

Project Objective

Measure HCHO and a suite of VOCs and CO to determine relative importance of *primary* and *secondary* sources of HCHO.

- Use correlations between HCHO and other species to reveal origins.
- Apply statistical methods such as principal component analysis to quantify what drives HCHO variability (meteorology, chemical tracers).

Karl et al., JGR, 2003 : TexAQS 2000 at La Porte

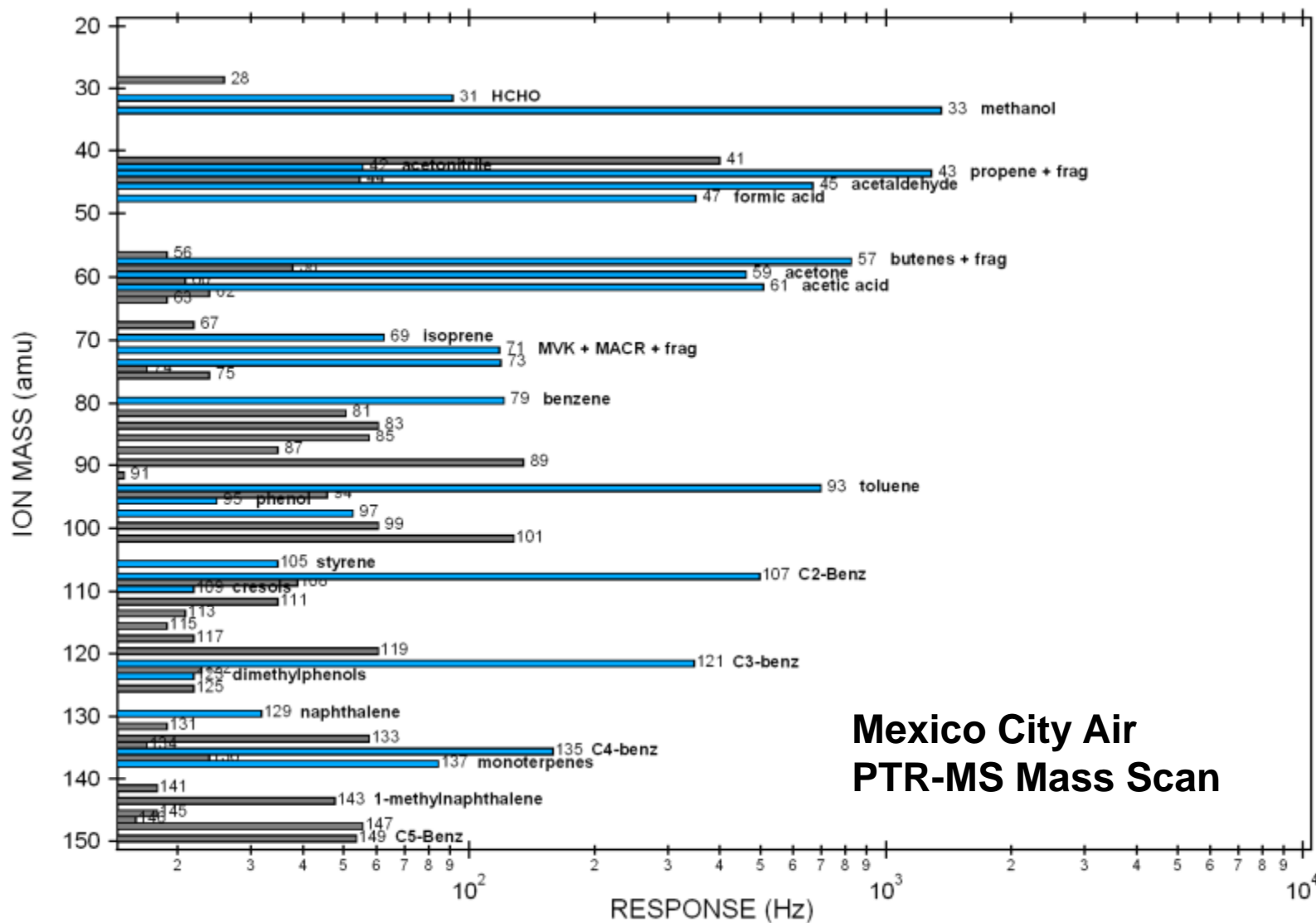
- Field measurements at Moody Tower(?) for 1 month as part of **FLAIR** (Formaldehyde and Olefins from Large Industrial Sources)

Outcome

- Determine relative roles of primary and secondary sources of HCHO.
- Identify impact of HSC emissions (primary and secondary HCHO) on HCHO budget.

Measurement Approach

Use PTR-MS instrument: $\text{H}_3\text{O}^+ + \text{R} \rightarrow \text{RH}^+ + \text{H}_2\text{O}$ (in-situ measurement)



Measure species in blue (~ 25 masses)

Measure HCHO correlation with other organics.

Proposed Tracer Mass List

Mass	Species	Sources
Oxygenated species		
31	formaldehyde	photoproduct & direct emissions
33	methanol	solvents
45	acetaldehyde	photoproduct
47	formic acid	O ₃ + alkene reaction product
59	acetone + propanal	solvents + photoproducts
61	acetic acid	photoproduct from CH ₃ C(O)OO + HO ₂
71	MVK + MACR	isoprene photoproducts
77	PAN: CH ₃ C(O)OONO ₂	photoproduct from CH ₃ C(O)OO + NO ₂
Aromatic compounds		
79	benzene	vehicle emissions / industrial
93	toluene	vehicle emissions / industrial
105	styrene	industrial
107	C₂ benzenes (C₈H₁₀)	vehicle emissions
121	C₃ benzenes (C₉H₁₂)	vehicle emissions
135	C₄ benzenes (C₁₀H₁₄)	vehicle emissions
129	naphthalene	vehicle emissions
95	phenol	vehicle emissions
109	cresols	toluene photoproducts
Natural VOC emissions		
69	isoprene	tree emissions
137	monoterpenes	tree emissions
Industrial tracers		
49	methyl mercapton	pulp and paper industry
54	acrylonitrile	air toxic
43	propene*	refineries
57	butenes*	refineries
Biomass burning tracers		
42	acetonitrile	plant material combustion

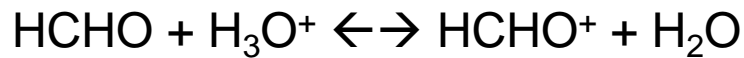
PTR-MS can measure a range of primary and secondary VOC tracers with good time resolution (~ 1 minute for entire mass list) = GOOD STATISTICS

Need good measurements of secondary tracers (oxygenated species).

bold = calibrated using compressed gas standard (naphthalene, phenol use relative response factors)

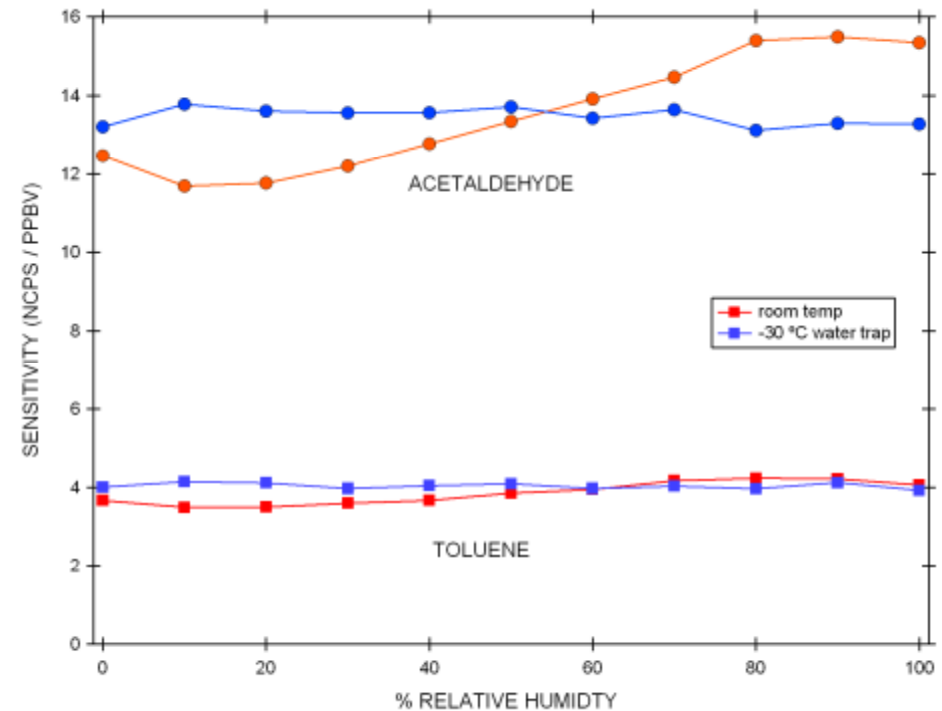
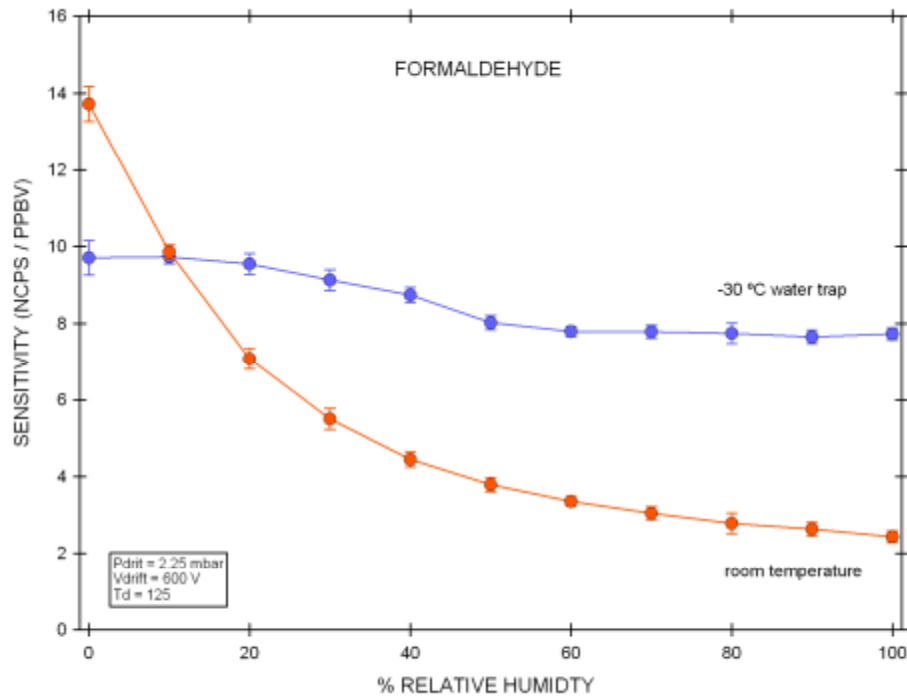
HCHO Measurement

Issue: water vapor dependent response
 - reduces sensitivity, variable calibration factor

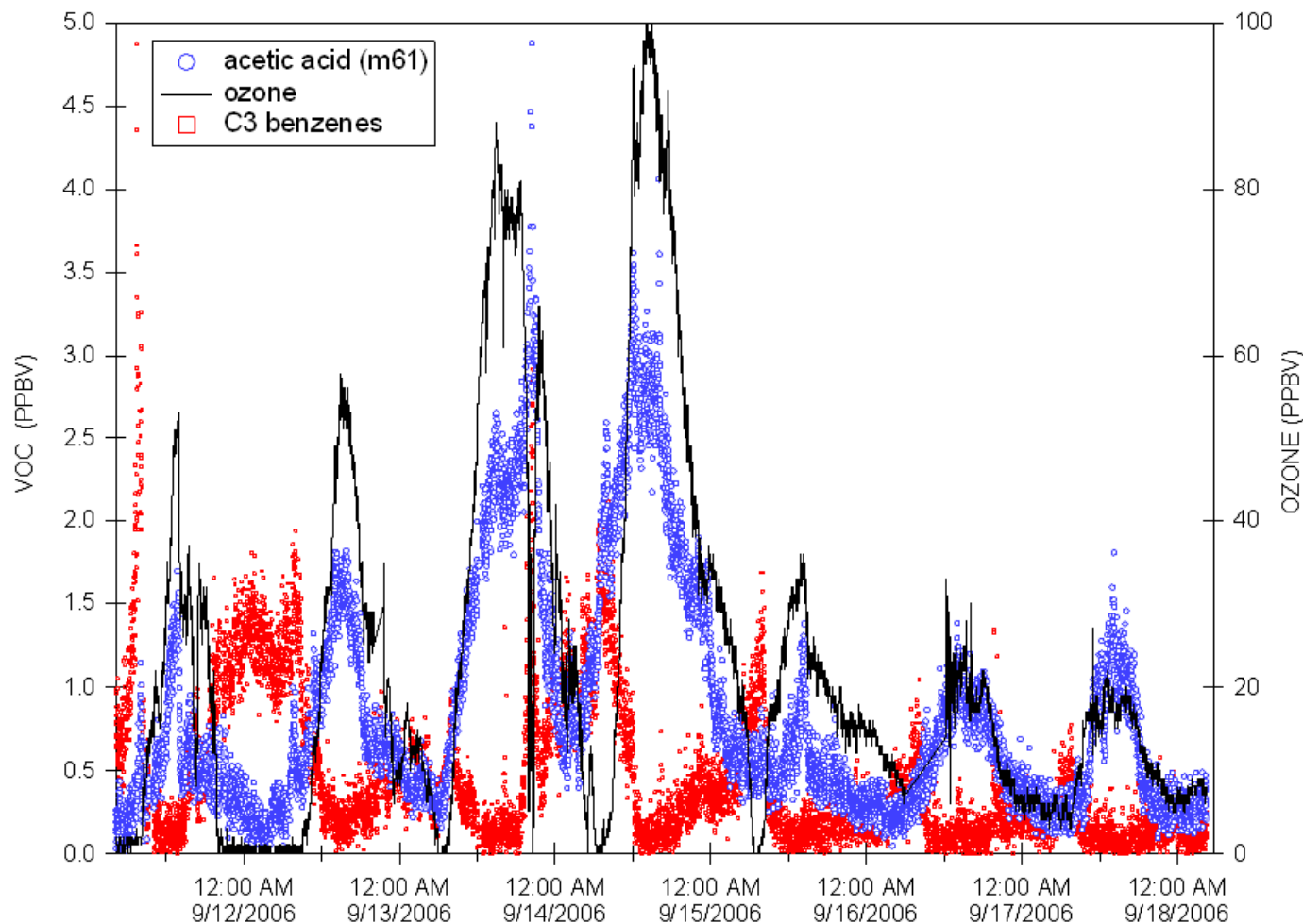


When humidity increases back reaction increases reducing HCHO⁺ count rates (Ionmata, ACP, 2008)

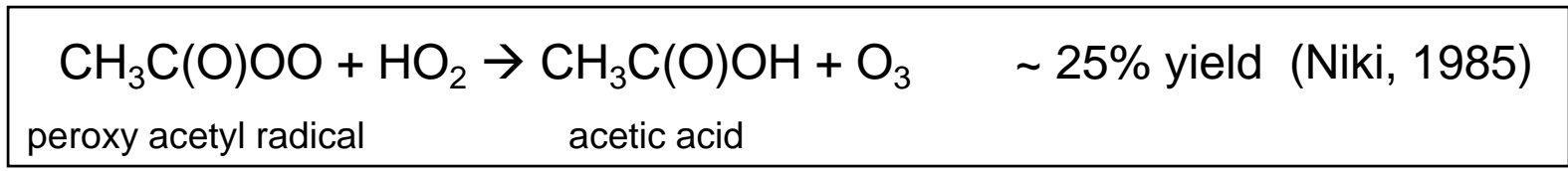
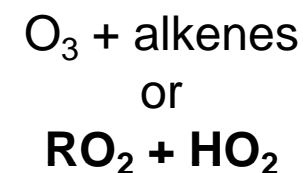
Another solution: Reduce humidity of sampled air, calibrate for HCHO using standards



Example Secondary Tracer: Acetic Acid at Bayland Park



Acetic acid behaves like ozone. Secondary product from:



Summary

- There is a need for an improved understanding of primary and secondary sources of HCHO and the impacts of HSC emissions on the HCHO budget.
- PTR-MS uniquely suited to measure HCHO and a range of VOC tracers to examine correlation between HCHO and VOC source tracers.
- We propose to use tracer relationships to identify primary and secondary origins of HCHO in a 1 month field study.