

**MDGC-MS-Olfactometry Based Odorant  
Prioritization: An Effective Bridge Between  
Sensory and Instrument Monitoring  
Protocols**

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# ODOR INVESTIGATIVE APPROACHES

## SENSORY ONLY

(Human 'Sensor', ASTM 679, Dynamic Dilution Olfactometry)

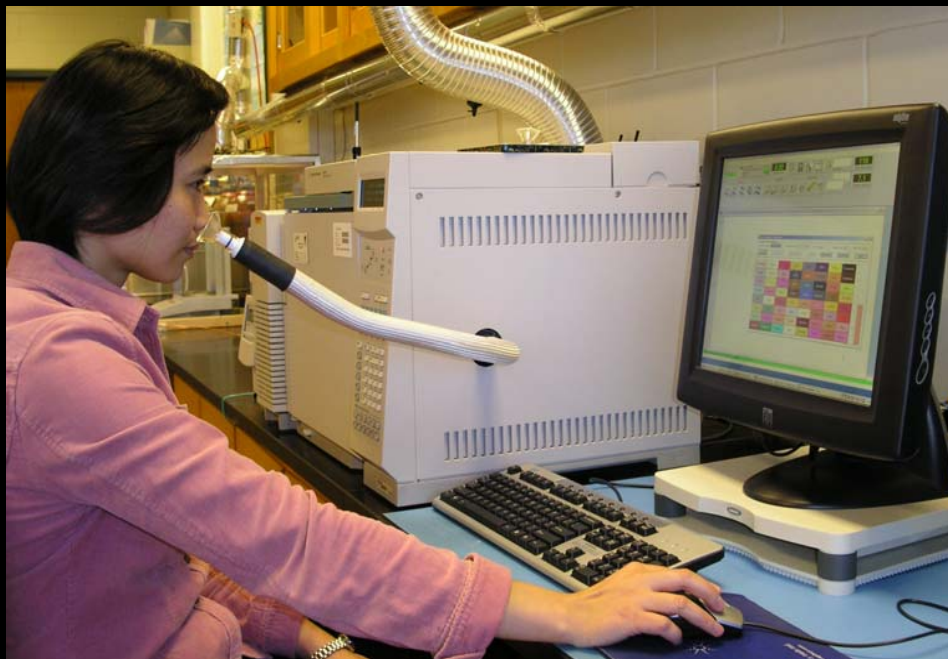
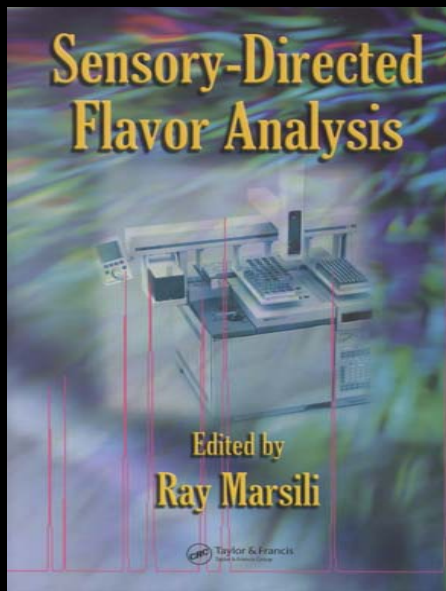
## SENSORY DIRECTED INSTRUMENTATION

(MDGC-MS-Olfactometry)

## INSTRUMENTATION ONLY

(GC, GCMS, Electronic nose etc)

# Sensory-Directed Flavor Analysis

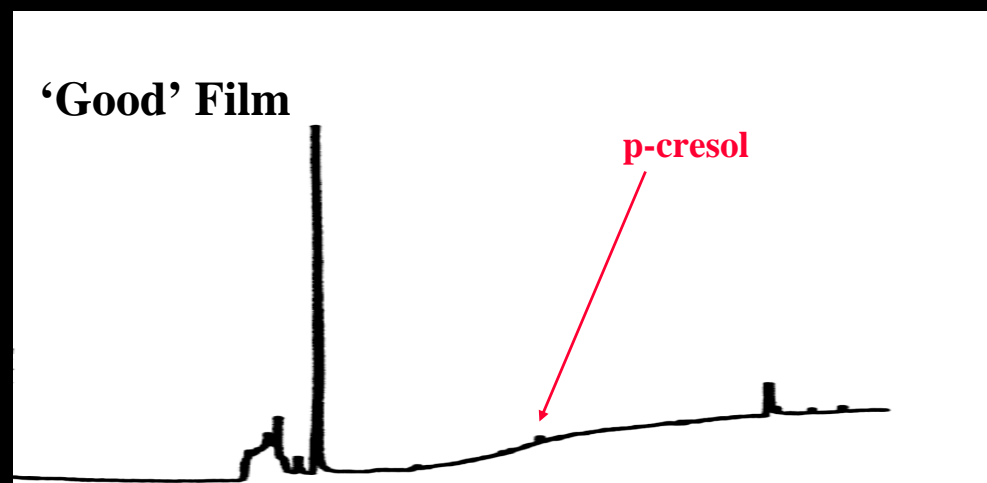
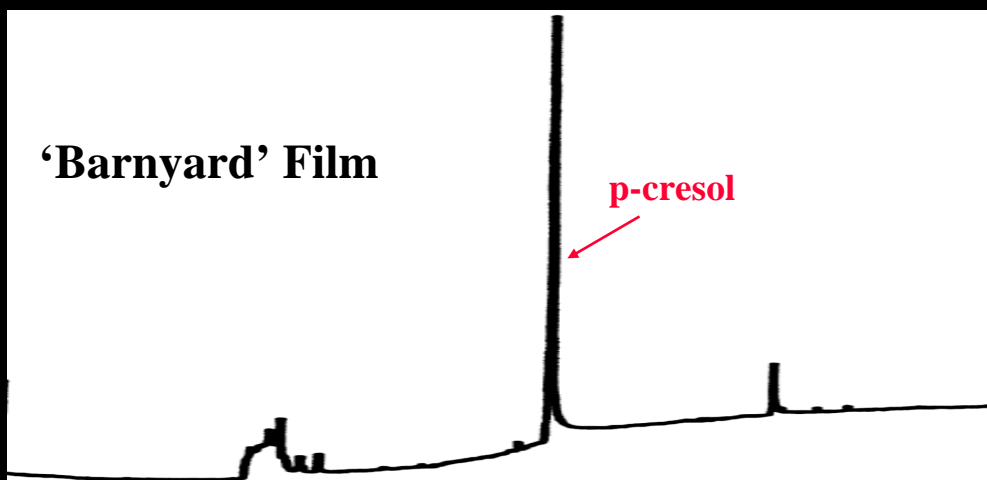


Chapter 4: An integrated MDGC-MS-Olfactometry approach to aroma and flavor analysis, David K. Eaton, Lawrence T. Nielsen and Donald W. Wright, Microanalytics, 2007.

# Character Defining Odorant Examples

SOURCE	ODORANT
Coconut, peach, whisky, oak	Various Lactones
Beet	Geosmin
Mushroom	1-Octene-3-ol
Cat Urine Marked Areas (feline derived)	_____thiol
Beer 'Skunky' Off-Flavor (light-struck)	3-Methyl-2-Butene-1-Thiol
Taco Shell Aroma	2-Aminoacetophenone
Mexican Free-tail Bat Colony Downwind	2-Aminoacetophenone
Cereal Packaging Film 'Barnyard' Off-Odor	para-Cresol
Swine Barn / Feedlot Downwind	para-Cresol

# Cereal Packaging Film – ‘Barnyard’ Malodor



## Excerpt from Project Report into Swine CAFO Study - 1996

.....“The molecular weight range of possible significance to the swine odor question may be considerably wider than I originally suspected. If, in fact, phenol and phenol substituted compounds (e.g. para-cresol or other cresol isomers) are significant contributors to the swine odor problem it is doubtful that they can be sampled from a polymer bag without discrimination induced by wall adsorption effects. I have previously observed this effect with compounds carrying much greater volatility than these and therefore must suspect that many of the higher molecular weight contributors are completely lost or preferentially reduced. I have not specifically evaluated Tedlar™ bags for this effect but based on previous experience with other polymer bags firmly believe that this effect should be suspected until proven differently.”....

## Technical References Addressing the Issue of Odorant Loss in Tedlar<sup>tm</sup> Bags

Keener et. al.; 2002; *Evaluation of thermal desorption for the measurement of artificial swine odorants in the vapor phase*; NC State, Transactions of the ASAE.

Koziel et. al.; 2005; *Evaluation of sample recovery of malodorous livestock gases from air sampling bags, SPME fibers, Tenax TA sorbent tubes and sampling canisters*; Texas A&M, JAWMA.

Trabue et.al.; 2006; *Bias of Tedlar bags in the measurement of agricultural odorants*; USDA-ARS Iowa, J of Environmental Quality.

Statements taken recently from the U.S. Pork Center  
web site [www.usporkcenter.org](http://www.usporkcenter.org)

Pork Industry Air Quality Research & Extension Needs and Priorities;  
Conference April 12, 2007, Clive, Iowa...

with respect to odor...

We Know: ....that, of the 400 or more odorants identified from swine manure, para-cresol is the primary contributor to the offensive odor associated with swine manure.

We Need: ....faster, real time, more accurate methods to measure and detect odors.

We Need: ....diet manipulation, new biochemical and microbiological methods to reduce para-cresol....

# Odor Sampling Strategy Development

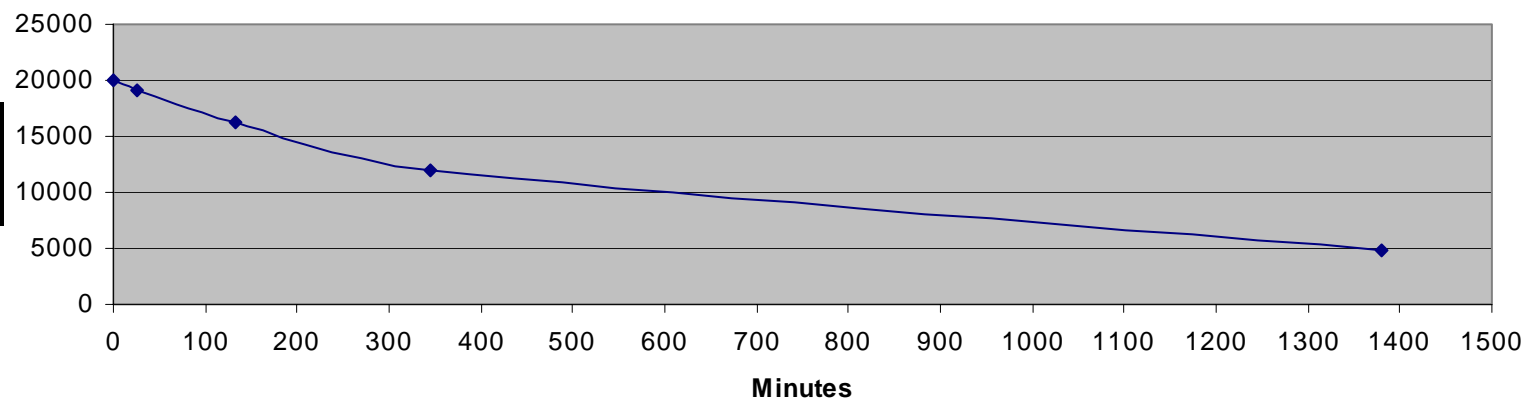
**Metalized FEP** versus Tedlar<sup>tm</sup>

# Metalized FEP Gas Sampling Bags

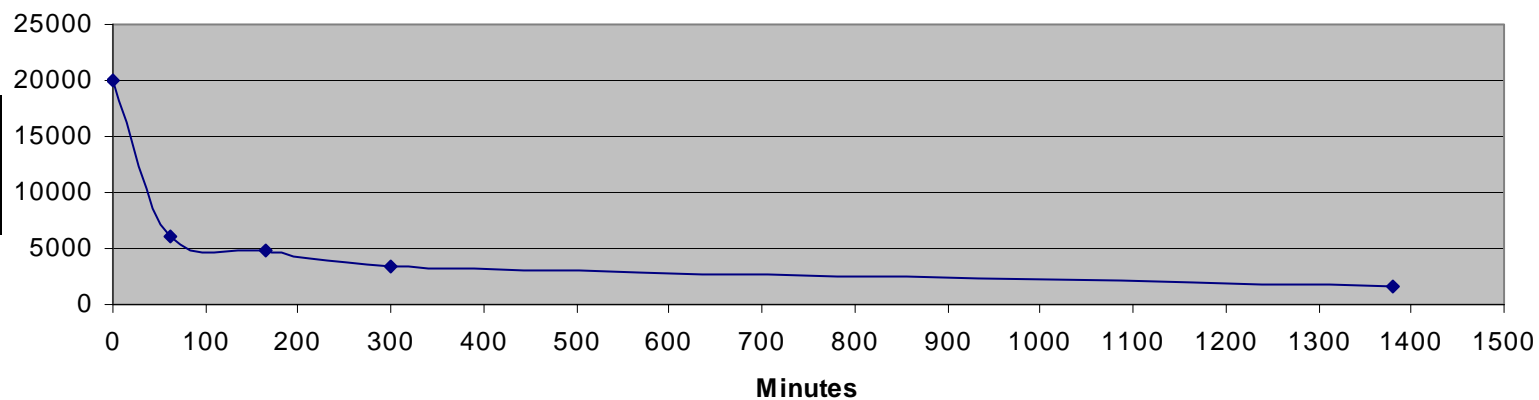


# p-Cresol Recovery – Metalized FEP vs Tedlar™ Bags

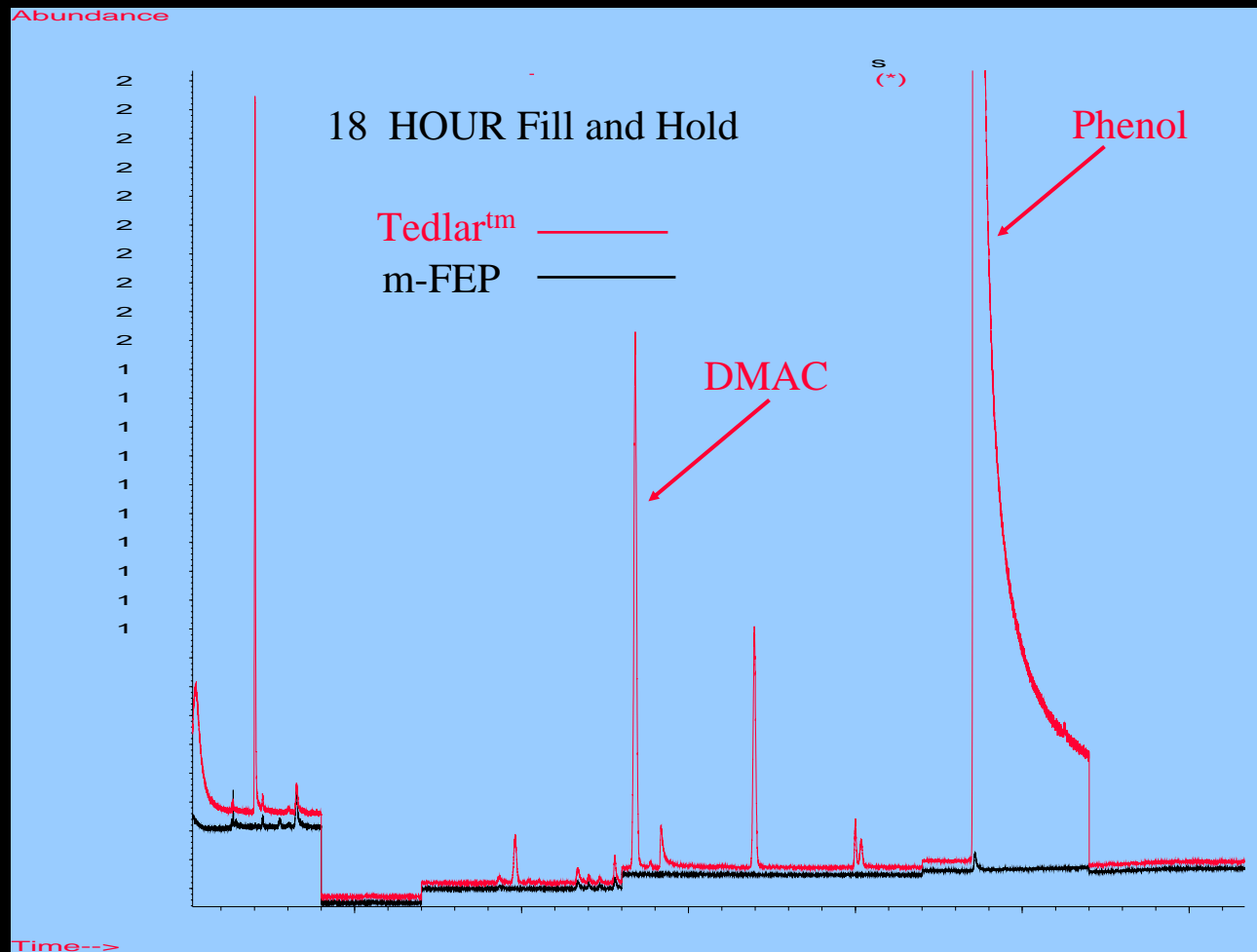
## p-Cresol Recovery (MFEP)



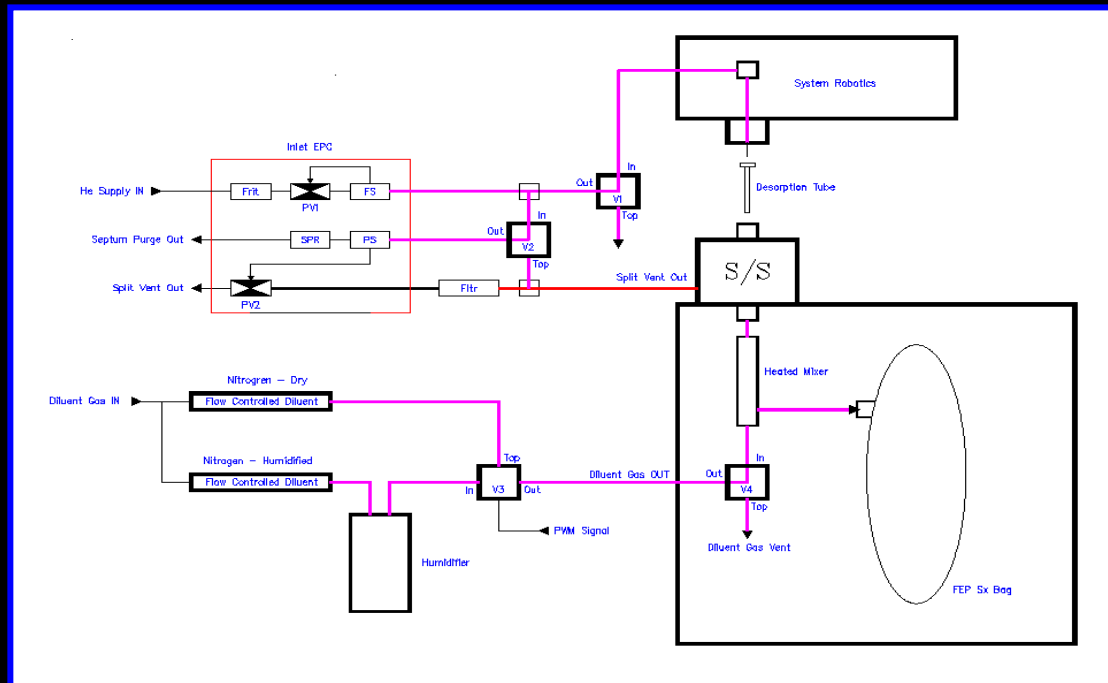
## p-Cresol Recovery (Tedlar Bag)



# Background Comparison: Tedlar<sup>tm</sup> vs Metalized FEP



# Odor Assessment System – Sorbent Tube Field Collection / Thermal Desorb Lab Reconstitution

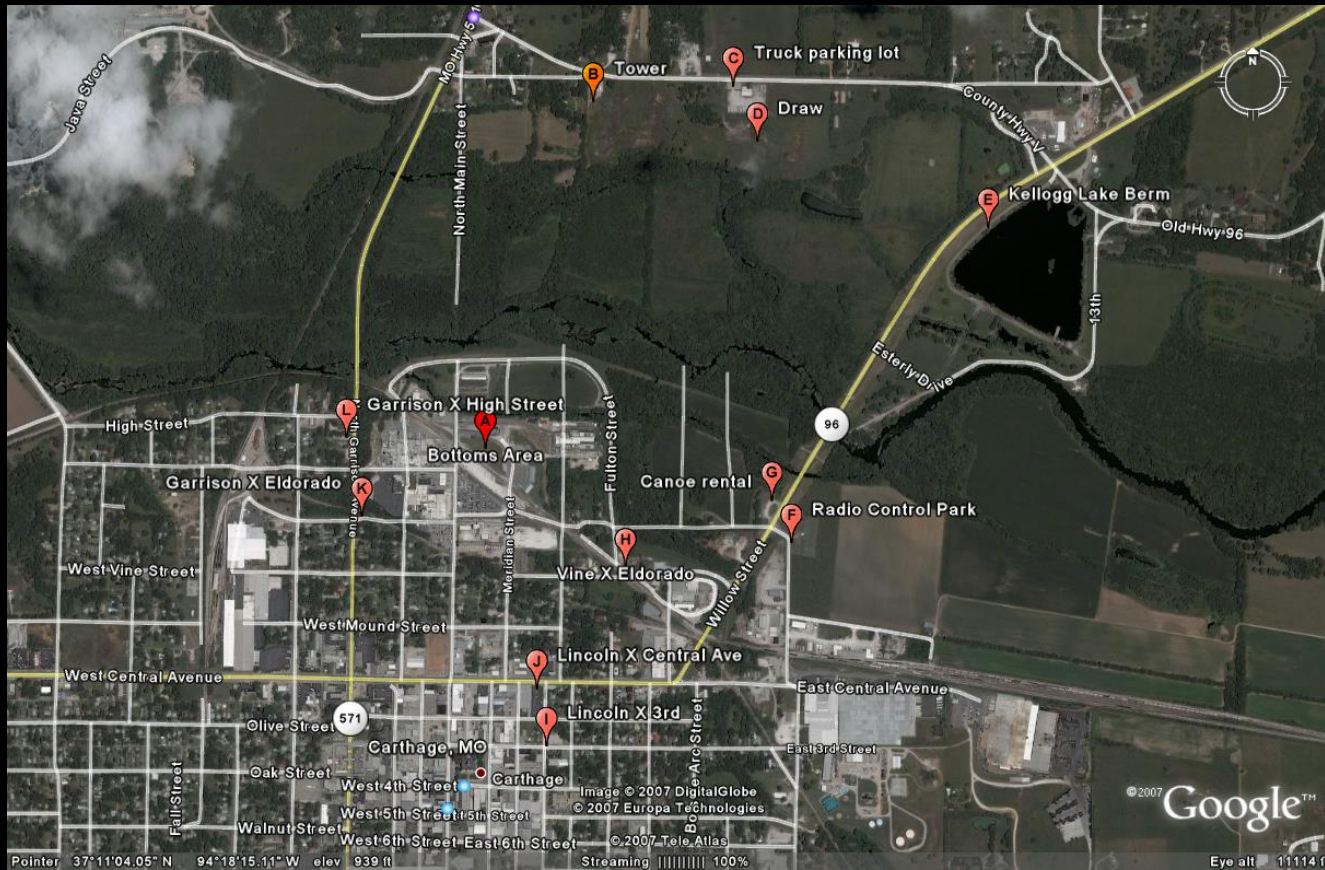




# Odor Sampling Strategy Development

## Transient Odor Events

# Carthage Industrial Bottoms Area – 1<sup>st</sup> Visit October 28<sup>th</sup> to November 1<sup>st</sup>



# First CBIA Site Odor Assessment

## Significant Problems and Hindrances

- ◆ Two of the CBIA industries were shut down during the first 2.5 days of site assessment visit. Interestingly, significant downwind odor events were coincidentally absent during this period.
- ◆ Many local officials and citizens were aware of the timing for the CBIA site odor survey.
- ◆ Passive SPME sampling approach shown to be lacking because of the transient 'burst' or 'wave' nature of the odor events.

# First CBIA Site Odor Assessment

## Significant Observations and Conclusions

- ◆ Repeated encounters with a distinct and consistent at-distance downwind odor event, described by this investigator as ‘sulfurous’ and ‘paper-mill like’.
- ◆ Lateral stratification of distinct and differentiable odor events from the CBIA.
- ◆ The ‘paper-mill like’ odor was perceived as priority by this investigator as a result of its reach, frequency of encounter and corroborating comments from a few knowledgeable local citizens.
- ◆ The at-distance odor plume was found to be remarkably narrow and transient in nature. Unlike CAFOs, encountered as brief ‘bursts’ or ‘waves’.
- ◆ Dimethyltrisulfide projected as an individual, priority ‘odorant-of-interest’ relative to the ‘sulfurous’, ‘papermill’ composite odor.

# Papermill Downwind Odor and Reduced Sulfurs

$\text{H}_2\text{S}$	hydrogen sulfide
$\text{CH}_3\text{SH}$	methyl mercaptan
$\text{CH}_3\text{SCH}_3$	dimethylsulfide
$\text{CH}_3\text{SSCH}_3$	dimethyldisulfide
$\text{CH}_3\text{SSSCH}_3$	dimethyltrisulfide
ETC	higher homologs

# Second CBIA Site Odor Assessment December 3<sup>rd</sup> to December 5<sup>th</sup>



# Conclusions Emerging From Three CBIA Site Odor Assessment Visits

- ◆ The need for an alternative to SPME as a sampling strategy for such transient, 'burst' type odor events.
- ◆ Dimethyltrisulfide projected as a **likely** individual, priority odorant relative to the perceived priority 'sulphurous' / 'paper-mill' downwind odor events.
- ◆ Reinforcement of the need for instrument based alternatives to current sensory methods for monitoring of transient downwind odor events.

# **Carthage Bottoms Area Odor Study: A Missouri Test Case for Odorant Prioritization as a Prelude to Instrument Based Downwind Odor Monitoring Protocol Development**

DON WRIGHT, Helen Wright - Don Wright & Associates, LLC, Georgetown, Texas; Anna Iwasinska, Fred Kuhrt - Microanalytics-MOCON, Round Rock TX; Jacek A. Koziel, - Iowa State University, Department of Agricultural and Biosystems Engineering, Ames, Iowa; Leanne Tippett-Mosby - Missouri DNR, Jefferson, Missouri

Proceedings of ASABE International Meeting in Rhode Island, June 2008

Full Manuscript Accessible at:

<http://www.plumechasers.com>



# Post-Phase I Transient Event Sampling Strategy Development

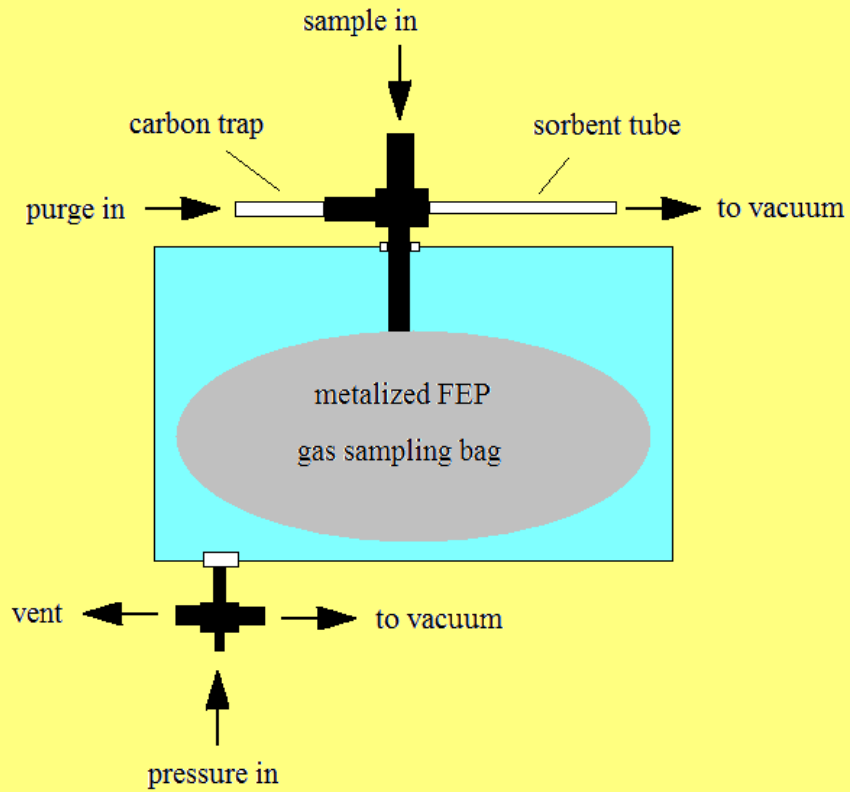
# Scale Model Transient Odor Event Generator



# Targeted Experimental 'Compressions'

Assessment Area	@ 1 sq. mile to @ .5 acre
Max Source to Receptor Distance	@ 1 mile to < 100 feet
Average Event Frequency	@ 2 per hour to >20 per hour
Travel Time to Survey Site	8+ hours to <5 minutes

## Proposed High-Speed Odor Event Sampler System



# Prototype Transient Odor Event Sampler



# Comparative Naphthalene Yields

Indirect 30 min SPME Fiber Exposure to < 2 Second Bag Collection

<b>Run #1</b>	10,524 count
<b>Run #2</b>	10,318 count
<b>Average</b>	<b>10,421 count</b>

Direct 3 min SPME Fiber Downwind Exposure

<b>Fiber #1</b>	2,624 count
<b>Fiber #2</b>	2,451 count
<b>Average</b>	<b>2,538 Count</b>

# Multi- Point Source Scale Model Transient Odor Event Simulator



# Summary

- ◆ Regardless of source, odor analysis is, first and foremost, chemical analysis; carrying the same constraints and limitations with respect to sample handling and storage.
- ◆ While always carrying the 'potential' for extreme complexity, the human odor response to real world odor sources is often remarkably simple; with both positive and negative impacts primarily driven by very small subsets of the total source emission.
- ◆ Regardless of surface treatment, extended storage of polar, high-impact semi-volatile odorants in the gas phase is ill-advised. An optimized whole-air odor sampling strategy is currently being evaluated whereby odorants are field collected onto an adsorbent bed, shipped and stored under refrigeration in advance of gas phase reconstitution; just prior to analysis or composite sensory assessment.
- ◆ A direct, SPME sampling approach was shown to be limited because of the transient, 'burst' or 'wave' nature of the odor events such as encountered downwind of the CBIA. Efforts are on-going to develop and validate an improved alternative for sampling such transient events.

# Acknowledgements

This work has been partially funded by the US Department of Agriculture under SBIR Phase II Grant – CSREES Award number 2007-33610-18619 to Microanalytics.

**However**

Any opinions, findings, conclusions, or recommendations expressed in this presentation are those of the author and do not necessarily reflect the view of the US Department of Agriculture

# CBIA Odor Issue Opinion ‘Absolutes’

- ◆ #1 . ‘It ain’t that ( ) bad; the real ( ) problem is the ( ) old ladies in town and their constant ( ) complainin’; It ain’t gonna kill ya’. (**irate citizen**).
- ◆ #2 . ‘The problem won’t go away as long as ‘Industry C’ remains in operation in the Bottoms Area’. (**engineer contractor**).
- ◆ #3 . ‘...we are not the primary [source]; there are downwind odors even when our operation is shut down...’. (**‘Industry’ official**).
- ◆ #4 . ‘I don’t know if you have been involved in environmental odor litigation but it is a very difficult issue to ‘get your hands around’; odor issues are very ‘squishy’; ‘like trying to grab water with your hands’..’. (**attorney, engineer representing one of the CBIA industrial operations**).
- ◆ #5 . ‘What an example of over-analysis.....’. (**anonymous – letter-to-editor Joplin Globe**)’.

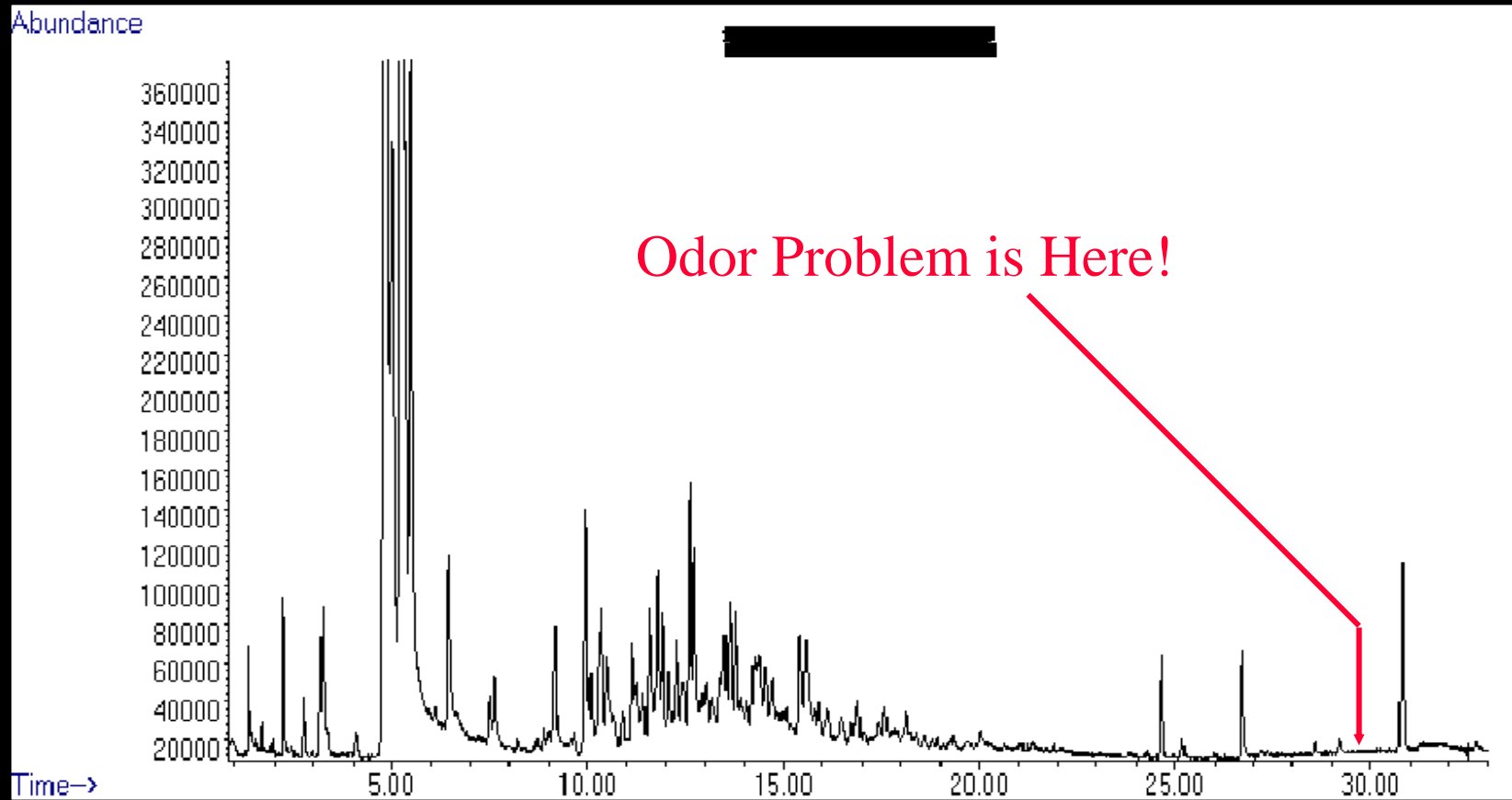


# Crisis-Driven Problem Solving

## Case Study – MDGC-MS-O Based Odor Quality Problem Solving

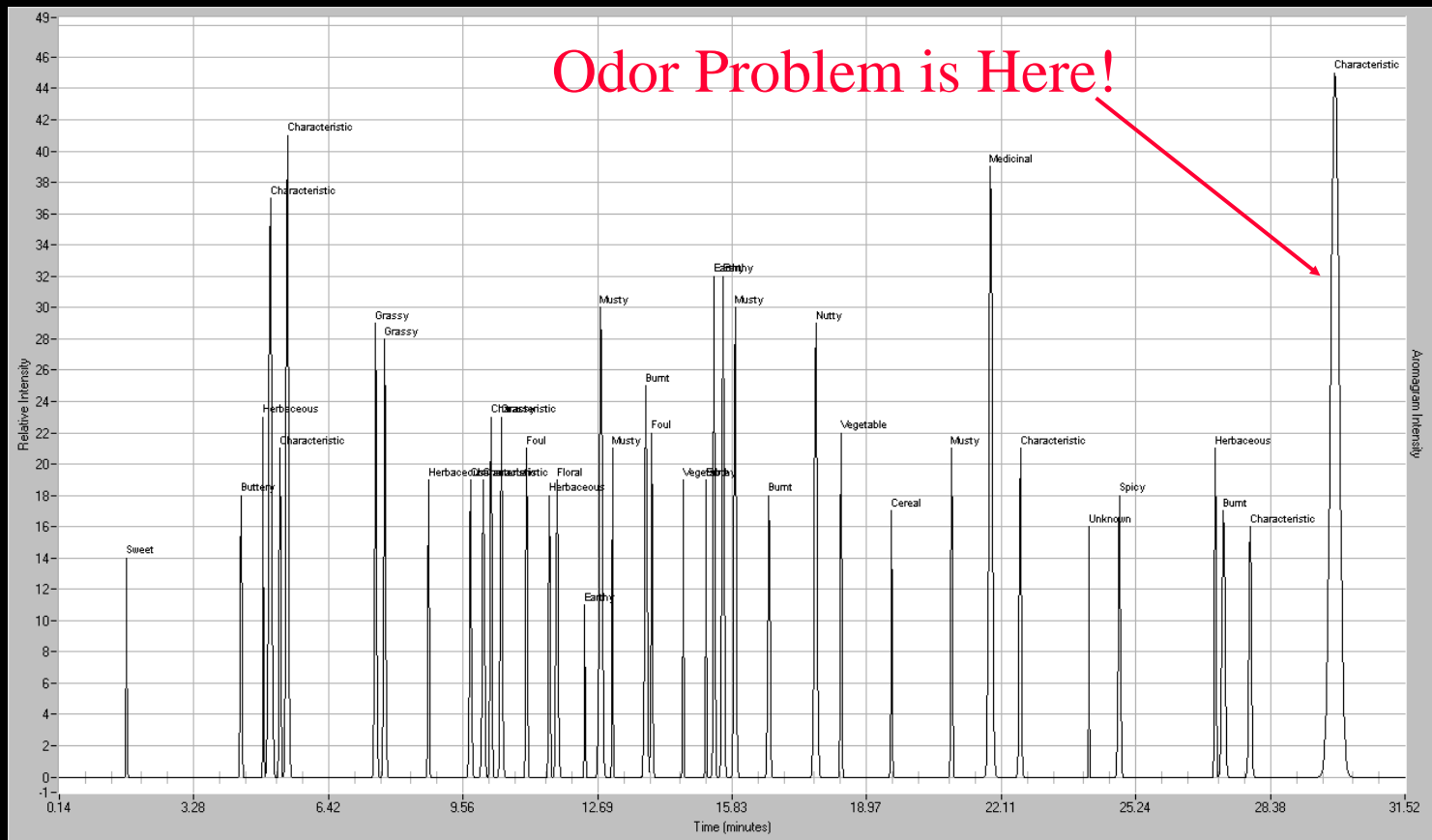
- ◆ Fortune 50 Corporation – health care field
- ◆ Odor quality problem ‘festering’ for 9 months
- ◆ Extensive internal task group studies conducted
- ◆ Problem investigated by 4 independent laboratories
- ◆ Accumulated reports @ 6 inches high (@ 10 pounds)
  
- ◆ MDGC-MS-O based primary odorant in < 2 hours

# Health Care Pack Volatiles MDGC Total Transfer – MS TIC



# Health Care Pack Volatiles

## MDGC Total Transfer – Aromagram



## Mal-odorant Density Profile Based on Target MS-SIM Electronic Response

Rank	Component	MS-SIM Response Ratio
1	Bottom component – bottom section	292X
3	Bottom component – top section	20X
4	Top component – top section	7X
6	Middle component – top section	1X



**‘Contrasting’  
Animal Odor Issues  
Mexican Free-tail Bat**

# Bracken Cave – Comal County, Texas



# Mexican Free-Tail Bats

## Evening Exodus from Bracken Cave



# SPME Fiber Sampling of Ventilation Shaft



 **THE END OF THE CAVE**  
OF BRACKEN BAT CAVE IS  
ABOUT 10 FEET SOUTH OF THE MINE  
SHAFT. BAT GUANO BLOCKS FURTHER  
EXPLORATION, BUT THE CAVE  
PROBABLY CONTINUES ABOUT  
ANOTHER 500 FEET TO THE SOUTH  
WHERE IT SHOULD END AGAINST THE  
BAT CAVE FAULT. THIS FAULT IS AN  
ANCIENT SHIFT IN THE EARTH'S CRUST  
WHERE THE CAVERNOUS ROCK THAT  
CONTAINS THE CAVE RESTS AGAINST  
LESS CAVERNOUS ROCK. THIS FAULT  
EXTENDS FOR SEVERAL MILES AND  
ALSO MARKS THE SOUTHERN END OF  
NATURAL BRIDGE CAVERNS.