

# Development of Methods to Characterize Emissions From Spray Polyurethane Foam Insulation

**Mark Mason**

**Symposium on Developing Consensus  
Standards for Measuring Chemical Emissions  
from Spray Polyurethane Foam Insulation**

**April 30, May 1, 2015  
[mason.mark@epa.gov](mailto:mason.mark@epa.gov)**

***Krebs, Barnes, Greenwell, Liu, Owens,  
Roache, Folk, Allen,  
Skarping, Dalene, Karlsson***



# Why Are There Concerns about SPF Insulation?

- SPF insulation is manufactured *on-site* from a complex mixture of chemicals, many with recognized occupational health hazards
- SPF is spray applied under pressure and heat, including exothermic reaction conditions, where exposures to chemicals and byproducts may be found in vapors, aerosols, dust, or on surfaces during and for a period of time after installation
- EPA and CPSC have received reports of incidents from consumers who have allegedly experienced health effects, including concerns for lingering odors, after SPF application
- Relationships between product application, curing, post-application exposures, including product off-gassing, and health and environmental outcomes are poorly understood

# EPA Research Objectives

- In collaboration with stakeholders, develop and demonstrate consensus test methods and models
  - What is emitted and what is the time course of emissions?
    - *Identify sources of variability and uncertainty*
- Use results to inform and guide decisions to eliminate and/or reduce risks

## EPA/ORD Research Approach

- Utilize test chambers to develop and demonstrate source emissions methods and investigate factors that impact emissions
  - Work from small to full-scale test environments
    - Initial focus on emissions immediately after application
    - Conduct pilot work with two-component low pressure systems
    - Adapt sampling and analysis approaches that maximize range and sensitivity for detection and quantification of potential emissions

## **Sampling and Analysis Approaches for Classes of Potential Emissions**

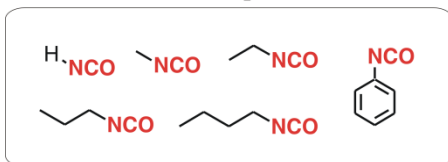
- Isocyanates collected on denuder/filter samplers followed by extraction, concentration and LC-MS/MS analysis (ISO 17734)
- VOCs, SVOCs collected on mixed bed porous polymer adsorbent samplers with TD-GC/MS analysis (WK 40293)
- Aldehydes collected on DNPH cartridges with analysis of extract by HPLC-DAD (ASTM D5197)
- Flame Retardants collected on PUF (air), and surface wipes with solvent extraction and GC/MS analysis

## Sampling and Analysis Approach for Isocyanate Emissions

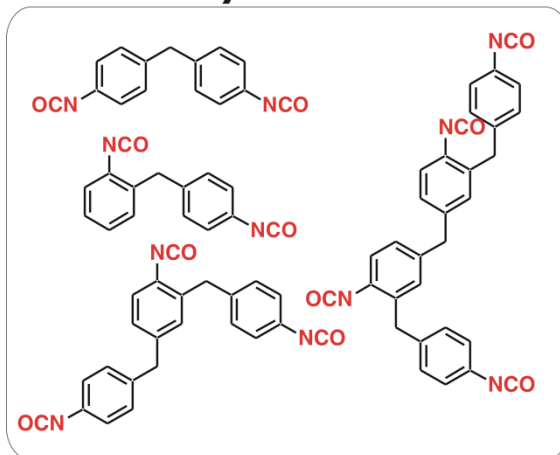
- Isocyanates collected on Di-n-butylamine (DBA)-treated denuder-filter samplers, extract analyzed by LC-MS/MS



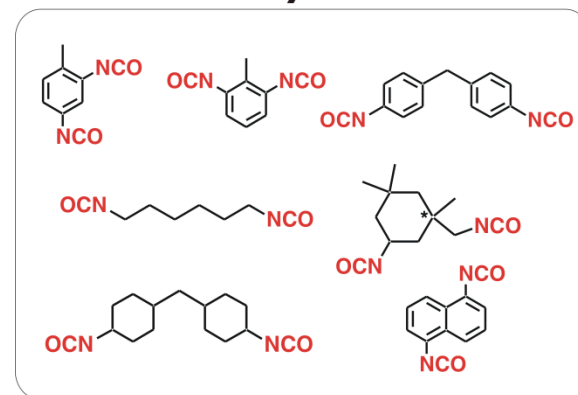
### Monoisocyanates



### Polymeric MDI



### Diisocyanates



## Quality Assurance & Quality Control Targets

Analytical Instrument	Parameter	Accuracy	Precision	Completeness
<b>LC-MS/MS</b>	Calibration correlation for target compounds	N/A	$R^2 \geq 0.95$	90%
	Pre- and post-calibration slope factor difference <sup>a</sup>	N/A	$\leq 20\%$	90%
	Performance Evaluation Samples (PES), low/medium/high concentrations	$\leq 30\% E_r$ <sup>f</sup>	N/A	90%
<b>TD-GC/MS</b>	Repeatability of internal standard (IS) injection	N/A	$\pm 20\%$	90%
	Linear regression, $R^2$	N/A	$R^2 \geq 0.995$	90%
	DCC <sup>b</sup> — all target compounds	$\pm 25\%$	N/A	90%
	IAP	$\pm 25\%$	$\pm 25\%$	90%
<b>GC/MS<sup>c</sup></b>	Calibration – relative standard deviation (RSD) triplicate results	N/A	$\leq 25\% \text{ RSD}$	90%
	DCC – all target compounds	$\pm 25\%$	N/A	90%
	Recovery of d15-Triphenyl phosphate concentration (RCS <sup>d</sup> )	60-140%	40%	90%
	IAP	$\pm 25\%$	$\pm 25\%$	90%
<b>HPLC/DA<sup>e</sup></b>	Calibration – RSD triplicate results	N/A	$\leq 20\% \text{ RSD}$	90%
	DCC – all target compounds	$\pm 15\%$	N/A	90%
	PES	N/A	$\leq 25\% \text{ RSD}$	90%
	IAP	$\pm 25\%$	$\pm 25\%$	90%

<sup>a</sup> Percent difference between pre- and post-calibration  $[(\text{pre}-\text{post})/\text{pre}]$  must be  $\leq 0.2$ .

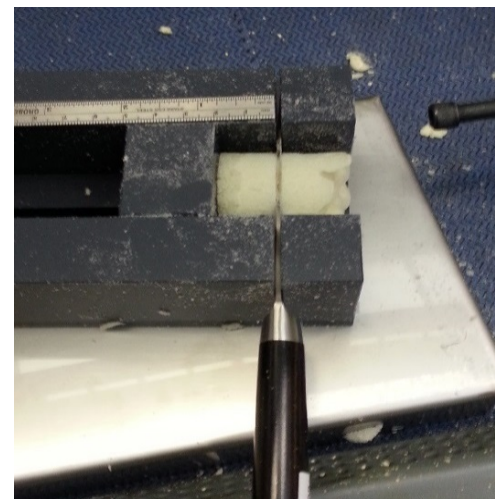
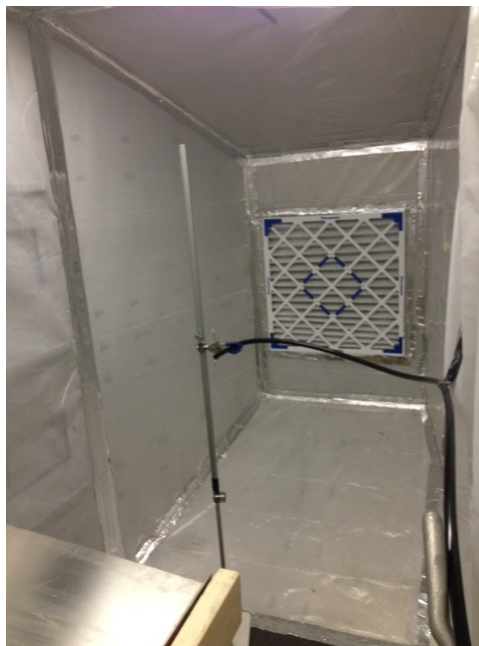
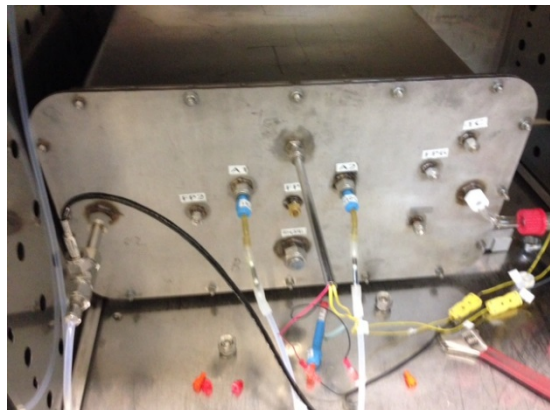
<sup>b</sup> Daily Calibration Check.

<sup>c</sup> For both PUF and wipe sample analyses.

<sup>d</sup> Recovery Check Sample.

<sup>e</sup> Diode-array.

<sup>f</sup> % Relative error



## Test System Development

Test System Development	Objective	Status
Isocyanate-specific emissions tool (PUFETS)	To identify and quantify primary SPF isocyanate emissions	On hold, issues with air flow, volatility of derivatizing agent
53 L electro-polished stainless steel chambers	Qualitative isocyanate and TCPF post application emissions characterization	Modifications made to chambers and to the isocyanate denuder sampler system
Micro chambers	To evaluate suitability for immediate post-application emissions characterization, scaling to full-scale environments	Several experiments conducted – evaluating reliability; sample prep, substrate, thickness, temperature effects

## Micro Chamber Scouting Tests

- Objectives
  - Gain insight into immediate post-application emissions
  - Investigate impact of temperature on emissions
  - Investigate variability between subsamples
- Methods
  - Product sprayed on release paper in tray
  - 45 mm diameter by 28 mm plugs cut from sample
  - Plugs placed in micro chamber cells at 25 and 40 °C with smooth side up (plug bottom)
  - Effective headspace 3.2 ml, air flow rate 120 ml/min
  - Samples collected periodically for 310 hours

# Spray Foam Samples in Micro Chambers for 25 and 40 °C Tests



## **Calculation of Emission Rate per ASTM D-5116** **(where concentrations are not quasi steady state)**

$$R = V*(dC/dt) + QC$$

**where:**

**R = emission rate ( $\mu\text{g/h}$ )**

**V = effective headspace volume in the micro chamber ( $\text{m}^3$ )**

**C = concentration ( $\mu\text{g}/\text{m}^3$ )**

**Q = air flow rate ( $\text{m}^3/\text{h}$ )**

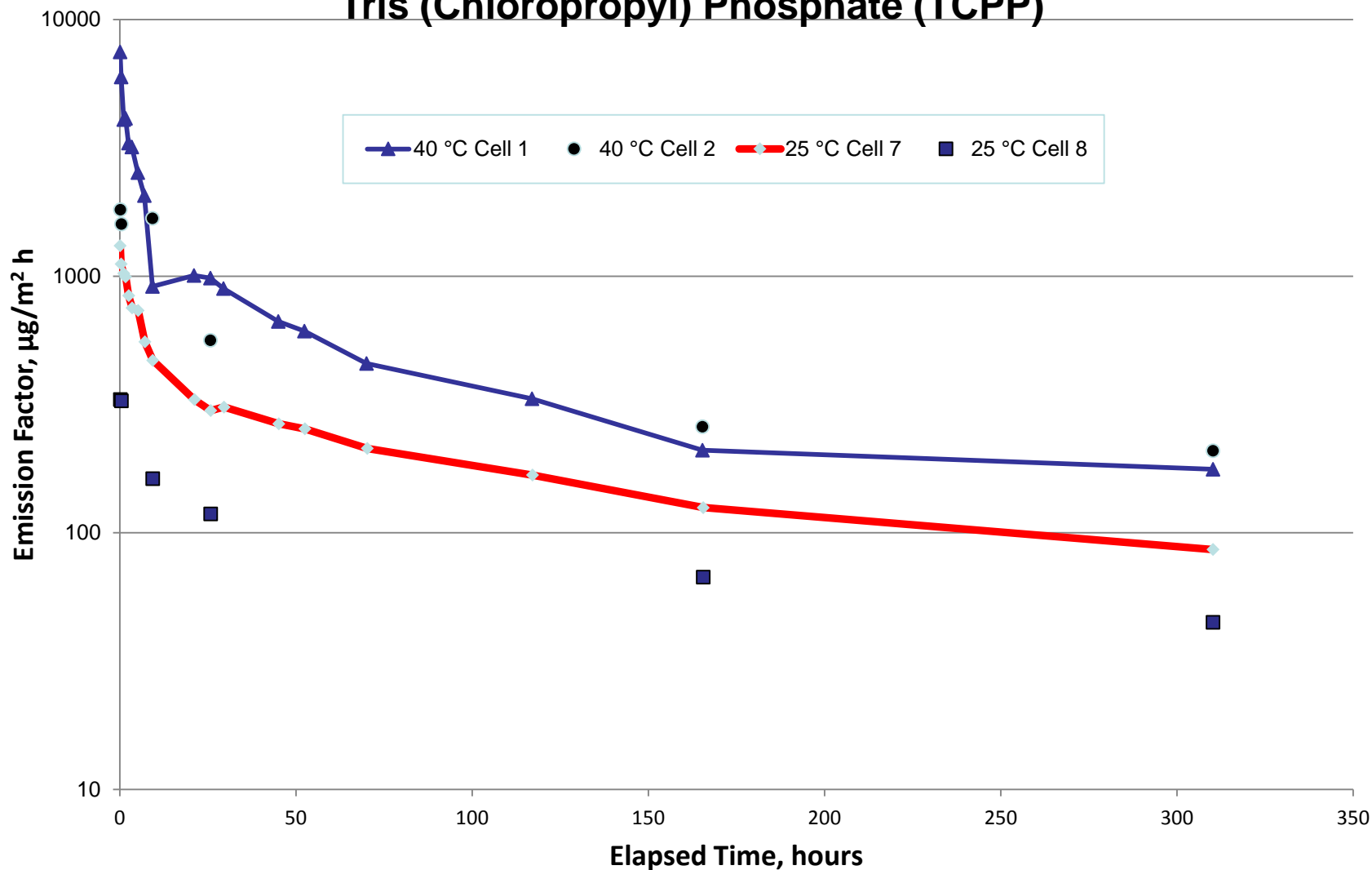
**t = time (h)**

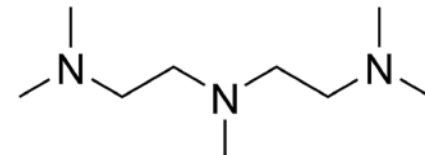
$$\text{Emission Factor } (\mu\text{g}/\text{m}^2/\text{h}) = R/S$$

**where:**

**S = sample surface area ( $\text{m}^2$ )**

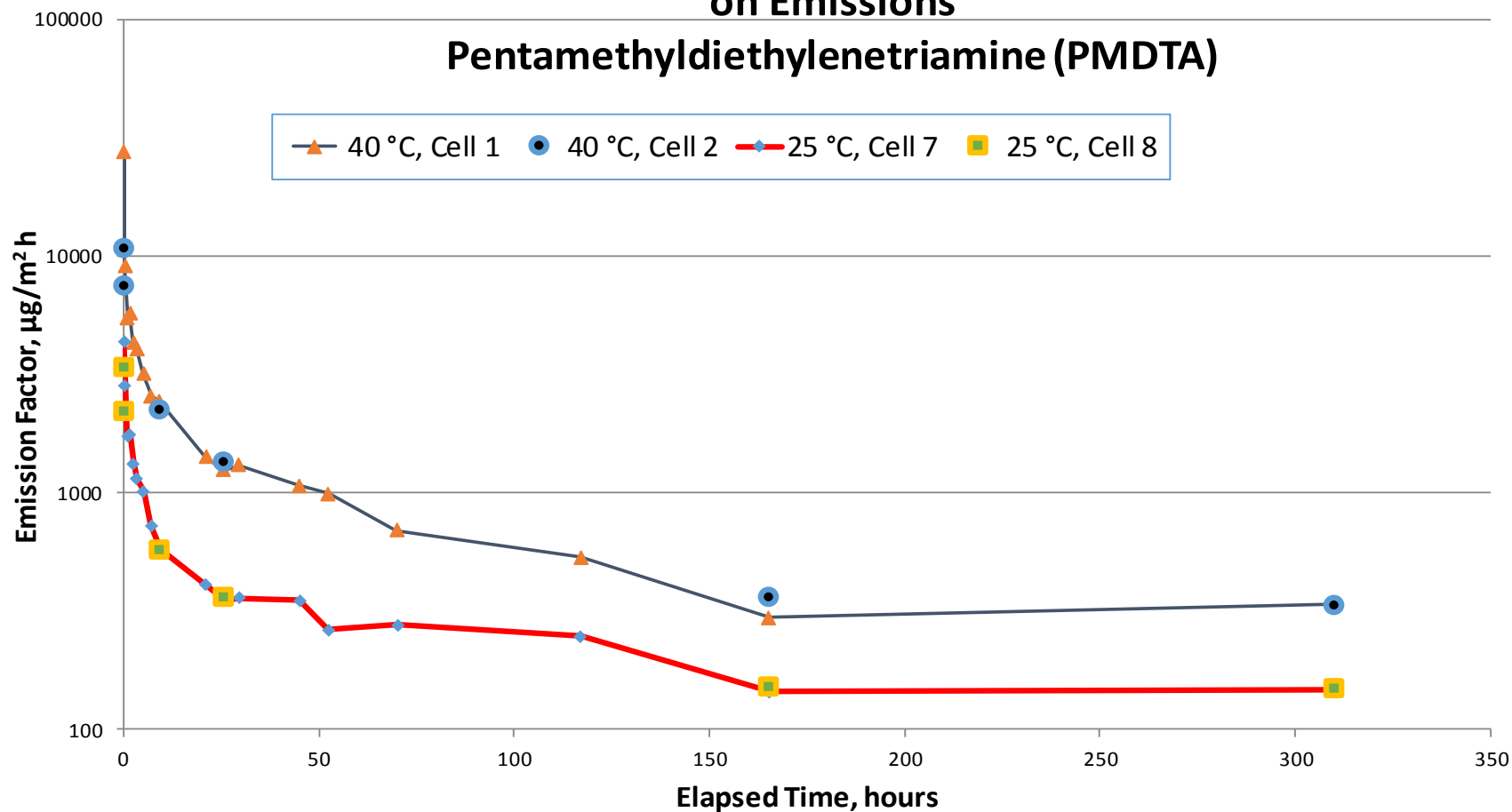
## Micro Chamber Temperature Comparisons Tris (Chloropropyl) Phosphate (TCPP)

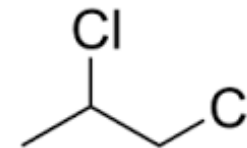




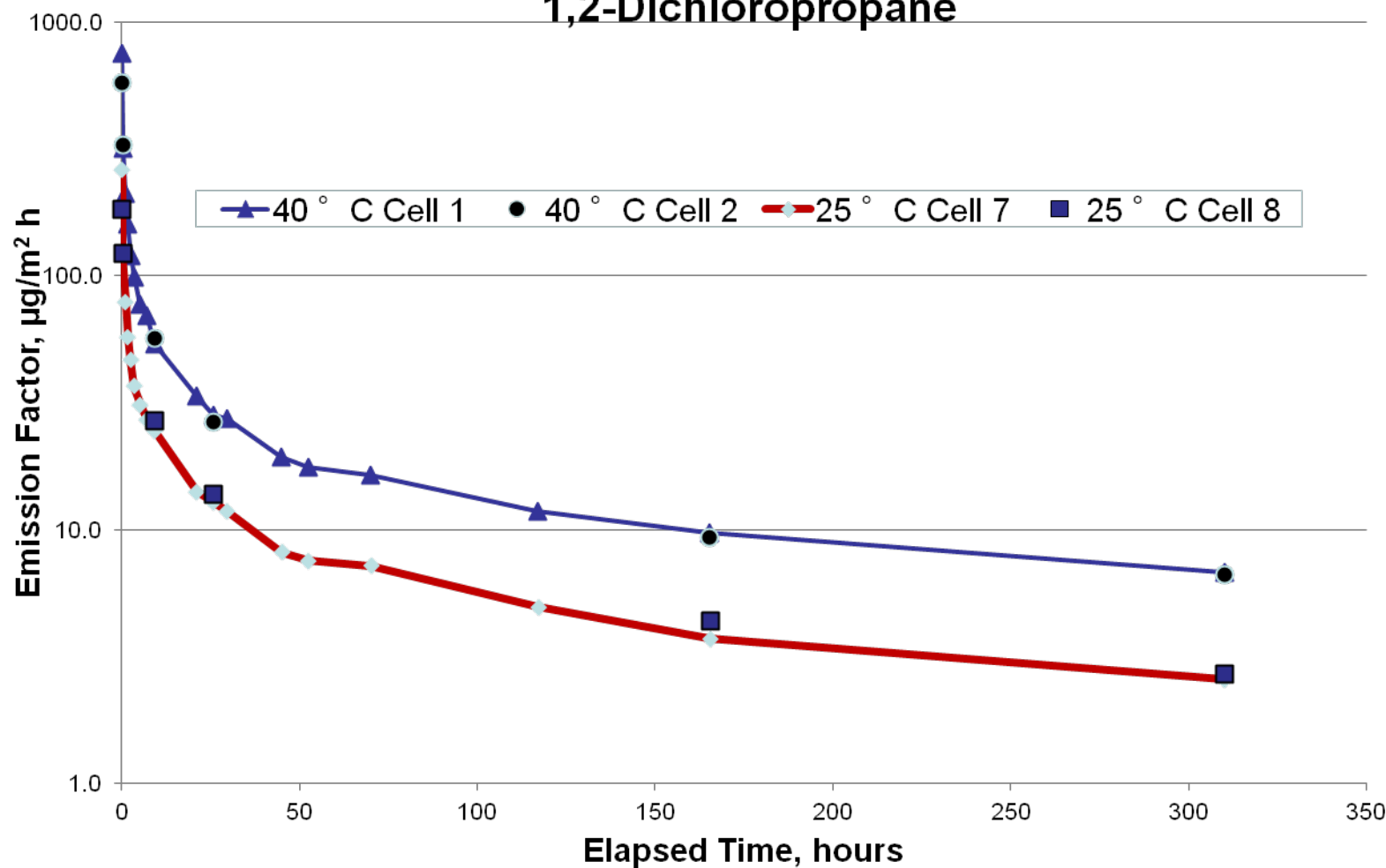
## Micro Chamber Temperature Scouting Test: Temperature Impact on Emissions

### Pentamethyldiethylenetriamine (PMDTA)





## Micro Chamber Temperature Impact on Emissions 1,2-Dichloropropane



## Comparison of TCP P Mass Leaving in Air and Mass Recovered from Micro Chamber Lid

	Cell #	Mass Leaving in the air (µg) in 310 h	Mass on Lid (µg)	Average ± Standard Deviation for three cells (µg)
40 °C	1	178.6	1.9	1.33±0.78
	2		1.65	
	3		0.44	
25 °C	7	75.7	0.19	0.98±0.98
	8		2.08	
	9		0.67	

## Observations from Micro Chamber Scouting Test

- Apparent initial emission factors are 1 to 2 orders of magnitude greater than emission factors observed after approximately 48 hours
  - Underscores need to understand emission and ventilation, natural and mechanical, during and following application
- Apparent emission factor increase of 2 to 3 times with increase in temperature from 25 to 40 °C
- Mass of TCP on inner surface of lid is about ~1% of mass emitted over 310 hours; cell to cell differences suggest need for improvement of the wipe technique

## Pilot Evaluation of Isocyanate Emissions in 53 L Emissions Test Chambers

- **Objectives:**

- Evaluate potential derivatizing agent (DBA) emissions from normal and low DBA denuder samplers at 25 °C
- Evaluate reproducibility of protocol
- Obtain qualitative insight into isocyanate emissions during curing phase
- Obtain limited VOC/SVOC emissions data to provide additional comparability data

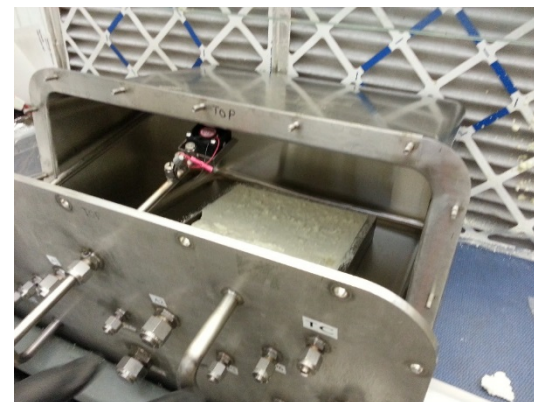
- **Approach:**

- Monitor DBA at outlet manifold during collection of background samples
- Conduct replicate tests; morning and afternoon SPF production with same source
- Utilize high chamber loading ratio ( $3 \text{ m}^2/\text{m}^3$ ) to maximize potential to quantify emissions
- Collect Tenax samples at 27 hours post application

SPF production  
in spray booth



Physical properties  
tray



Transferring sample  
tray to small chamber



## Physical Properties Data

- Morning application

- Density: 2.42, 2.45 lbs/ft<sup>3</sup>
- Application depth: 4.4 ± 0.8 cm (n = 30)
- Adhesion and cohesion tests: passed
- Observations: uniform cell structure, no apparent air inclusions

- Afternoon application

- Density: 3.01, 2.61 lbs/ft<sup>3</sup>
- Application depth: 3.3 ± 0.6 cm (n = 30)
- Adhesion and cohesion tests: passed
- Observations: uniform cell structure, no apparent air inclusions, some larger cells near substrate

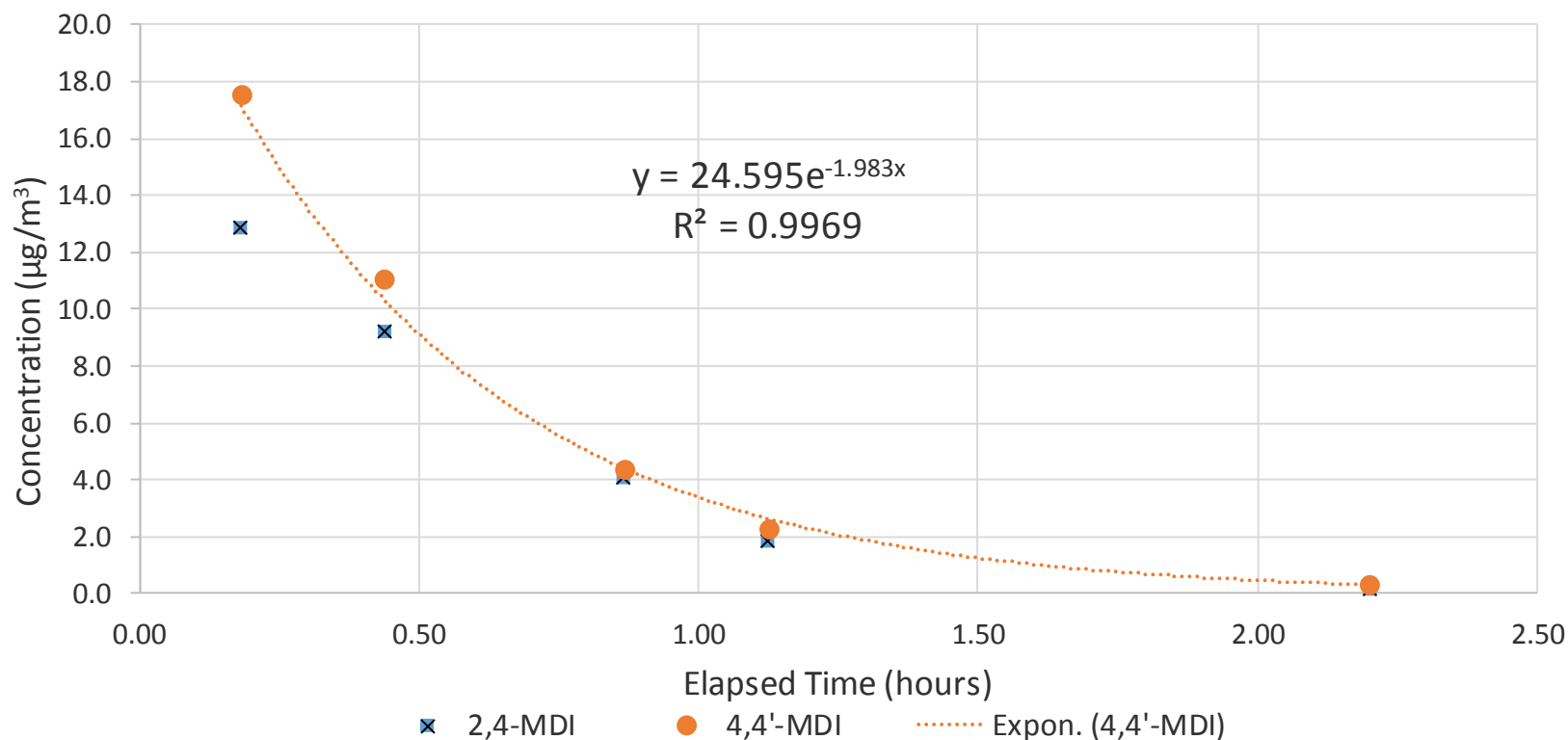
## Comparison of Morning and Afternoon Chamber VOC/SVOC Concentrations in the Small Chamber 27 Hours After Application

	Morning Application (ST7)		Afternoon Application (ST8)		Ratio
	Sample A	Sample B	Sample A	Sample B	Afternoon/ Morning
	$\mu\text{g}/\text{m}^3$	$\mu\text{g}/\text{m}^3$	$\mu\text{g}/\text{m}^3$	$\mu\text{g}/\text{m}^3$	
<b>Allyl Chloride</b>	190.8	192.2	362.8	337.4	1.8
<b>1,4-Dioxane</b>	134.5	131.7	783.3	772.5	5.8
<b>PMDTA</b>	506.8	537.1	8999.3	9235.7	17.5
<b>Sum TCPP</b>	199.5	208.5	252.1	267.8	1.3

## Isocyanate Concentrations Observed in 53 L Chamber High Loading 3 m<sup>2</sup>/m<sup>3</sup>, 1 air change per hour, 25 °C

Sample Description		MIC	PHI	2,4-MDI	4,4-MDI
		µg/m <sup>3</sup>	µg/m <sup>3</sup>	µg/m <sup>3</sup>	µg/m <sup>3</sup>
0.2 Hr	Morning	-	-	12.87	17.55
	Afternoon	3.19	-	-	-
0.5 Hr	Morning	1.06	2.36	9.24	11.07
	Afternoon	2.14	-	-	-
1.0 Hr	Morning	0.65	1.20	4.08	4.37
	Afternoon	1.19	-	-	-
1.2 Hr	Morning	-	-	1.87	2.29
1.3 Hr	Afternoon	0.89	-	-	-
2.3 Hr A	Morning	-	-	-	0.33
2.5 Hr A	Afternoon	-	-	-	-
2.3 Hr B	Morning	-	-	0.18	0.33
2.5 Hr B	Afternoon	-	-	-	-

## Exponential Fit to 4,4' Chamber Concentration 25 °C, 50% RH, and 1 Air Change per Hour



## QA Markers for Duplicate Chamber Tests

	<b><u>Morning Application (ST7)</u></b>	<b><u>Afternoon Application (ST8)</u></b>
Duplicate 2 hr ASSET™ samples	4,4-MDI good precision (0.33/0.33 µg/m <sup>3</sup> ) 2,4-MDI good precision (ND/0.18 µg/m <sup>3</sup> )	Both duplicates ND for isocyanates
Application duplicates	---	All ± 30% except for 3-ring MDI at 36%
DBA back diffusion duplicates	All ND, except for one collected with original ASSET™	---
C3 duplicates (at 27 hr)	RSD < 12% for all compounds	RSD < 12% for all compounds

### MARKES C3 Thermal Desorption (TD)

DCC	All PASS, except for one compound (allyl chloride) in one DCC failed by 0.4%
Field Blanks for C3	All ND
Calibrations	R <sup>2</sup> > 0.99

### ASSET™ Samplers

Chamber Background Blanks	ND for isocyanates
Field Blanks	All ND, except EIC detected at 6 ng on one blank
Calibrations	R <sup>2</sup> > 0.99; one calibration point failed the pre/post ratio criterion
Spike recoveries	All PASS

# Conclusions

- Pilot small chamber tests:
  - Provide qualitative insight into gas-phase isocyanate emissions and highlight the need to
    - Characterize diisocyanate (and other VOC/SVOC) application phase emissions in full-scale experiments
    - Develop better understanding of MDI and pMDI fast-reacting aerosols – what is their role in exposure to isocyanates, how long do they persist?
    - Develop a better understanding of the apparent brief mono isocyanate emissions during cure phase
  - Indicate a need for A to B ratio feedback during application for the two component low pressure systems
  - And indicate a need for improved understanding of performance of these systems in the field

## Conclusions and Implications for Research Needs

- The Micro chamber systems provide a very useful tool for rapid identification and quantification of many SPF emissions
  - Data should be useful for identification of off-ratio product emissions
  - Evaluation of emissions from new formulations
  - Evaluation of changes in emissions over time as materials age
- For interpretation and use of emissions data
  - Need a demonstrated modeling approach to relate emissions to potential exposures and assess and guide risk management
    - Model inputs needed for emissions over time, transport factors, partitioning to surfaces, other factors that impact exposure