engineering laboratory

Developing a Reference Material for VOC Emissions Testing

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U.S. Department of Commerce

Acknowledgements

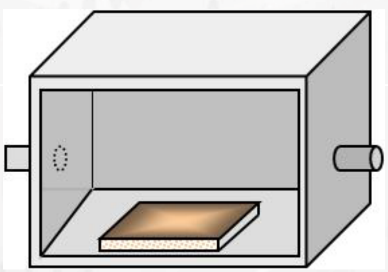
VirginiaTech

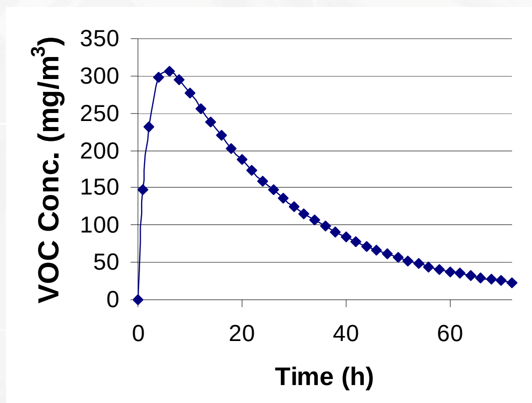
- John Little, Steve Cox, Zhe Liu

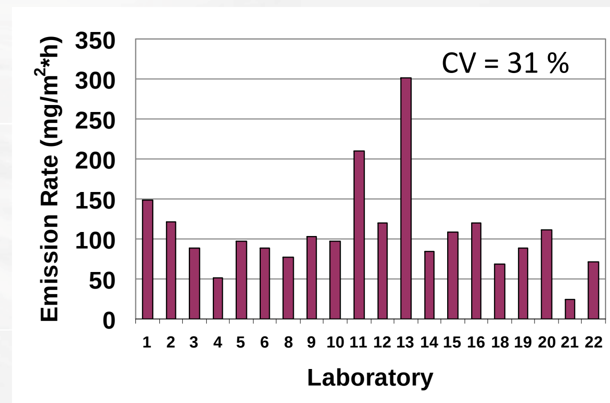
- Air Quality Sciences
- BAM – German Federal Institute for Materials Research and Testing
- Berkeley Analytical Associates
- National Research Council Canada

Problem – Building Materials Perspective

- VOC emissions from building materials have been measured since the late 1970s.
  - Proliferation of “green” labeling programs
  - Many different chamber emissions test methods with no standard approach for test method validation







What is the true value?

Can the variability between labs be improved?

Reference Material Development

<u>Key Definitions</u>:

Reference material: a material or substance with one or more property values sufficiently **homogeneous** and well established to be used for the calibration of an apparatus, the assessment of a measurement method, or for assigning values to materials. *[ISO VIM: 1993, 6.13* [7] *]*

Reference value: a best estimate of the **true value** and associated uncertainty provided on a NIST certificate where all known or suspected sources of bias have not been fully investigated by NIST.

Desired Qualities of Reference Materials

- Independent knowledge of emission rate
- Easily reproducible with consistent performance
- Factors affecting emission rate well understood
- Mimics mass transfer processes of indoor materials (may require several materials)
- Sized for small and large chambers
- Emits a range of VOCs
- Stable with a predictable shelf-life

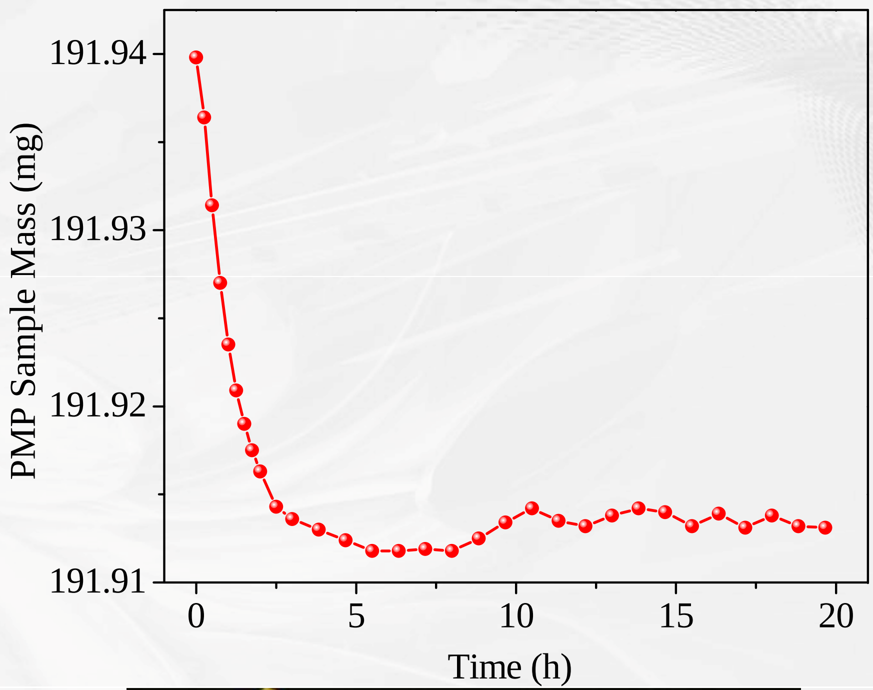
Reference Material Development Approach

- Select a suitable material
- Load the material with VOC at constant concentration
- Distribute reference material to different laboratories for chamber emission tests

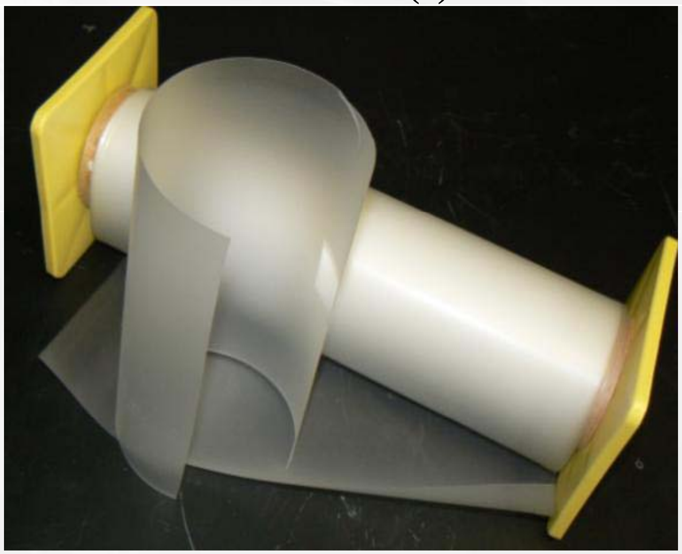
- Establish “reference value”
  - NIST-only measurement
  - Inter-laboratory measurements
  - Predict the emission profile of the material with mechanistic model using independently measured material characteristics.

Material Selection

- Uniformity
- Purity
- Stability
- Similar emission profiles to indoor VOC sources

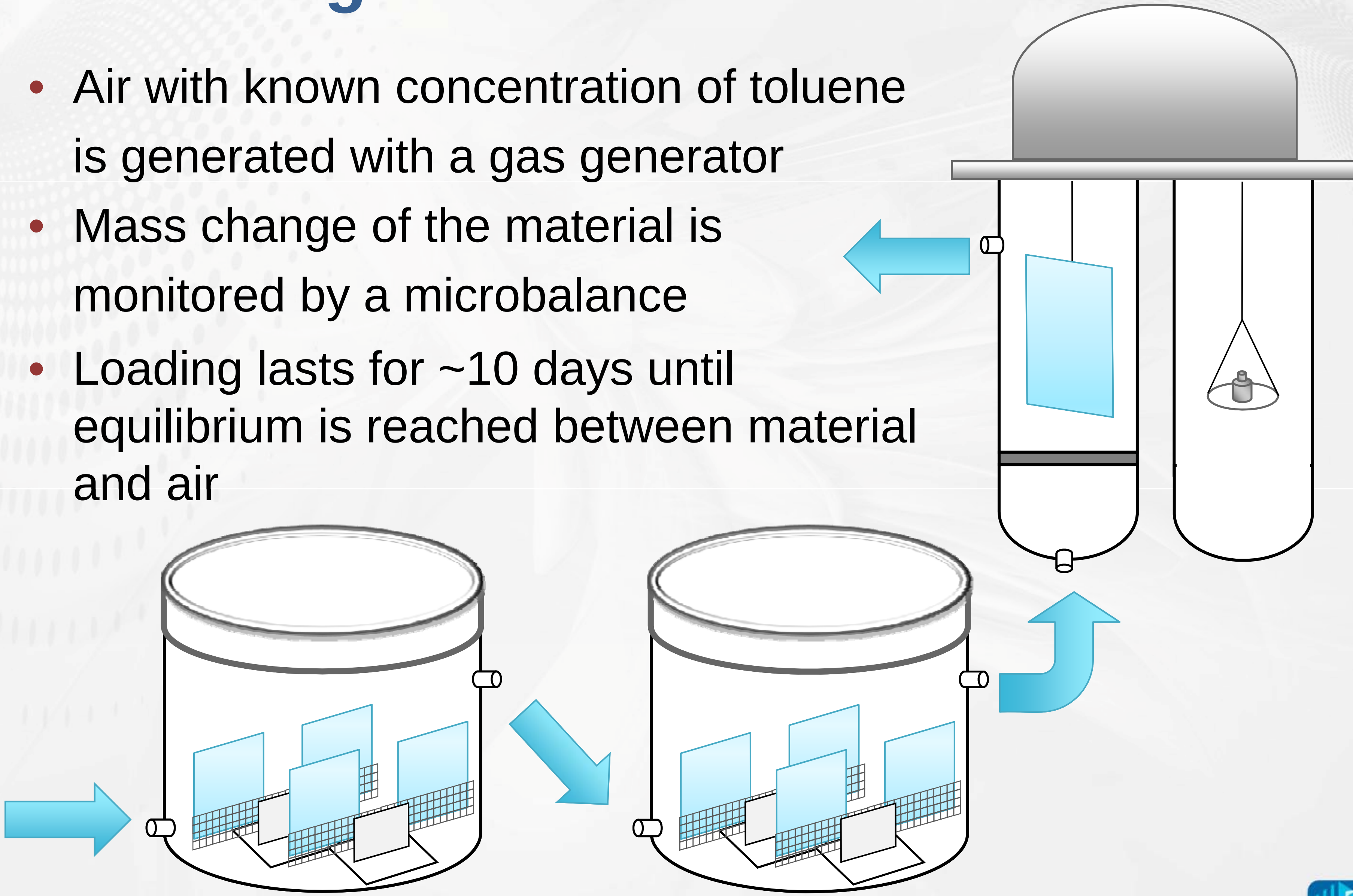


- Polymethylpentene (PMP)

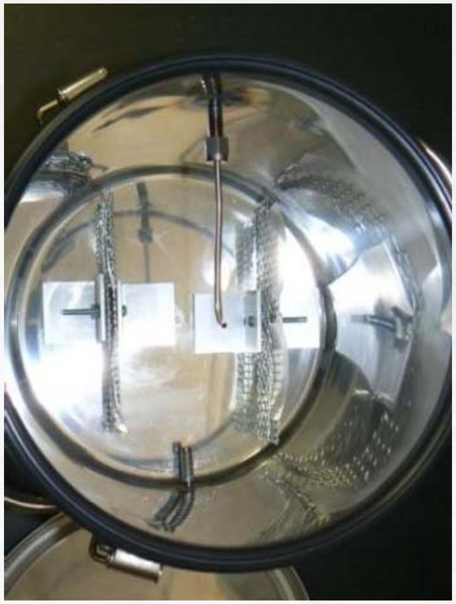


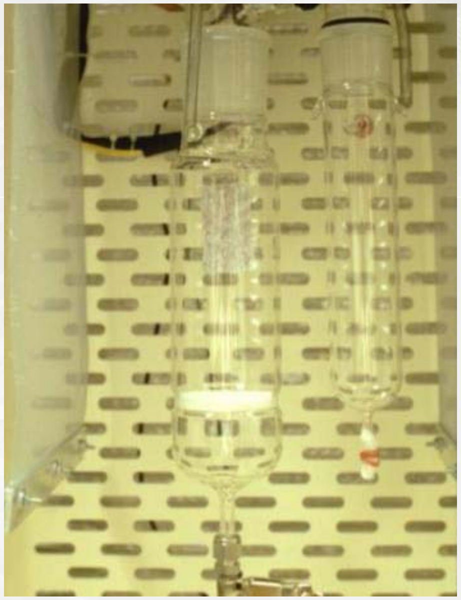
Loading VOC into the Material

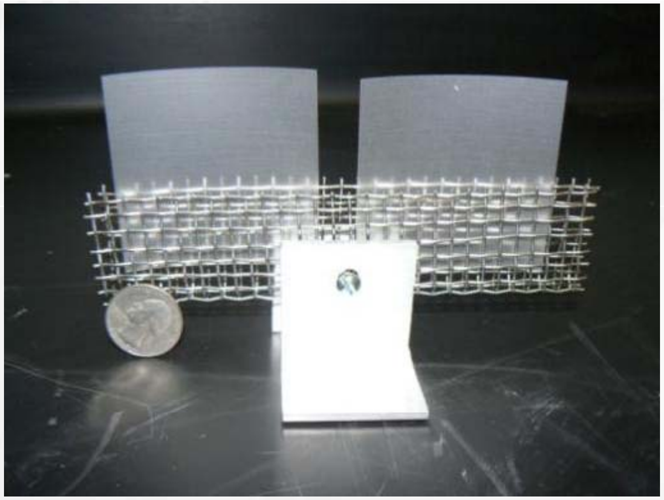
- Air with known concentration of toluene is generated with a gas generator
- Mass change of the material is monitored by a microbalance
- Loading lasts for ~10 days until equilibrium is reached between material and air



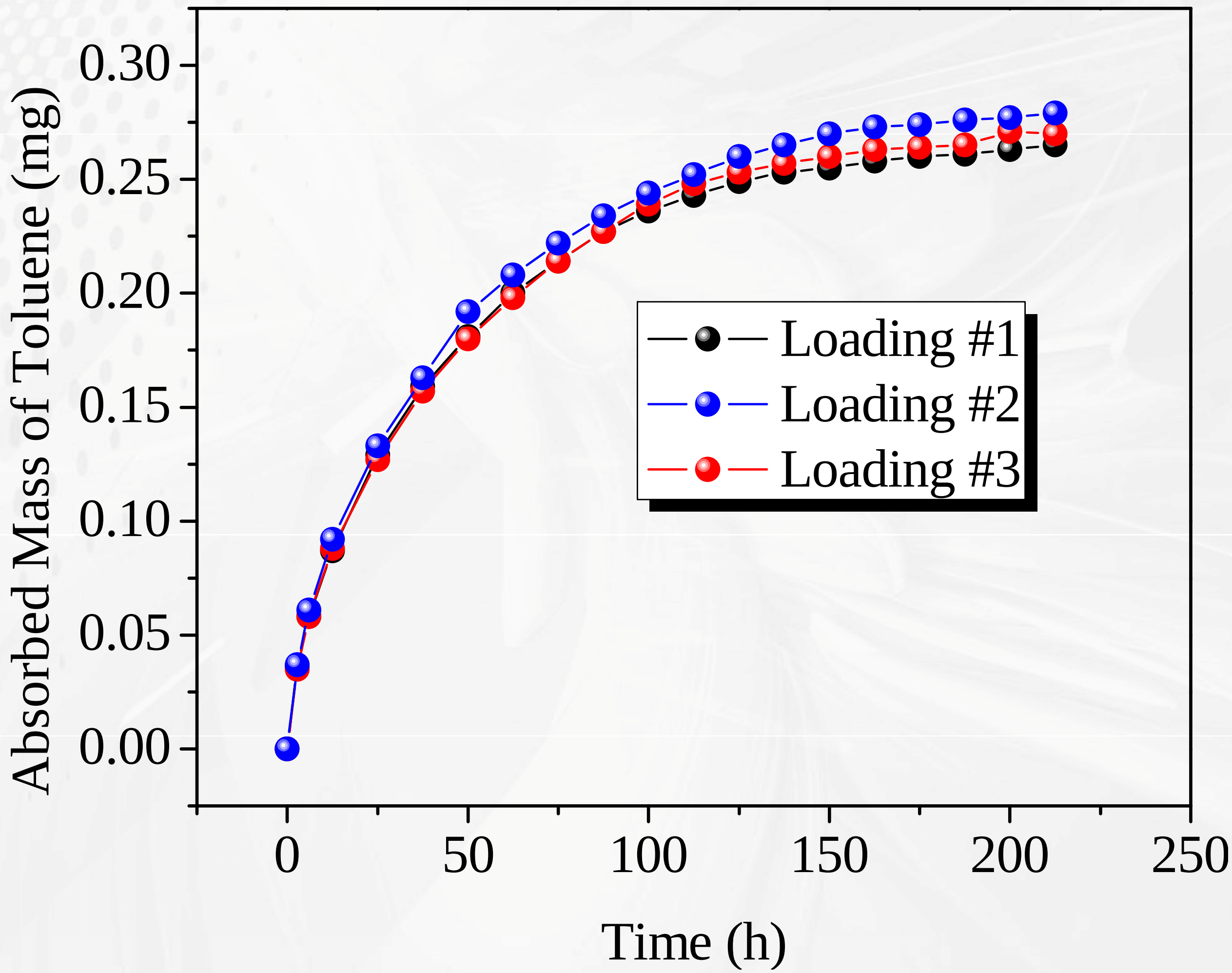
Loading VOC into the Material







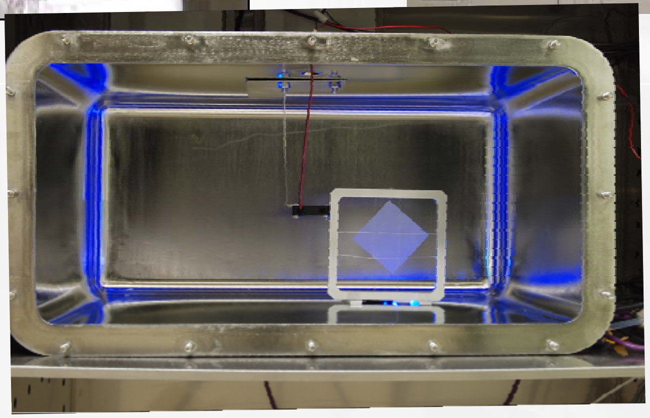
Loading VOC into the Material



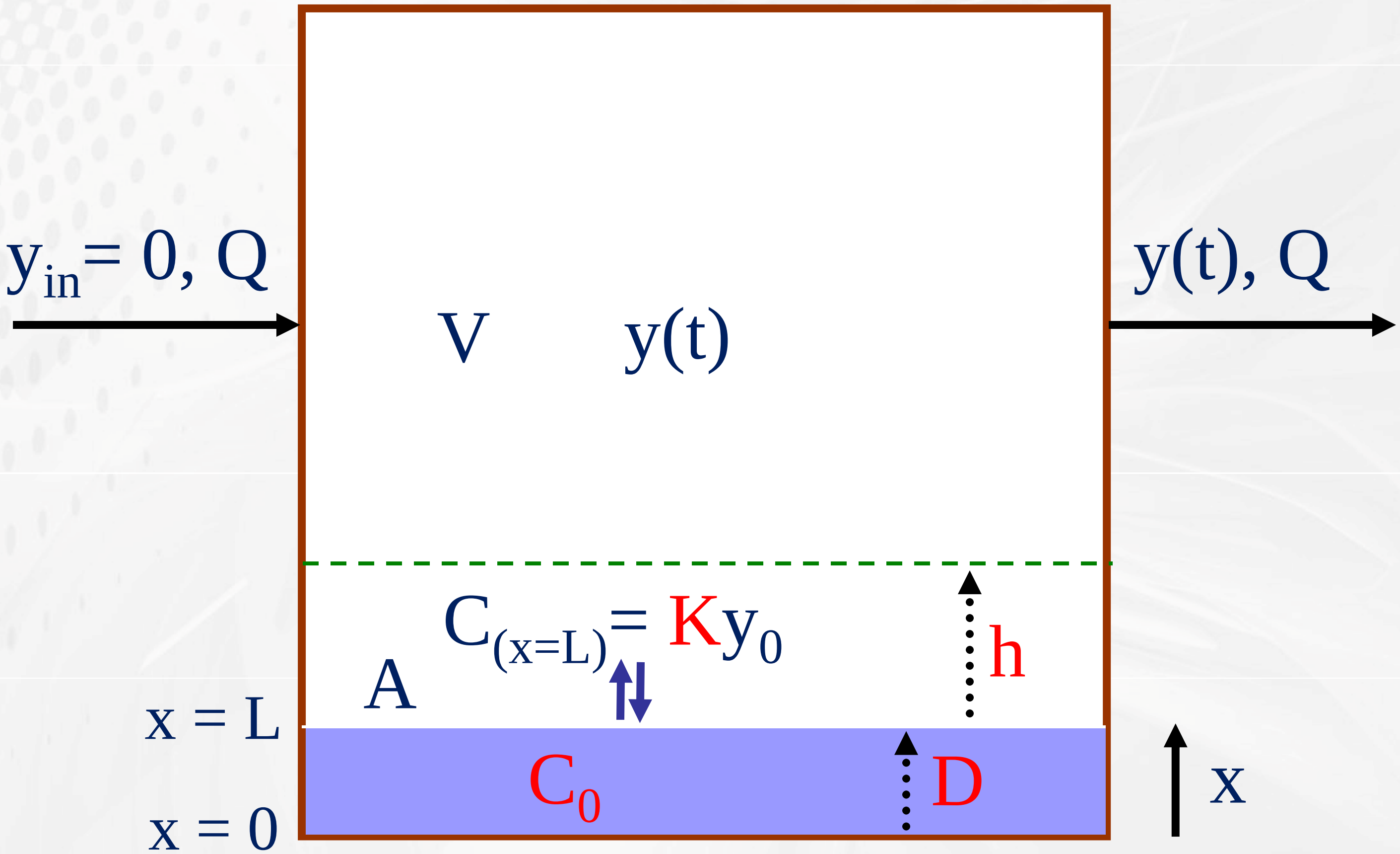
Distributing Loaded Materials

Emission Chamber Test

- ASTM Standard Guide for Small-Scale Environmental Chamber Determinations of Organic Emissions from Indoor Materials/Products (ASTM D5116-10)



Predicting Emission Profiles



Predicting Emission Profile

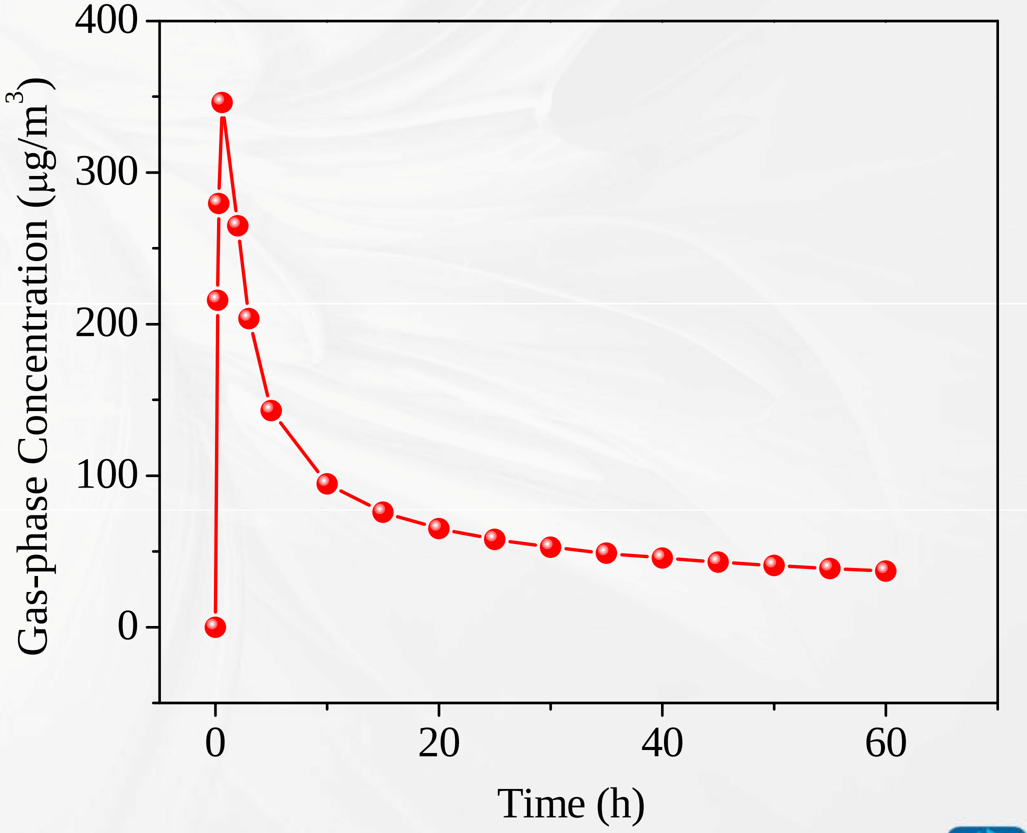
$$C(x,t) = 2C_0 \sum_{n=1}^{\infty} \left\{ \frac{\exp\left(-Dq_n^2 t\right)\left(h - kq_n^2\right)\cos(q_n x)}{[L\left(h - kq_n^2\right)^2 + q_n^2 (L + k) + h]\cos(q_n L)} \right\}$$

$$h = \frac{Q}{ADK}$$

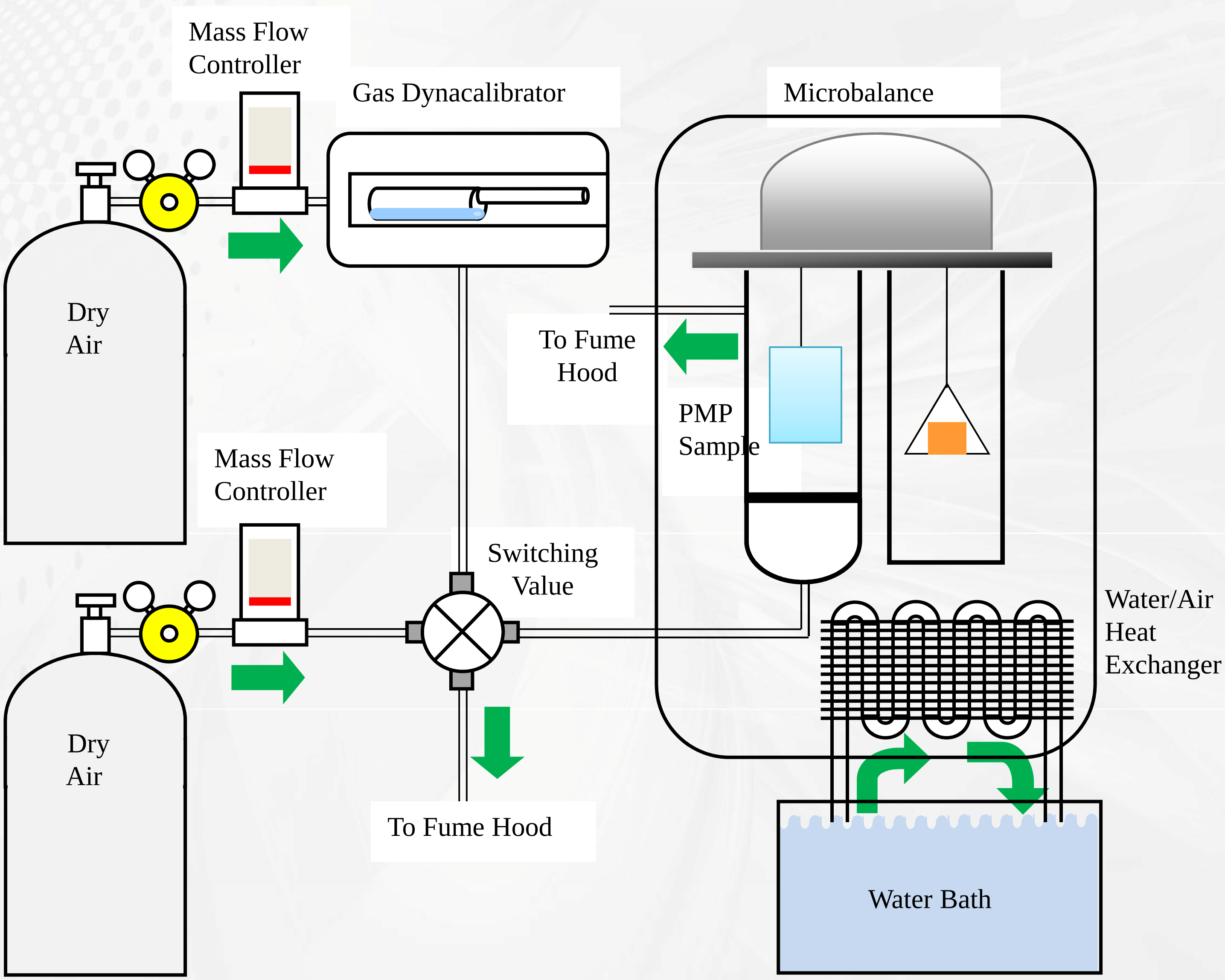
$$k = \frac{V}{AK}$$

$$q_n \tan(q_n L) = h - kq_n^2$$

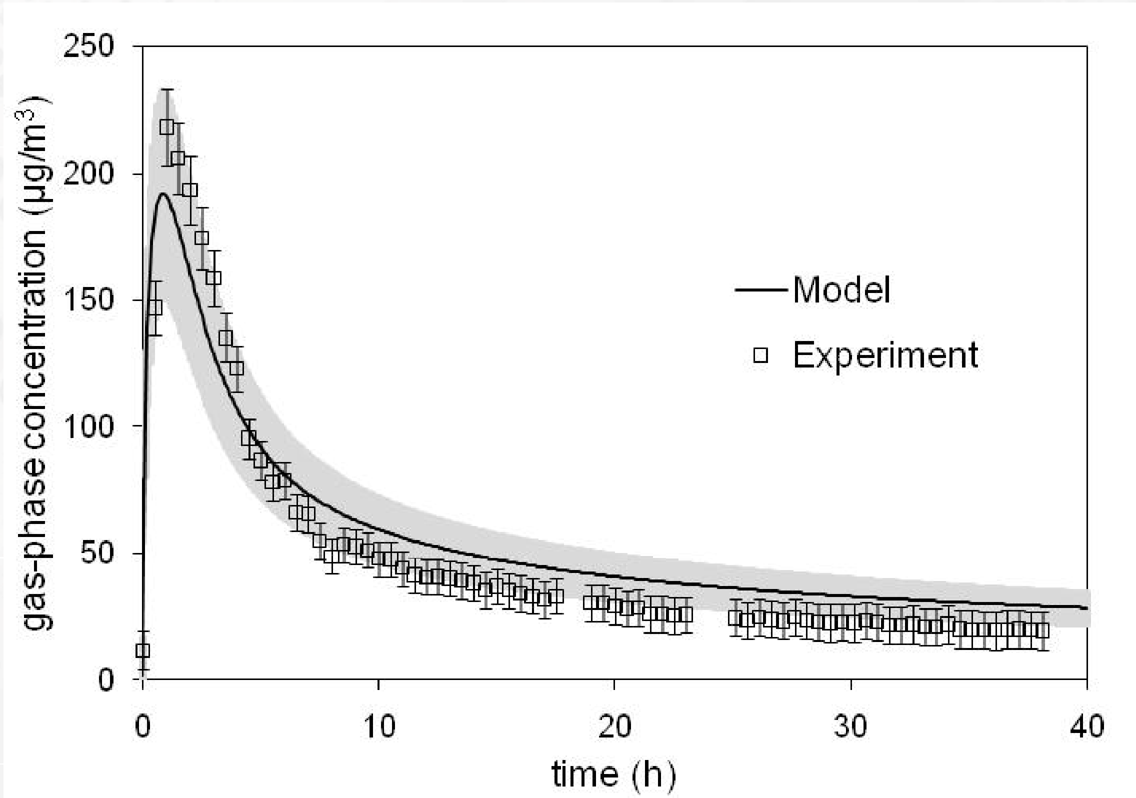
$$y = \frac{C|_{x=L}}{K}$$

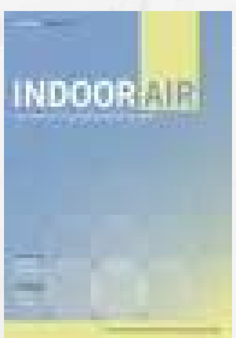


Characterizing Emission Parameters



NIST Chamber and Model Results





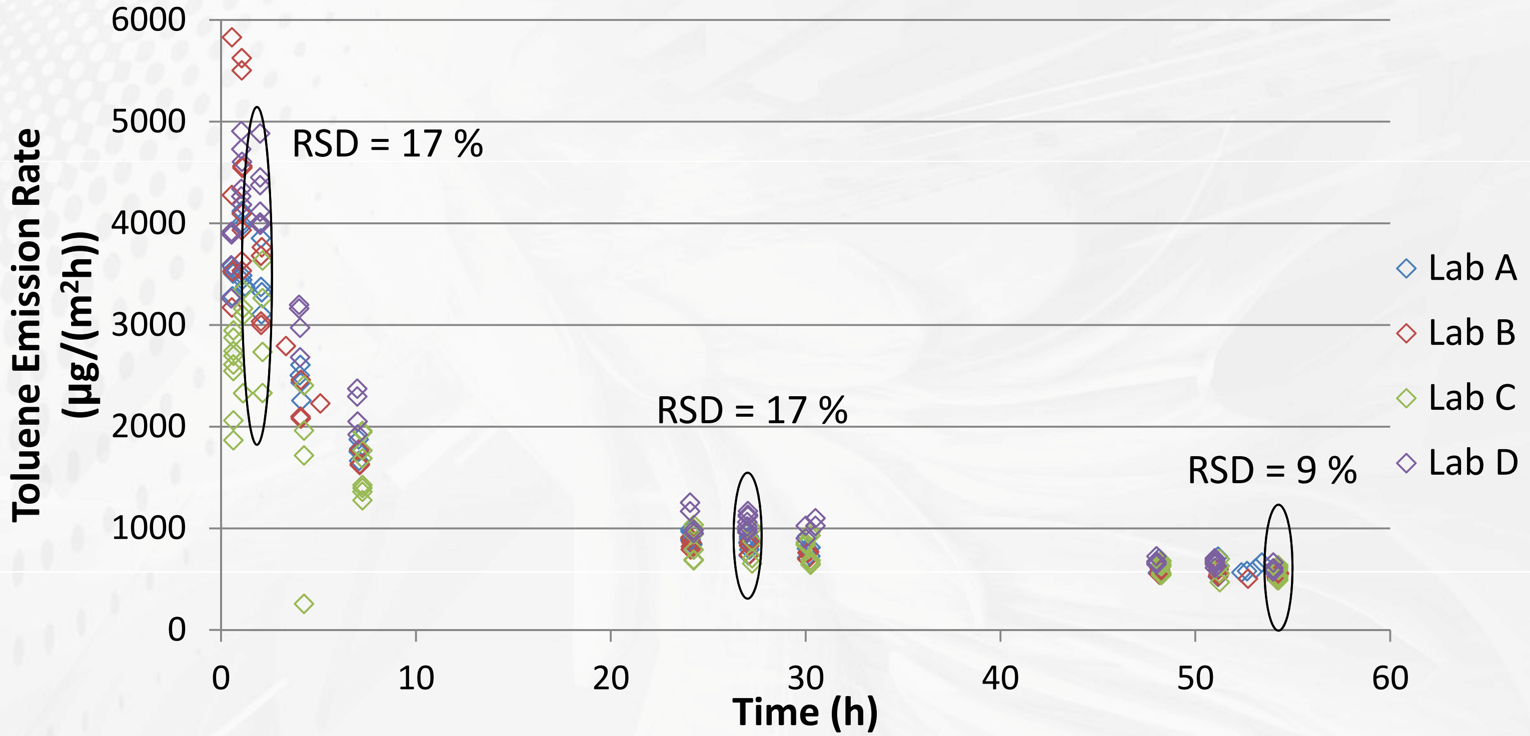
Publication:

Cox, S.S., Liu, Z., Little, J.C., Howard-Reed, C., Nabinger, S. and Persily, A. (2010) “Diffusion-controlled Reference Material for VOC Emissions Testing: Proof of Concept,” *Indoor Air* **20**: 424 – 433.

Pilot Inter-laboratory Study #1

- Four North American laboratories (chamber volumes 0.05 m^3 to 0.086 m^3)
- Each lab tested 4 reference films (2 films from 2 production batches)
- Specified
  - Chamber conditions: temp = 23 °C, RH = 50 %, airflow rate = 0.065 m^3/h, mixing fan = off
  - Test method: sample preparation and orientation in chamber, sample collection times (11 samples collected between 0.5 h – 54 h), liquid standard to check analytical calibration

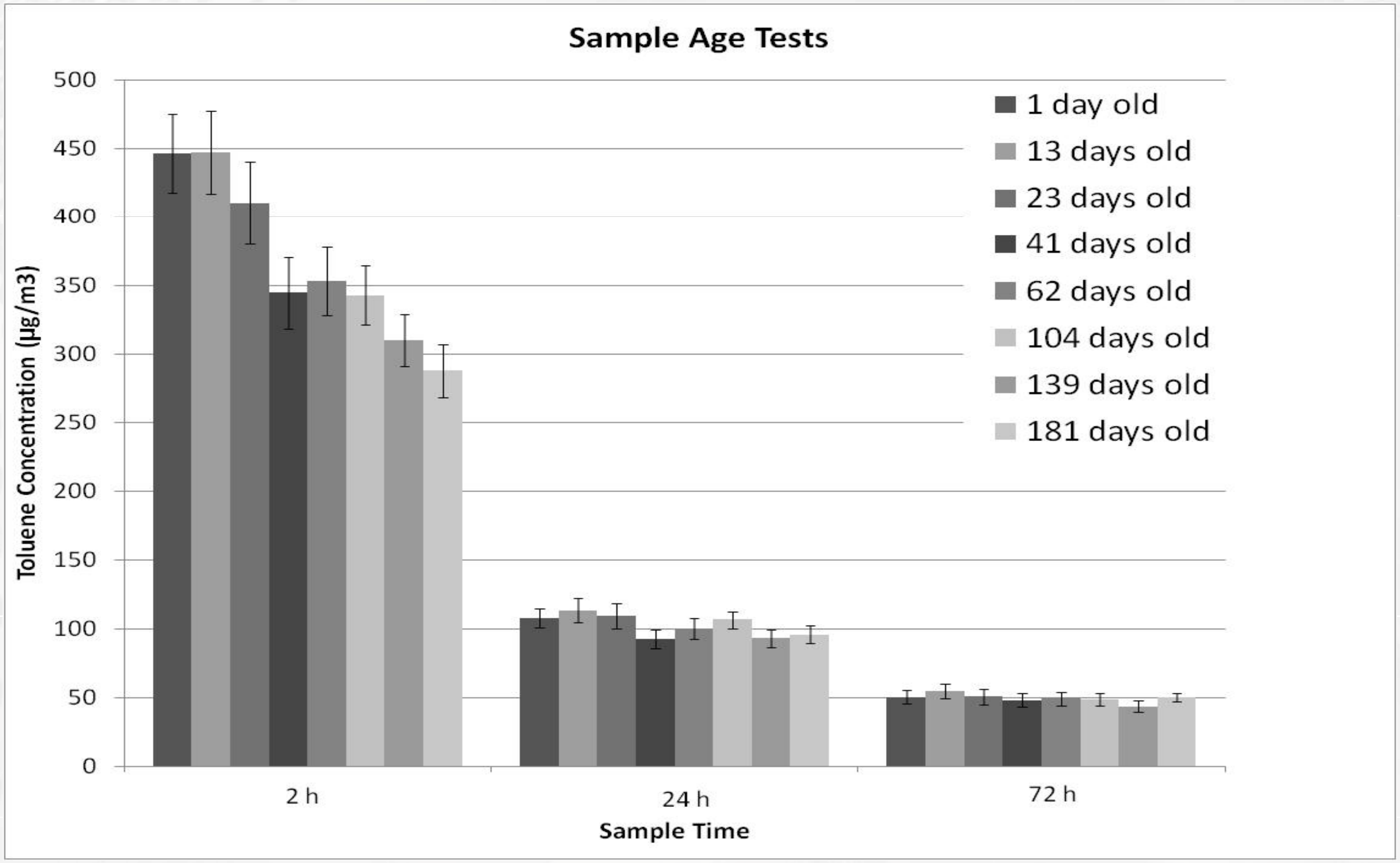
Pilot ILS #1 Results



Publication:

Howard-Reed, C., Liu, Z., Benning, J., Cox, S., Samarov, D., Leber, D., Hodgson, A., Mason, S., Won, D., and Little, J.C. (2011) "Diffusion-controlled Reference Material for VOC Emissions Testing: Pilot ILS," *Building and Environment*.

Factor Tests: Sample Age



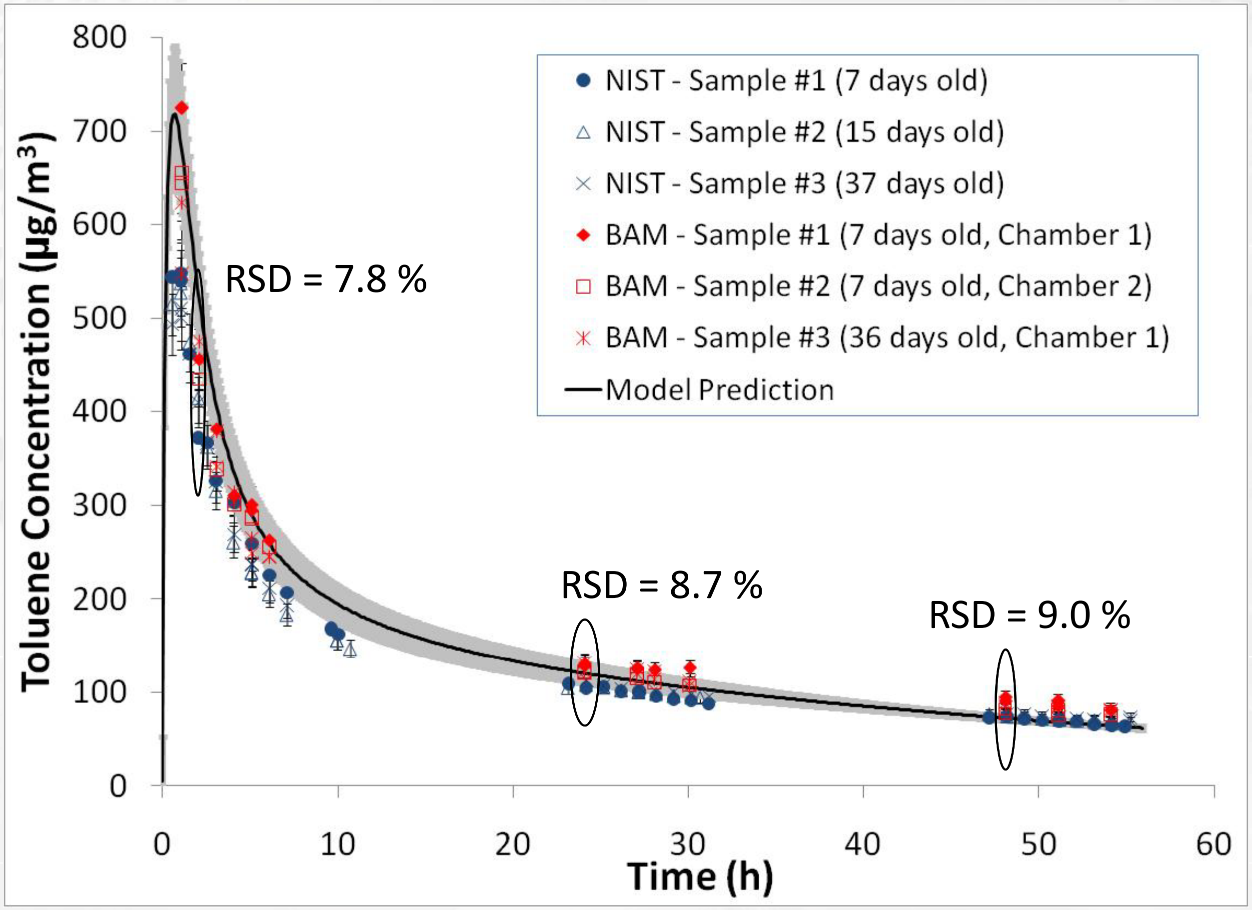
Publication:

Howard-Reed, C., Liu, Z., Cox, S.S., Samarov, D., Leber, D., and Little, J.C. (2011) “Assessing the shelf-life of a prototype reference material for product emissions testing,” in Proceedings of Indoor Air 2011, June 2011.

Pilot Inter-laboratory Study #2

- NIST (51 L chamber) and BAM German Federal Institute for Materials Research and Testing (24 L chamber)
- Each lab tested 3 reference films (all from the same batch)
- Specified
  - Chamber conditions: temp = 23 °C, RH = 50 %, airflow rate = 0.065 m^3/h, mixing fan = on
  - Test method: sample preparation and 2-side orientation in chamber, sample collection times (11 samples collected between 0.5 h – 54 h)

Pilot ILS #2 Results



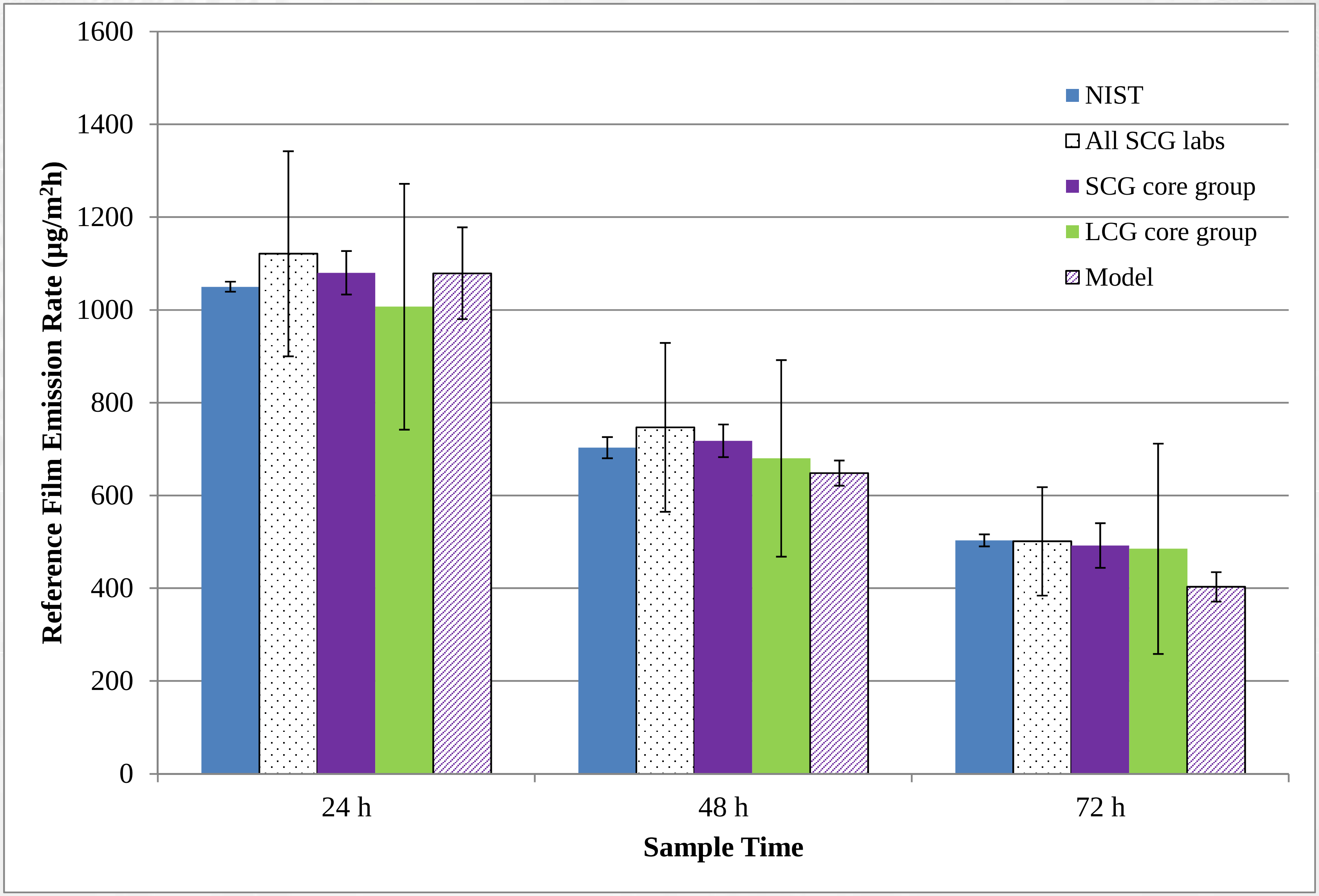
Publication:

Howard-Reed, C., Liu, Z., Cox, S.S., Little, J.C., Horn, W., Wilke, O., Wiegner, K., and Persily, A. (2011) "Inter-laboratory study approach to validate the performance of a prototype reference material for product emissions testing," in Proceedings of Indoor Air 2011, June 2011.

International Inter-laboratory Study

- 14 laboratories representing 7 countries
- 10 “small” chambers and 4 “large” chambers
- Each lab ran 2 reference film tests (all films made in the same batch)
- Specified
  - Chamber conditions: temp = 23 °C, RH = 50 %, airflow rate = 0.055 m^3/h for small chambers and 0.30 m^3/h for large chambers
  - Test method: sample preparation and 2-side orientation in chamber, sample collection times (duplicate samples collected at 24 h, 48 h, and 72 h)

International ILS Emission Rate Comparison



Next Steps

- Further improvement tests underway
  - Improved packaging
  - Temperature, RH, airflow effects on emissions
- Add more chemicals to the film
  - Formaldehyde
  - Butanol
  - Dodecane
- Transition to production phase