

**National Ambient Air Monitoring Conference**

**Technical Session: Air Toxics**

# **Characterizing the Short-Term Temporal Stability of Volatile Organic Compounds in Stainless Steel Canisters**

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**This work was performed by Battelle  
under contract to the U.S. Environmental  
Protection Agency**

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Battelle Collaborators: Laura Aume, Ian Macgregor, Robert Woodruff**

# Motivation

- Since 2003, the U.S. EPA has operated the National Air Toxics Trends Stations (NATTS) monitoring program
- On a quarterly basis, NATTS laboratories receive and analyze a single-blind proficiency test (PT) sample in order to assess the extent of *analytical bias*
- Laboratories are obligated to perform only a single analysis of the PT sample
- The temporal stability of some VOCs is uncertain and may impact bias assessment

Analytical bias represents the difference between the laboratory's measurement and the sample's assigned target value

# Objectives of this analysis

1. Investigate the short-term stability of trace-level VOCs collected in stainless steel canisters
2. Assess how stability affects the results reported for VOCs within the NATTS PT program

# Methods

- NATTS PT cycle: Quarter #1 of Calendar Year 2013
- Battelle prepared/shipped canisters containing 15 VOCs
  - Nominal spiked concentration of ~1.2 ppb
  - FSL and Summa canisters
  - Filled at 30 psia
  - Shipped to 29 laboratories (NATTS, non-NATTS, reference labs)
- Each laboratory was to perform **three replicate analyses**:
  - Temporal replicate #1: As soon as possible upon receipt of canister
  - Temporal replicate #2: ~7 calendar days after the first analysis
  - Temporal replicate #3: ~7 calendar days after the second analysis.



# Participating Laboratories

Lab ID	Location	Lab Name	Affiliation
01-01	Providence, RI	RI Dept of Health, Air Pollution Laboratory	NATTS
01-04	North Chelmsford, MA	US EPA Region 1 Lab	NATTS
01-05	Augusta, ME	Maine DEP Air Lab	Non-NATTS
02-01	Rensselaer, NY	NYS DEC	NATTS
03-01	Baltimore, MD	MDE Air Toxics Lab	NATTS
03-02	Richmond, VA	Division of Consolidated Labs (VBRP#6)	NATTS
03-03	Harrisburg, PA	PA DEP, Bureau of Air Quality	Non-NATTS
04-01	Tampa, FL	Pinellas County DEM AQD	NATTS
04-02	Chesterfield, SC	SCDHEC/DAQA	NATTS
04-04	Atlanta, GA	GA DNR, EPD Laboratories	NATTS
04-06	Raleigh, NC	NC DENR	Non-NATTS
04-08	Davie, FL	Broward County Environmental Laboratory	Non-NATTS
04-09	Research Triangle Park, NC	US EPA NRMRL	Reference Lab
05-03	Mayville, WI	Wisconsin DNR	NATTS
05-04	St. Paul, MN	MPCA	Non-NATTS
05-07	Groveport, OH	Ohio EPA	Non-NATTS
05-08	Chicago, IL	US EPA R5 Chicago Regional Laboratory	Non-NATTS
06-01	Houston, TX	Texas CEQ Air Laboratory	NATTS
07-02	Coralville, IA	State Hygienic Lab, Univ. of Iowa	Non-NATTS
09-03	San Francisco, CA	BAAQMD	NATTS
09-06	San Diego, CA	San Diego APCD	Non-NATTS
09-08	Diamond Bar, CA	South Coast AQMD Laboratory	NATTS
09-09	Carson, CA	JWPCP Water Quality Laboratory	Non-NATTS
09-10	Sacramento, CA	CARB Organic Laboratory	Non-NATTS
10-02	LaGrande, OR	Oregon DEQ	NATTS
11-01	Morrisville, NC	ERG	NATTS
N/A	Folsom, CA	Eurofins Air Toxics <sup>b</sup>	Reference Lab

# Study facts

- Battelle received data from 14 NATTS laboratories, 11 non-NATTS laboratories, and 2 reference laboratories.
- 5 laboratories (4 NATTS, 1 non-NATTS) reported measurement only at the first time point
- The 2 reference laboratories each received 2 canisters
  - Served as confirmatory analyses and for determining target conc.
- 1 NATTS laboratory performed analyses and reported results for two different instruments
- Some laboratories chose to reduce the canister pressure prior to analysis

# VOCs

Analyte	# Laboratories with Data	Target concentration, ppb	% recovery compared to nominal
Acrolein	17 (15 for trends)	1.39	116
Benzene	19	1.16	96
1,3-Butadiene	19	1.22	102
Carbon Tetrachloride	19	1.29	107
Chloroform	19	1.28	107
1,2-Dibromoethane	17	1.13	94
1,3-Dichloropropene - <i>cis</i>	16	1.03	86
1,3-Dichloropropene - <i>trans</i>	16	1.15	96
1,2-Dichloropropane	15	1.16	97
1,2-Dichloroethane	18	1.13	94
Dichloromethane	19	1.34	112
1,1,2,2-Tetrachloroethane	15	1.14	95
Tetrachloroethylene	19	1.12	93
Trichloroethylene	19	1.11	93
Vinyl chloride	19	1.29	108

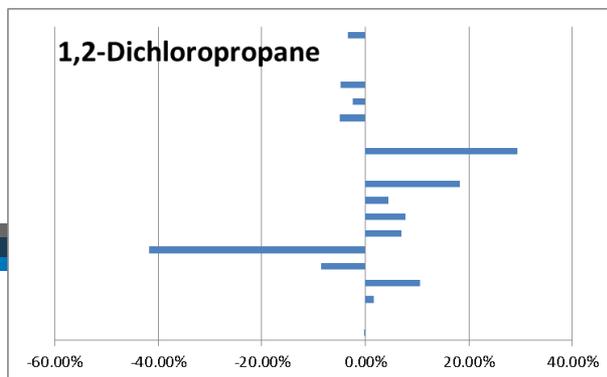
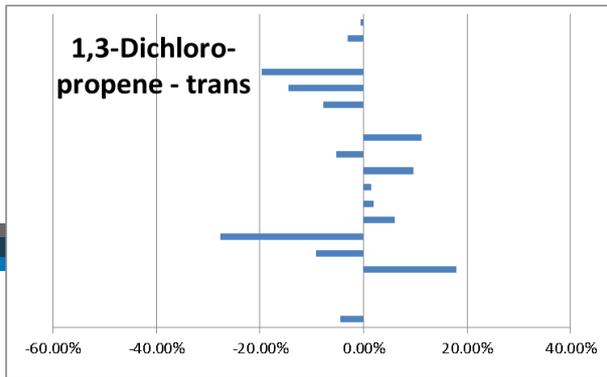
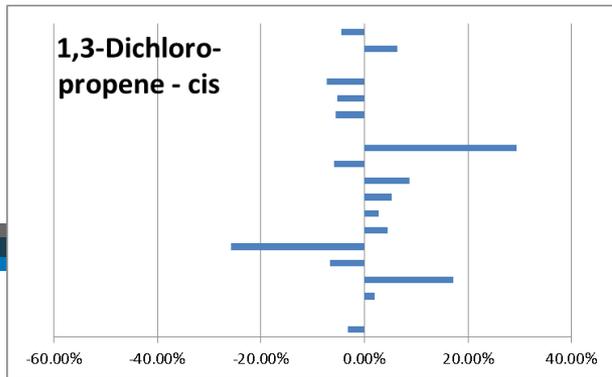
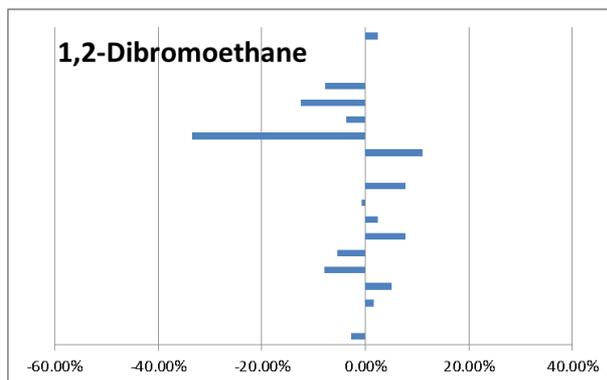
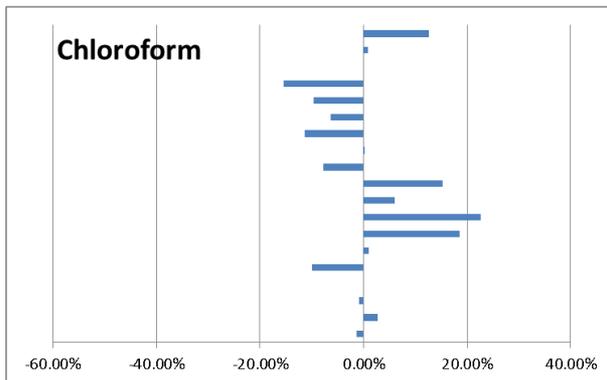
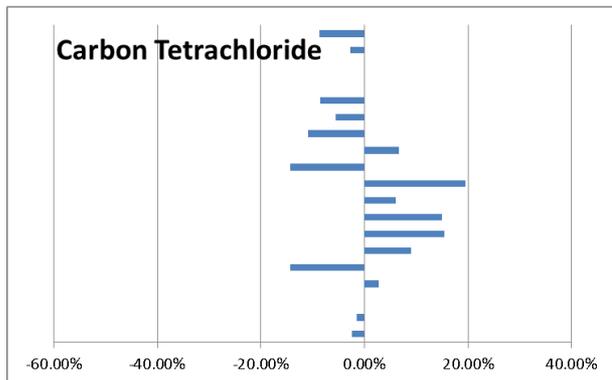
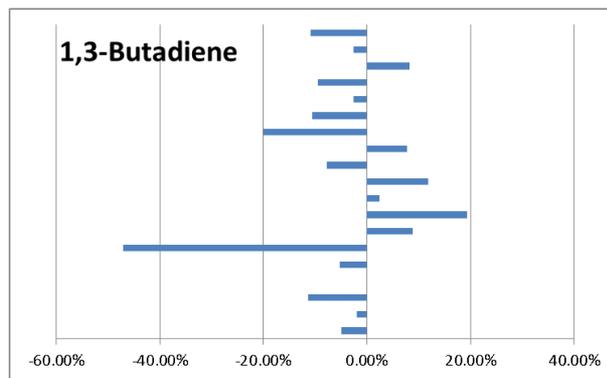
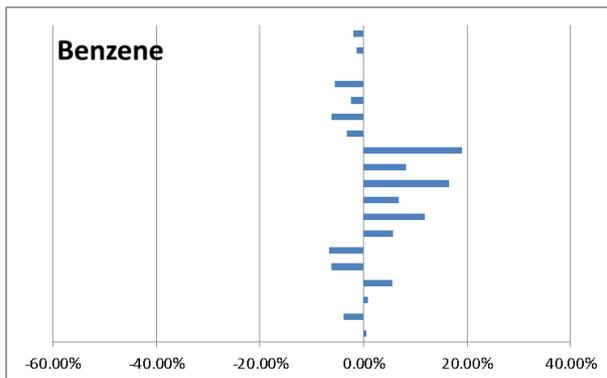
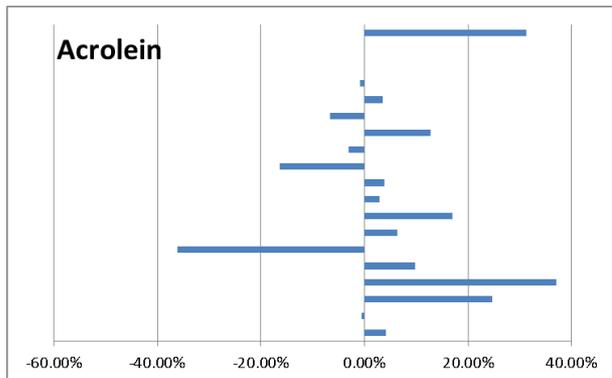
# First Data Analysis

How does the percent change in concentration over time differ between canister types and whether or not the canister pressure was reduced?  
Is this percent change negative over time?

$$\% \text{ change} = (\text{Replicate \#3} - \text{Replicate \#1}) * 100 / (\text{Replicate \#1})$$

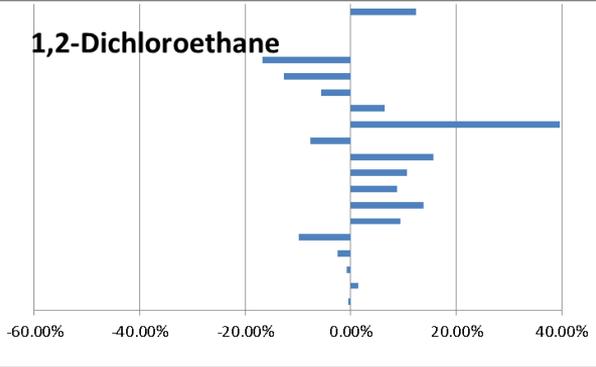
- Analysis of variance (ANOVA) models (one- and two-way)
- No significant relationship between canister type and pressure reduction indicator was observed
- Statistical test of model's intercept term determined whether percent change was significantly less than 0%

# Percent Change from Replicate #1, by Laboratory

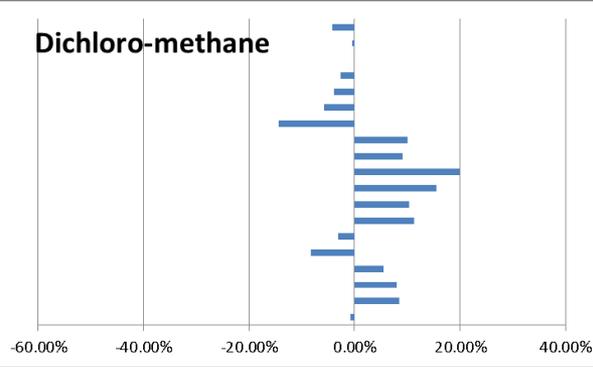


# Percent Change from Replicate #1, by Laboratory

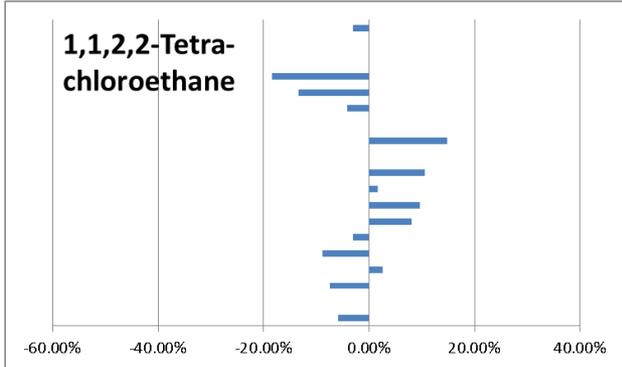
1,2-Dichloroethane



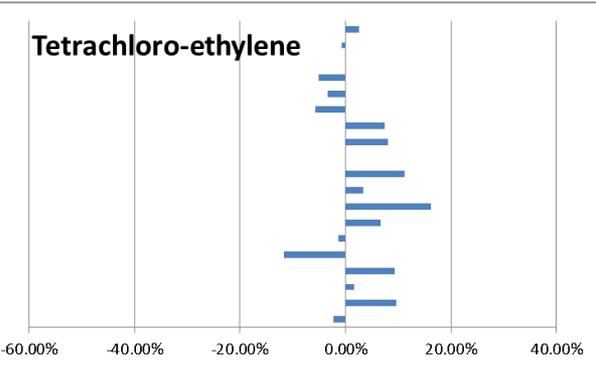
Dichloro-methane



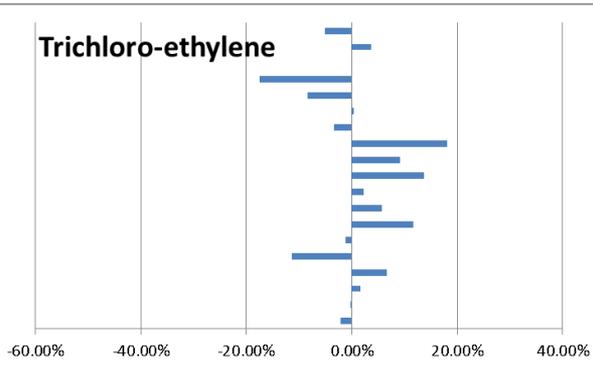
1,1,2,2-Tetra-  
chloroethane



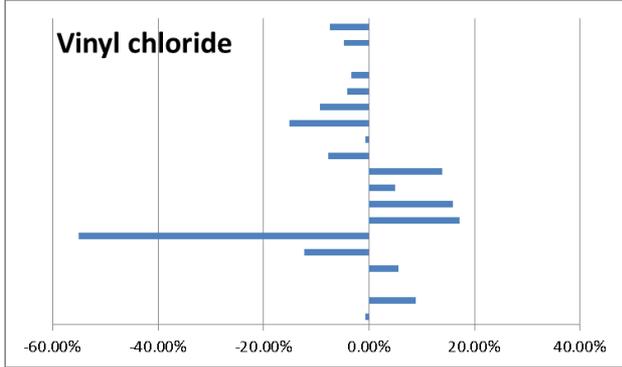
Tetrachloro-ethylene



Trichloro-ethylene



Vinyl chloride



# Extent of Consistent Trend Over Three Time Points

Analyte	# Labs with Non-Increasing Trend	# Labs with Non-Decreasing Trend	# Labs with Mixed Trend
Acrolein	2	4	11
Benzene	3	4	12
1,3-Butadiene	6	2	11
Carbon Tetrachloride	6	4	9
Chloroform	3	4	12
1,2-Dibromoethane	4	1	12
1,3-Dichloropropene - <i>cis</i>	3	4	9
1,3-Dichloropropene - <i>trans</i>	3	2	11
1,2-Dichloropropane	3	3	9
1,2-Dichloroethane	4	5	9
Dichloromethane	2	5	12
1,1,2,2-Tetrachloroethane	3	2	10
Tetrachloroethylene	1	5	13
Trichloroethylene	1	2	16
Vinyl chloride	4	2	13

# Key Results of First Data Analysis

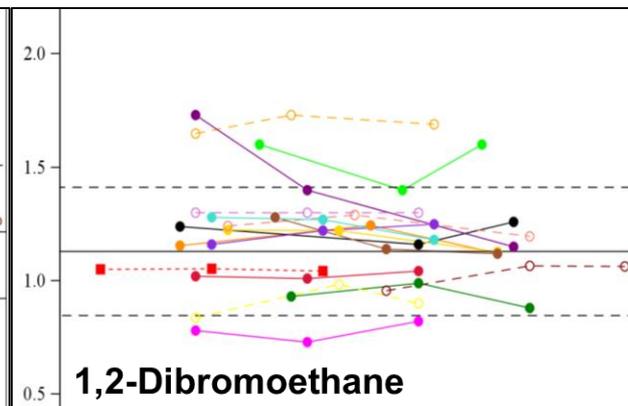
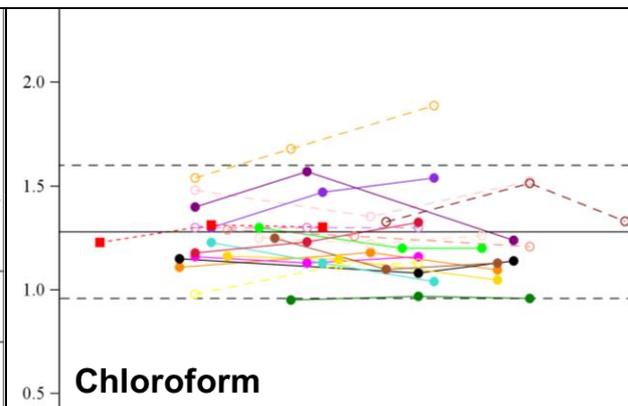
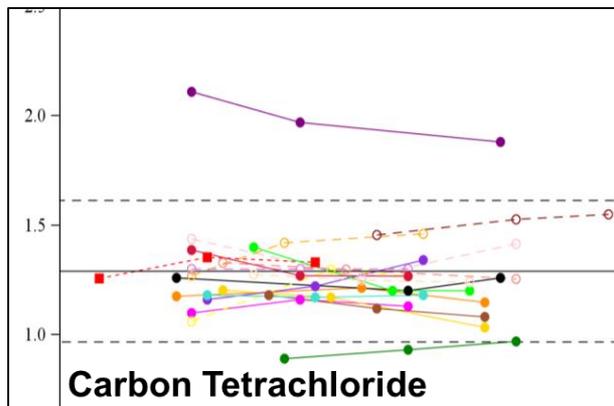
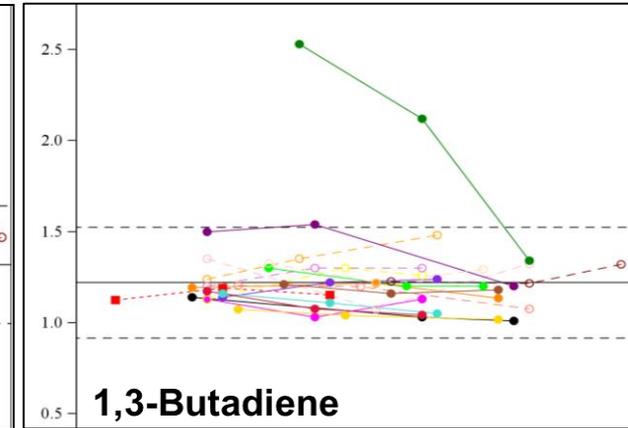
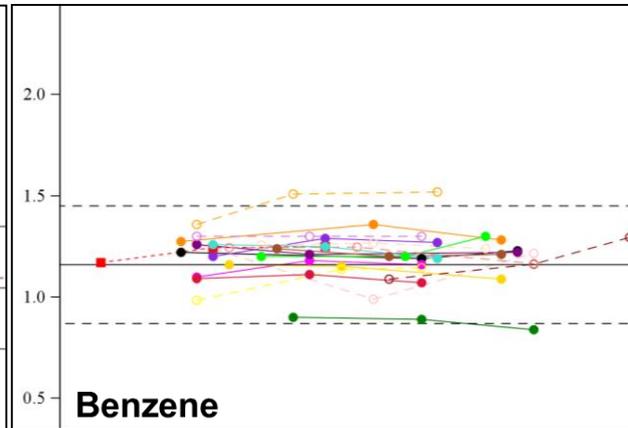
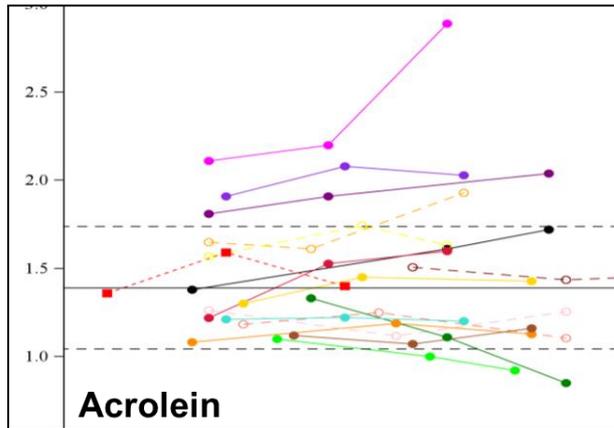
- ANOVA did not find percent change to be significantly less than zero
- ANOVA found no significant differences in percent change between the two canister types or presence vs. absence of pressure reduction
- Average and median percent change values were
  - Consistently  $> 0$  for Summa canisters (10-11 labs)
  - Consistently  $< 0$  for FSL canisters (6-8 labs)

# Second Data Analysis

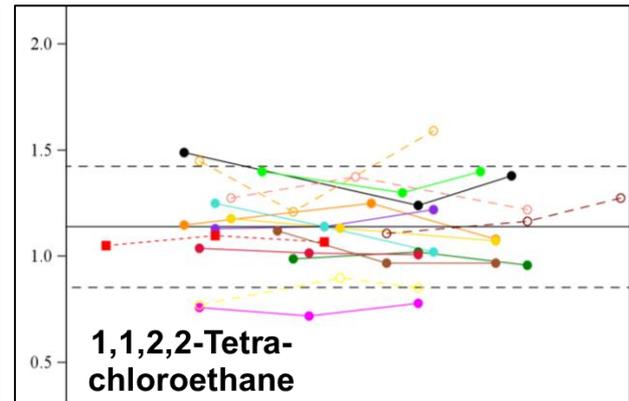
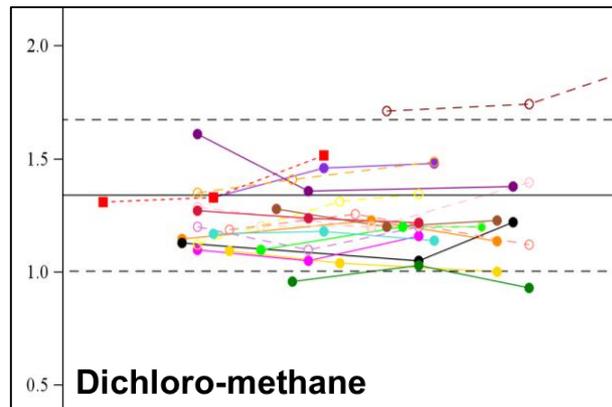
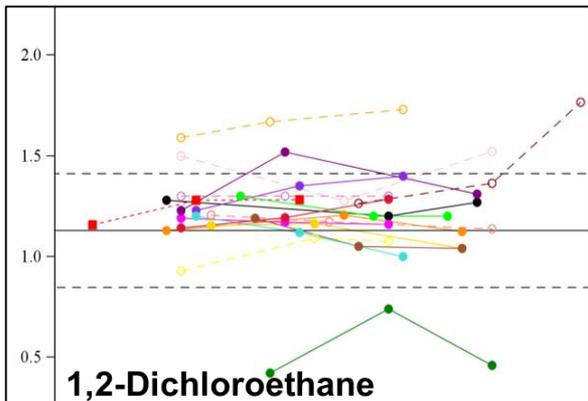
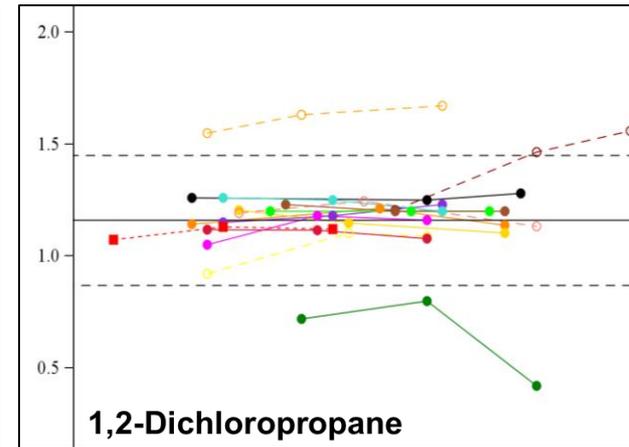
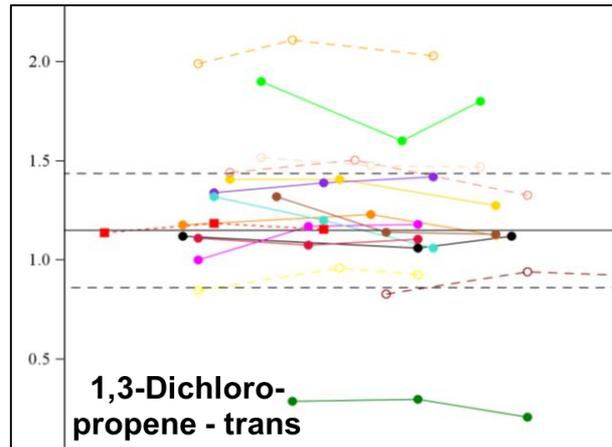
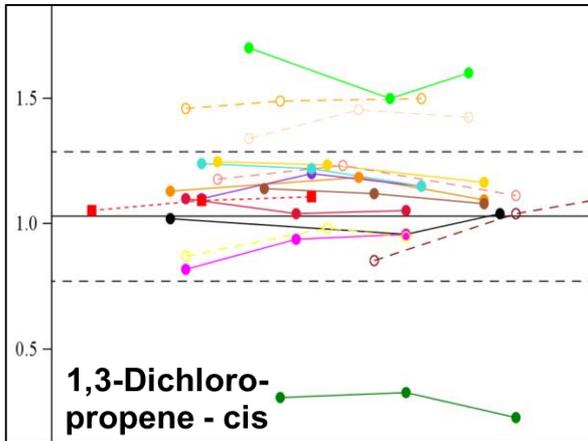
Does a significant relationship exist between measured concentration and the number of days since the canister was prepared?

- ANOVA/regression model with number of days, canister type, and reduced canister pressure indicator included
  - Model accounts for the inherent correlation present among repeated measurements within a laboratory
  - Model fitted for each VOC
  - Test of significance performed on the slope parameter associated with number of days

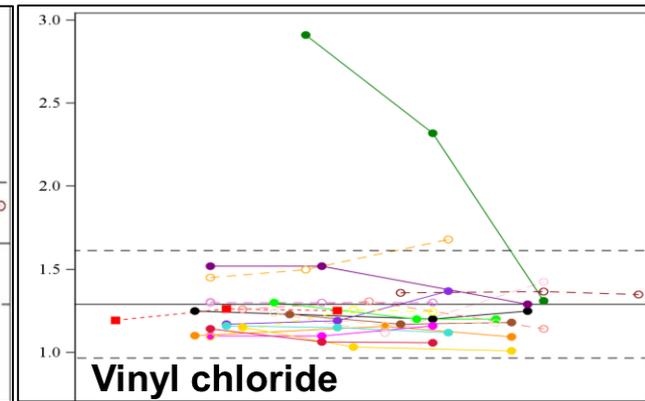
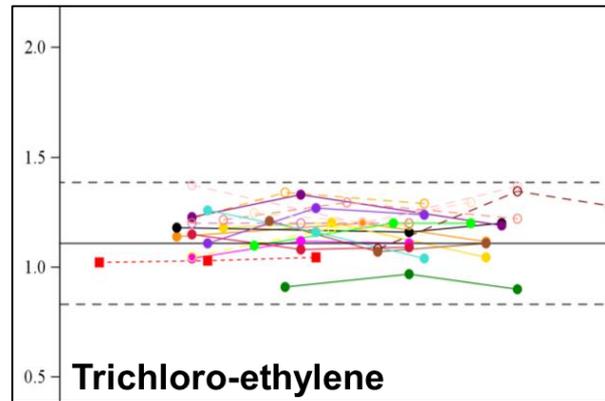
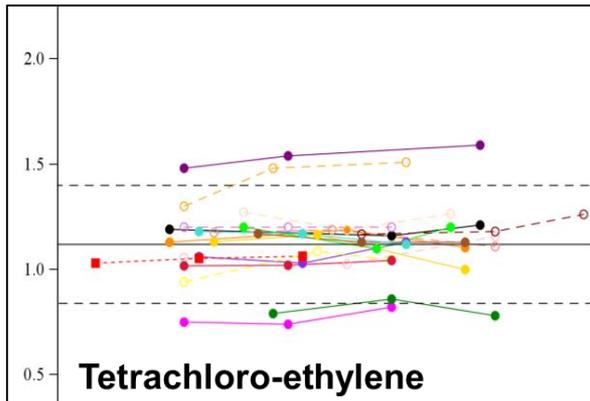
# Plots of Conc. vs. Elapsed Time (Days) Since Canister Preparation



# Plots of Conc. vs. Elapsed Time (Days) Since Canister Preparation



# Plots of Conc. vs. Elapsed Time (Days) Since Canister Preparation



- Trends in VOC concentrations over 2-3 weeks are negligible
  - No significant association between VOC concentration and time (based on ANOVA model)
- Generally consistent profiles among labs (with some exceptions)
- Greater lab-to-lab variability in trends for acrolein compared to, say, benzene

# Key Findings

- No significant decrease in VOC concentrations occurred on average between the time of canister sample preparation and when the last of three replicate analyses was completed (generally within 30 days).
- Average percent change in VOC concentrations over about a two week period was not significantly impacted on average by the elapsed time from sample preparation, nor by canister type or by pressure reduction.
- While qualitative trends were observed in VOC recovery over time for certain laboratories and VOCs, evidence was insufficient to indicate a statistically significant trend in a typical laboratory.

# Thank you

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