Characterizing Influence of PTFE-coated Neoprene Pump Diaphragm Material on Trace Gas Measurements

Kyle Petersen[1,2], Scott Clingan[1,2], Isaac Vimont[2], Stephen Montzka[2], Molly Crotwell[1,2], Brad Hall[2]
[1]-CIRES, University of Colorado, Boulder, USA; [2] -NOAA/ESRL/GML, Boulder, USA

Introduction

Continuous monitoring of our atmosphere through discrete air sampling is an essential activity to the mission of NOAA's Global Monitoring Laboratory (GML), allowing for the characterization of atmospheric composition. Ensuring samples are representative of original composition is critical to the integrity of the long term records produced by GML. Scientists at GML analyze ~70 trace compounds whose atmospheric mole fractions range between 100's of micromoles per mole (10^{-4} mol mol^{-1}) down to 100's of femtomoles per mol (10^{-13} mol mol^{-1}). Sample capture, storage, and transport have the potential to influence and contaminate sample analytes. It is critical that we understand and characterize the influence of all components in the sampling system when selecting equipment. Typically, piston-driven diaphragm pumps are used to draw the sample through a long inlet suspended above the ground and pressurize the air into a stainless steel or borosilicate glass flasks for future analysis. Because all sampling pumps of this type use semi-permeable polymers, there is potential for these materials to affect some of the analytes measured by GML.

Objective:

To compare a KNF UN86 pump equipped with a PTFE coated Neoprene diaphragm on trace gas measurements carried out by two of GML's GCMS instruments (identified as M3 and Perseus (PR1)). Design and build a lab test system that simulates pressure and flow conditions of GML field installations that collect flask samples.

Experiment Design

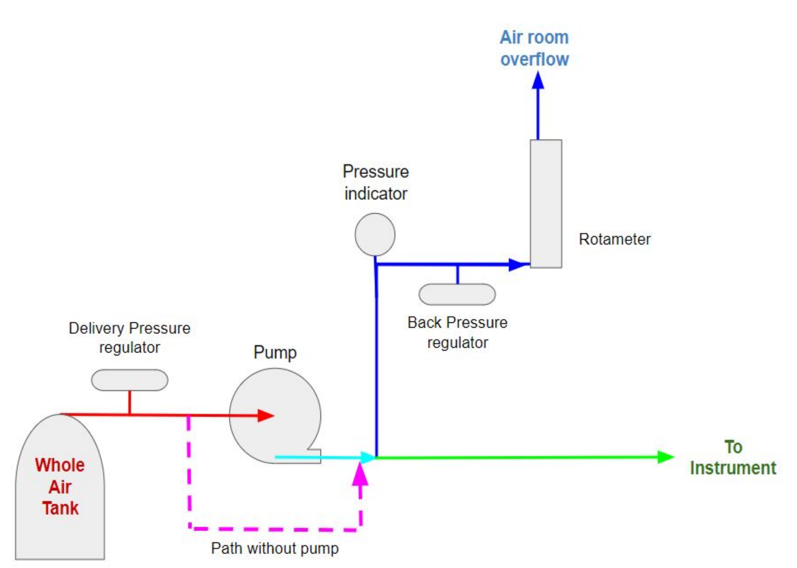

Figure 1: Line Diagram of Experimental Setup

Figure 2: KNF UN86 Diaphragm Gas Pump

Figure 1 illustrates the basic setup used to test the influence of the pump.

- Dry, ambient air pumped at Niwot Ridge pressurized into a bare-aluminum 29L cylinder to ~2000 psig w/ regulator
- KNF UN86 gas pump S/N 1.19381330
- Back pressure regulator
- Over flow rotameter
- ⅛" ID stainless steel tubing connecting all components

Test Configurations

	Configuration A (Reference State) Sampling system without pump	Configuration B Low Temp High Flow Entire Sampling System	Configuration C High Temp High Flow Entire Sampling System	Configuration D High Temp Low Flow Entire Samping System
Flushing Flow	1 lpm until 3 min prior to sampling	Pumped turned on after previous injection for warm-up 1 lpm until 3 min prior to sampling	Pumped turned on after previous injection for warm-up 1 lpm until 3 min prior to sampling	1 lpm
Sampling Flow	4 lpm, 3 minutes prior to, and during sampling	4 lpm, 3 minutes prior to and during sampling 1 lpm after sampling	4 lpm, 3 minutes prior to and during sampling 1 lpm after sampling	1 lpm
Back Pressure	7 psi for entire time	7 psi for entire time	30 psi for entire time	30 psi for entire time

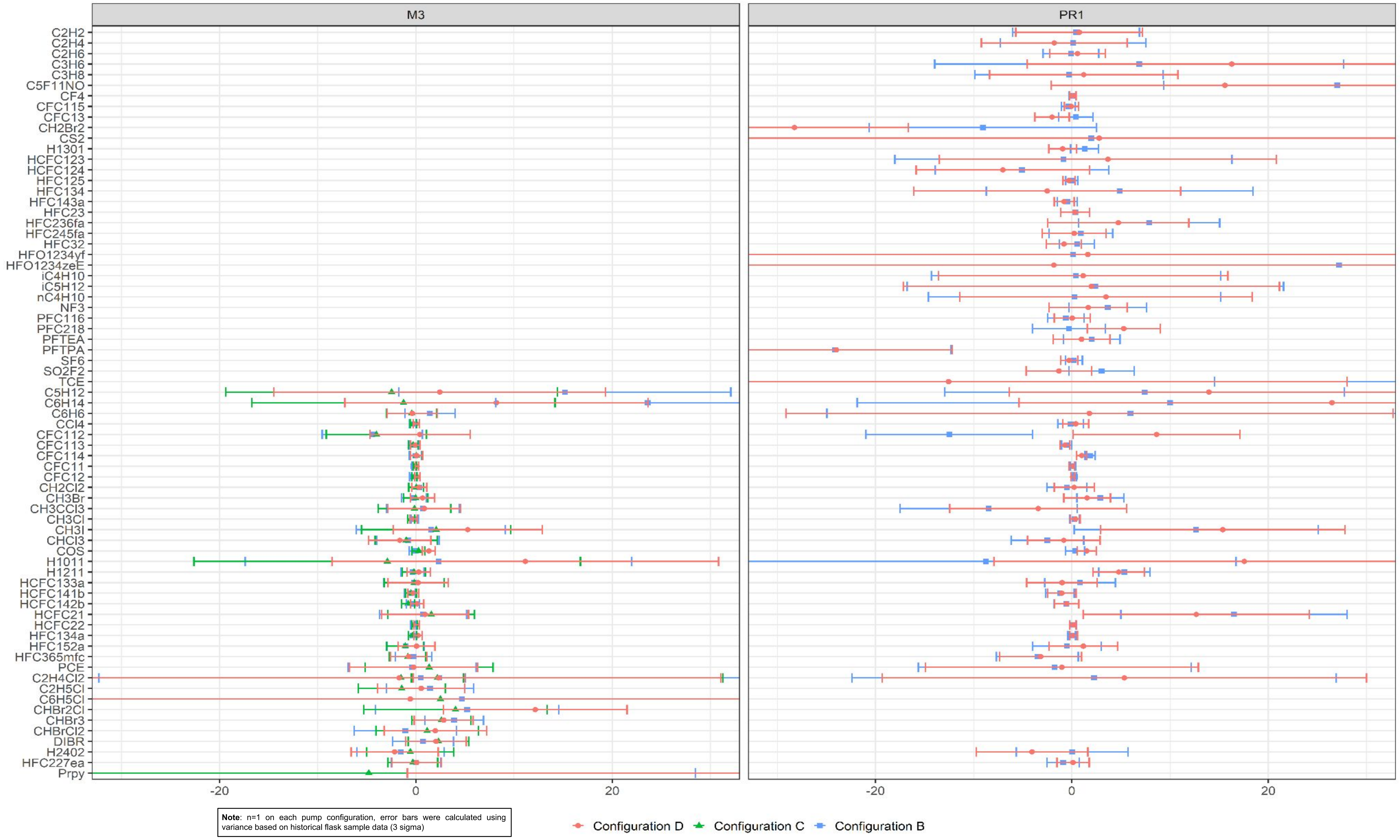

Table 1: Combined results for analytes that showed statistical change in composition

	C6H14	CCl4	CFC112	CFC113	CFC114	CFC11b	CFC12	CH3Br	CH3Cl	CH3I	COS	H1211	HCFC141b	HCFC142b	HCFC21
M3	Mixed Results	Mixed Results	No statistical impact	No statistical impact	No statistical impact	Mixed Results	Mixed Results	No statistical impact	Mixed Results	No statistical impact	Mixed Results	No statistical impact	Mixed Results	Mixed Results	No statistical impact
PR1	No statistical impact	No statistical impact	Statistical change on all runs	Statistical change on all runs	Statistical change on all runs	No statistical impact	Mixed Results	Mixed Results	No statistical impact	Statistical change on all runs	Mixed Results	Statistical change on all runs	No statistical impact	No statistical impact	Statistical change on all runs

No statistical impact (green)
Mixed Results (orange)
Statistical change on all runs (enhancement or degradation) (red)

Summary and Conclusions

- Most compounds only saw small changes (%-based) in response.
- Compounds that show large changes were mostly statistically insignificant due to large uncertainty for these compounds.
- Some compounds showed statistically significant enhancements AND degradations, but were inconsistent between configurations.
- Compounds that were shared between PR1 and M3 were not consistently statistically significant between instruments.
- Both instruments saw at least one configuration of statistically significant change on the following:
  - CFC 12
  - COS
- M3 did not show statistical differences on any compound for ALL configurations
- PR1 saw statistical differences on the following compounds for ALL runs (excluding shared compounds in Table 1)
  - PFTPA
- No compound saw significant change for both instruments for all configurations.

Future Work

- Conduct more testing utilizing larger sample size and more reference gas injections.
  - This was a large limitation on determining variance of % difference response.
  - This is why flask variance data was used to determine instrumentation precision on each sample.
- Track compound enhancement/degradation trends with pump run time.
  - This would help us identify if pumps require a "burn in" time period, and where offsets (if any) would stabilize
- Prepare both instruments to determine calibrated mole fractions for each compound to better understand potential for impact on flask samples.
- Conduct detailed intercomparison with previous pump tests that have been conducted by GML
- Review literature on out/in-gassing behavior of PTFE and Neoprene to determine if any compounds are more susceptible to influence of these materials.
- Conduct tests utilizing different concentrations of compounds to determine if any seasonal considerations need to be accounted for in flask analysis.
- Continue to monitor mole fractions at site of installation for any abrupt changes.