Ensuring High-Quality Data from NOAA's GC-MS PERSEUS Instrument

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Introduction

• NOAA/ESRL/GMD collects routine air samples in programmable flask packages (PFPs) from sites across North America and glass and stainless steel flasks across the globe.

• These sites include profiles in small aircraft (Fig. 1, blue diamonds), stationary locations at tall towers (green triangles), and cooperative fixed sites (red circles).

• Sampled flasks and PFPs are returned to Boulder, Colorado where they are measured for a suite of halocarbons, hydrocarbons, and sulfur-containing compounds.

• Data quality assurance (QA) and quality control (QC) are fundamental parts of these long-term data records.

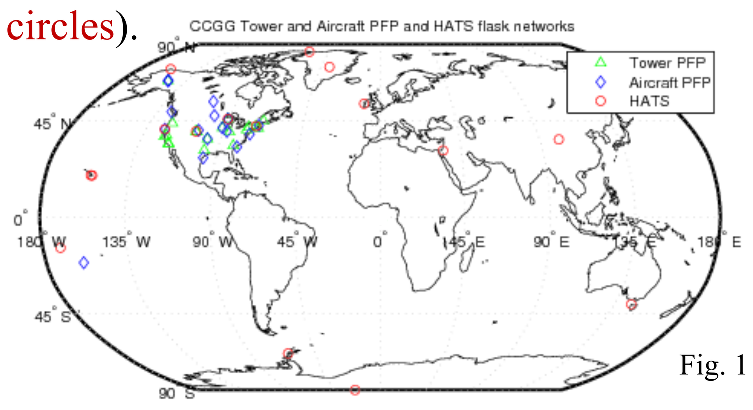


Fig. 1

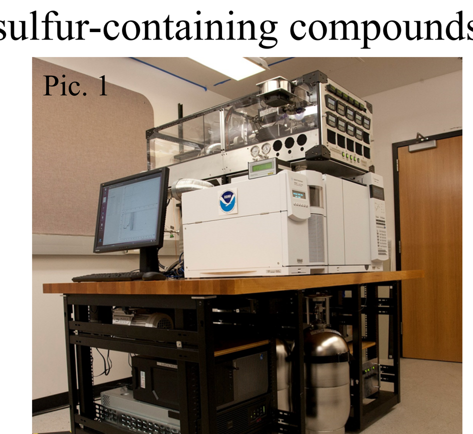
Measurement Techniques

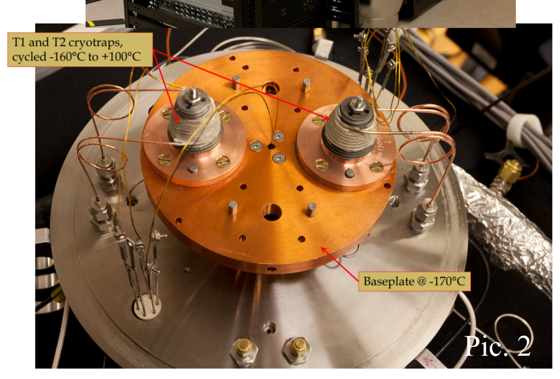
• A new gas chromatography-mass spectrometry (GC-MS) analytical system for Preconcentration of Environmentally Relevant Species (or PERSEUS) was completed in October 2014 (Pic. 1, 2 and Fig. 2).

• Since October 2014, almost 27,000 discrete air samples have been measured on PERSEUS for:

- 10+ hydrocarbons (e.g., ethane, propane, benzene)
- 35+ halocarbons (e.g., CFCs, HCFCs, HFCs, PFCs)
- 3 sulfur-containing compounds (e.g., OCS, SF_6, SO_2F_2)

Pic. 1





Pic. 2

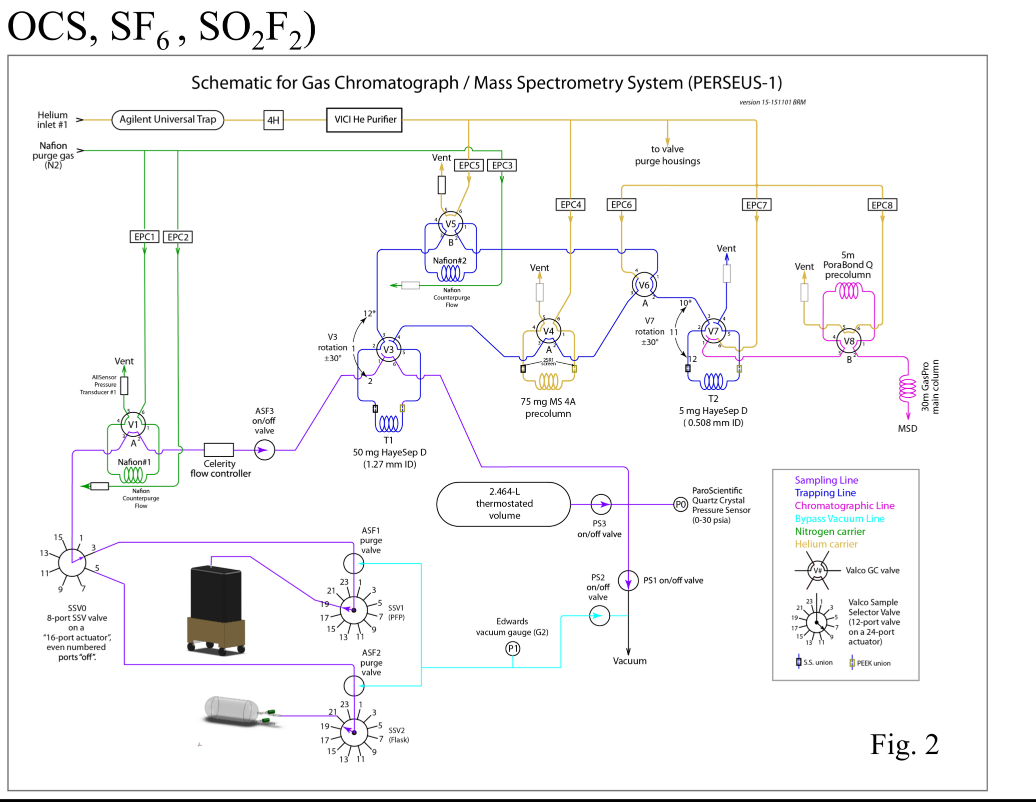


Fig. 2

Data Quality Control

• **Stripcharts**

24 diagnostic traces are stored in the form of a stripchart for every sample analyzed. Fig. 3 shows a stripchart with irregular T1 temperatures, potentially causing poor results for some of the early eluting analytes.

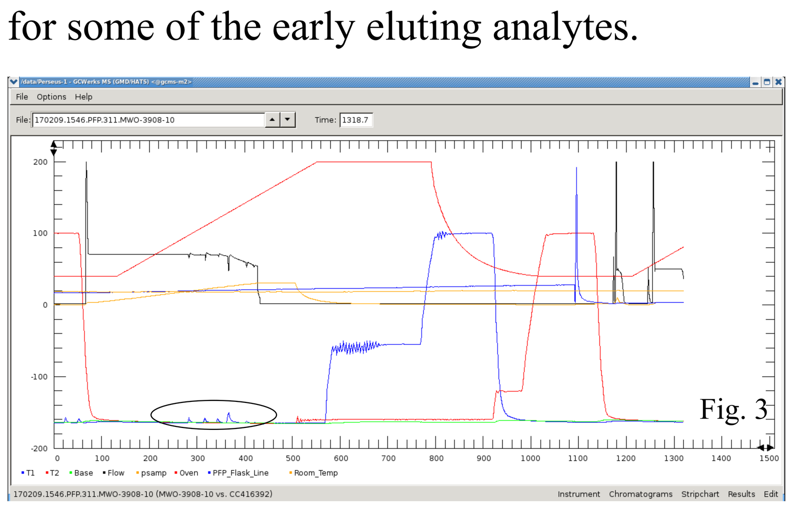


Fig. 3

• **Blank corrections**

Blanks are run twice per day and all measurements are corrected based on an interpolation between blanks (Fig. 4).

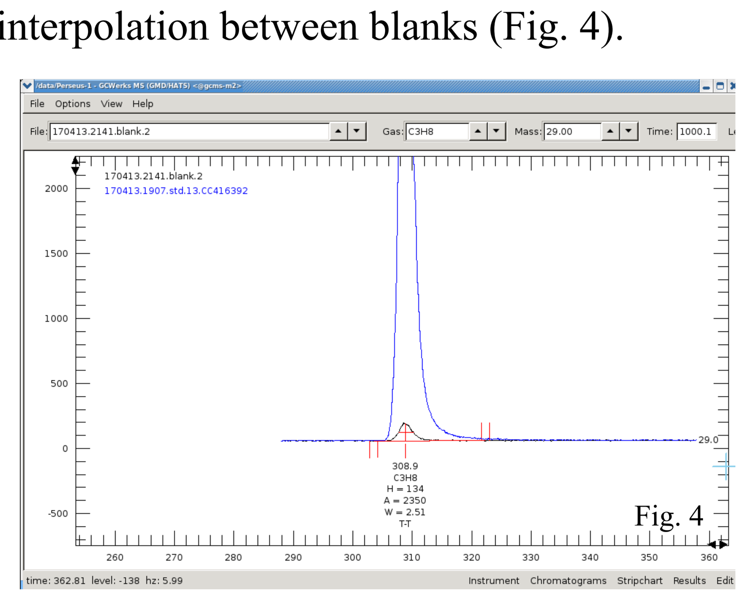


Fig. 4

• **Unexplained measurement problems**

Fig. 5 shows lab air contamination of HFC-152a standards when canned spray products are used near the measurement lab.

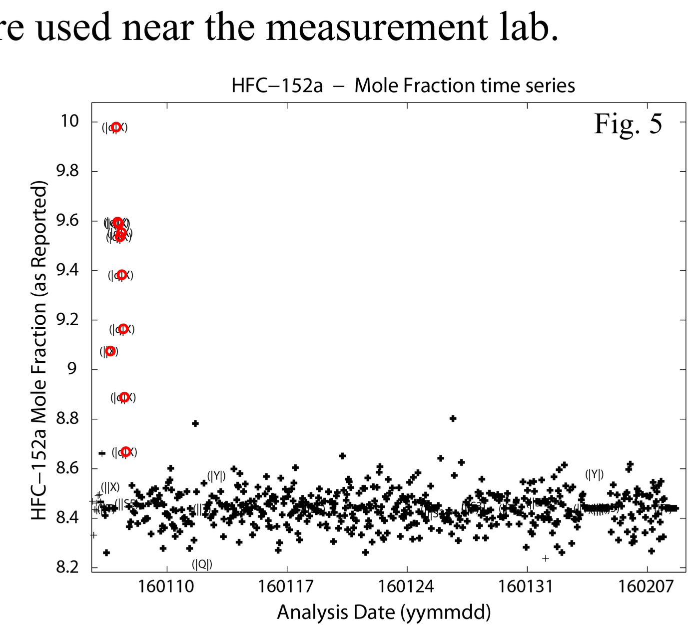


Fig. 5

• **Leak identification - collection**

Halon-1211 fire extinguishers were installed at the tower PFP sites to help identify leaks or problems in the sample collection system. Fig. 6 shows enhancements in H-1211 coinciding with the installation of a new chiller at Park Falls, Wisconsin (LEF).

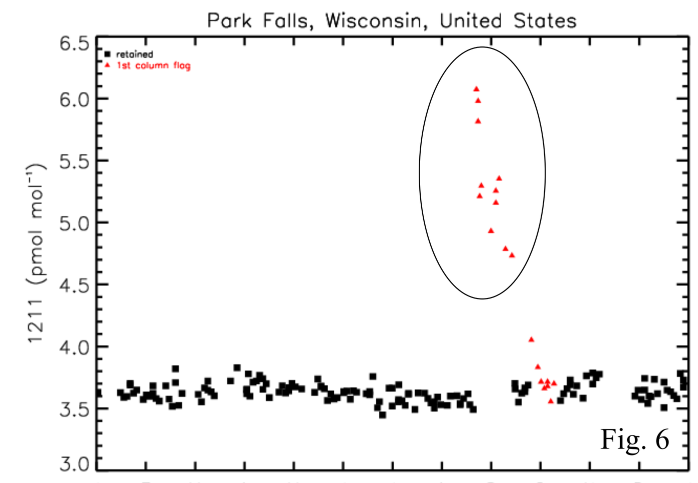


Fig. 6

• **Contamination – collection**

Toluene contamination from new materials in the PFP pumping units is shown in Fig. 7.

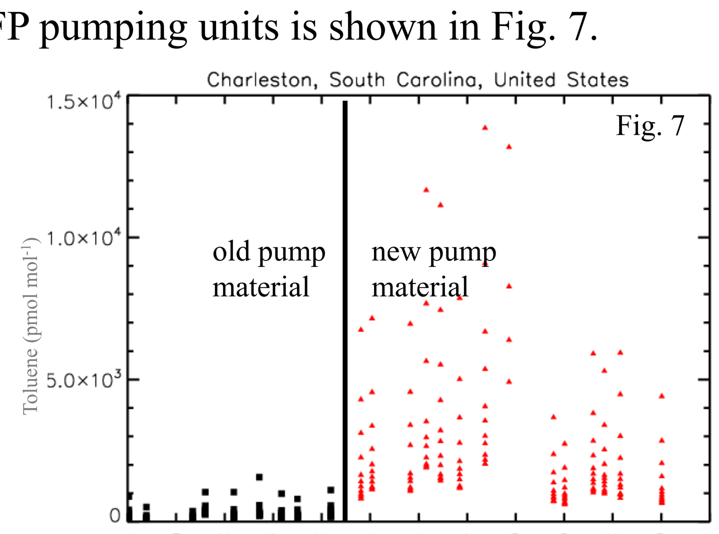


Fig. 7

• **Co-located samples**

Both glass and stainless steel flasks are collected at Cape Kumukahi, Hawaii with different pumping systems. Fig. 8 shows CH_2BrCl contamination in the glass flasks (black symbols).

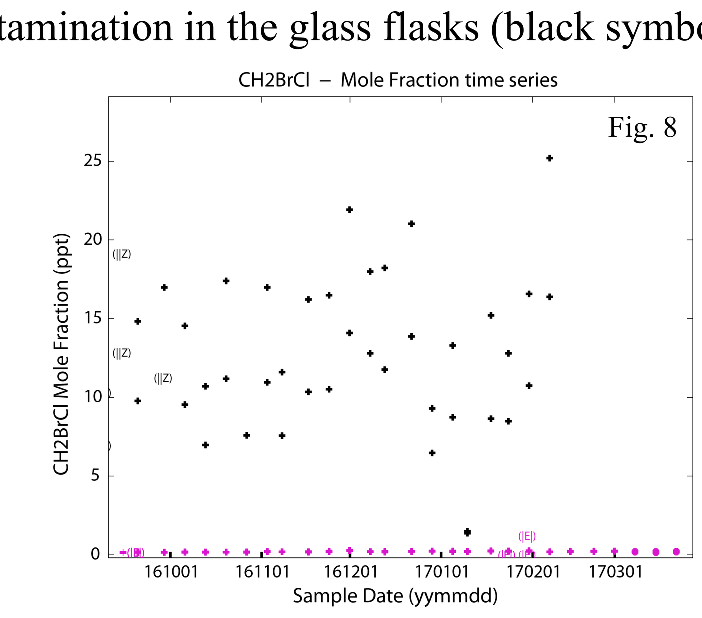


Fig. 8

Summary and Conclusions

• **Data from NOAA/ESRL/GMD's air sampling networks are vital to large-scale studies of halocarbons and hydrocarbons.**

• **To be most effective, these long-term data records must be carefully scrutinized so samples with collection or measurement problems are identified.**

• **Quality assurance and quality control (QA/QC) are performed with several different methods and programs developed at GMD and SIO. This includes:**

- Monitoring sample water vapor content, system diagnostics, and system nonlinearities.

- Comparing results from independent measurement systems and different sampling methods.

- Conducting routine tests of equipment and routine analyses of archive tank air.

Remaining Issues and Future Plans

• **Assign uncertainties for reported PERSEUS analytes.**

• **Apply corrections to PERSEUS analytes affected by nonlinearity.**

• **Convert to new tagging software for sample collection problems (CCGG samples only).**

• **Continue to compare results with independent measurement labs.**

• **Continue to learn about the instrument as we perform more tests.**

Data Quality Assurance

• **Instrument long-term reproducibility**

Archive tanks are measured routinely on PERSEUS to monitor long-term reproducibility. The ±0.015 ppt standard deviation of SF_6 differences between an initial analyses and all subsequent analyses of 24 different tanks proves our high reproducibility for this analyte (Fig. 9).

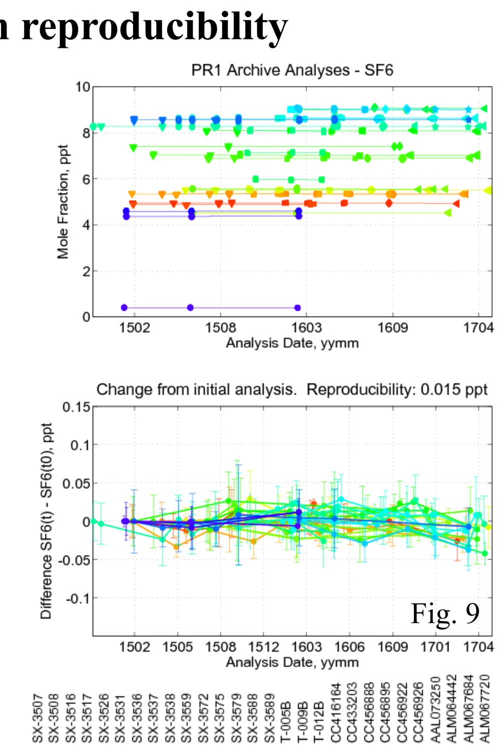


Fig. 9

• **System nonlinearities**

A 'linear response' instrument exhibits the same normalized sensitivity across a range of analyte mole fractions observed in the field. We use two independent methods to test the system linearity:

1) Vary the moles of analyte in our 'sample' by varying the amount of sample volume injected (Fig. 10, blue dots), spanning 10% to 500% of the standard injection (black dot).

2) Measure four tanks of real air with gravimetrically-known analyte ratios (red dots).

The good agreement between the two independent methods confirms the validity of the techniques. We can then use this fitted function (blue line) to correct our data to reduce this bias.

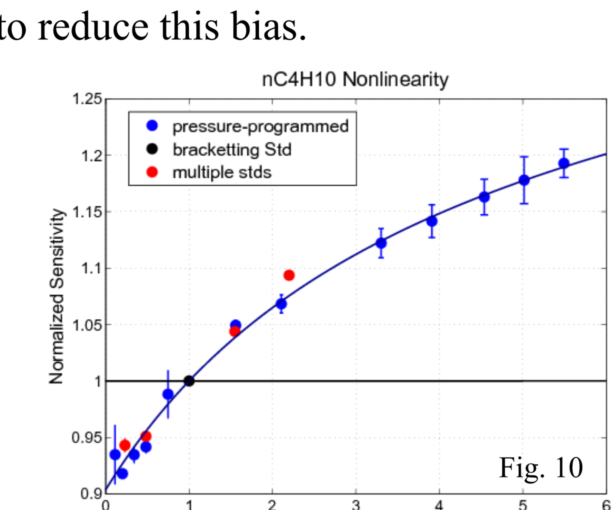


Fig. 10

• **Peak identification**

Fig. 11 shows the peak identification process for CH_2Br_2. Real air from NWR (top) is compared to a synthetic mixture of pure CH_2Br_2 in zero air (middle) to verify that we get the same analyte spectra. This allows us to choose the most abundant ion that doesn't show coelution in real samples. We also compare to the NIST spectra (bottom).

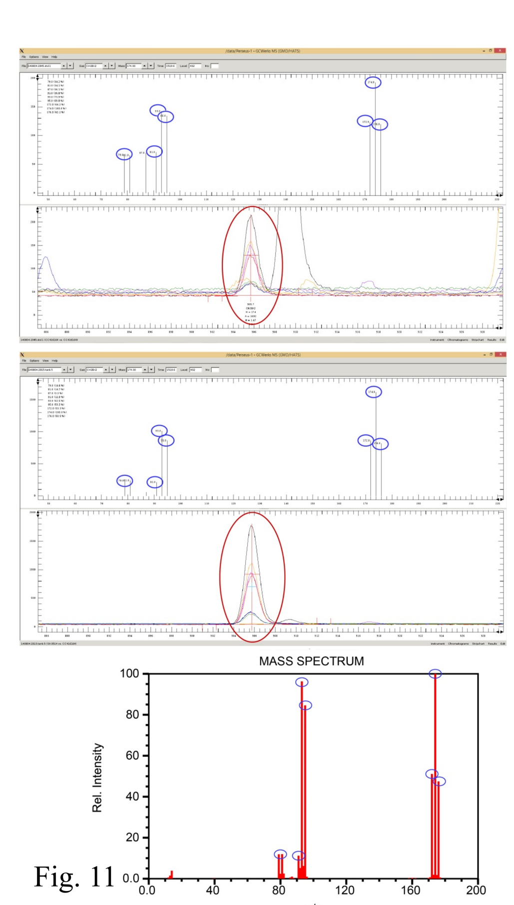


Fig. 11

• **Sample water vapor content**

All samples are dried in a two-step process involving Nafion dryers (Fig. 2). Water vapor in the MSD strongly affects analyte sensitivity. Therefore, drying all samples to the same low dew point (Fig. 12) makes the comparison of dry standard gas to moist field samples a more valid comparison.

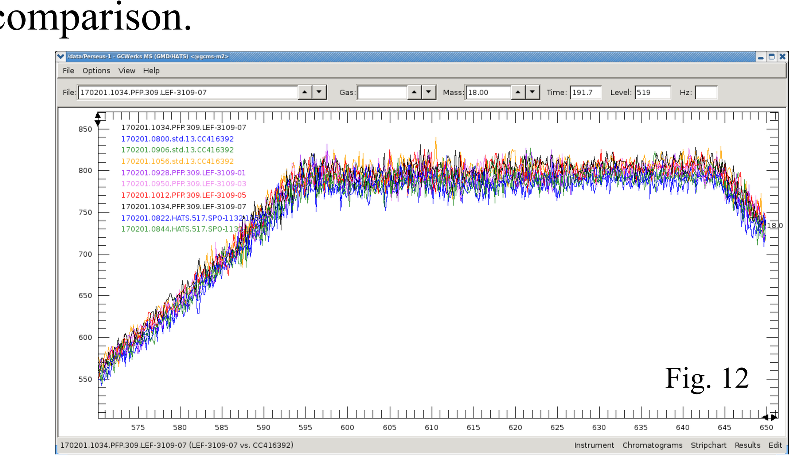


Fig. 12

• **Inter-laboratory comparisons**

Fig. 13 shows mean SF_6 differences between the CCGG MAGICC system and PERSEUS for the same air samples. This meets the WMO recommendation of compatibility of 0.02 ppt.

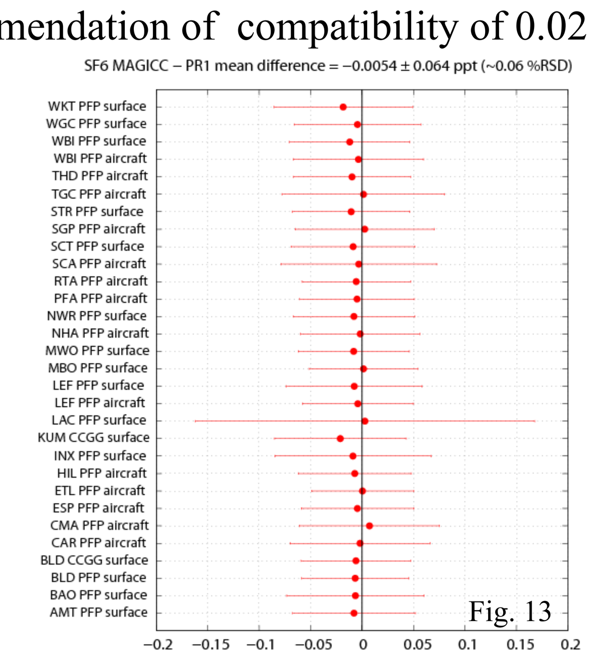


Fig. 13

• **Sample storage tests**

A typical lag time between sampling of PFPs in the field and subsequent analysis on PERSEUS is ~3 weeks. To evaluate the stability of the sample, we perform QA tests. A typical PFP test includes the following:

1) PFP flasks are filled with the same NWR air and measured as soon as possible (Fig. 14, blue +).

2) PFP is measured again after ~30 days of storage.

3) We compare the difference between the 30-day and the initial measurement to look for losses or enhancements that are due to storage (red +).

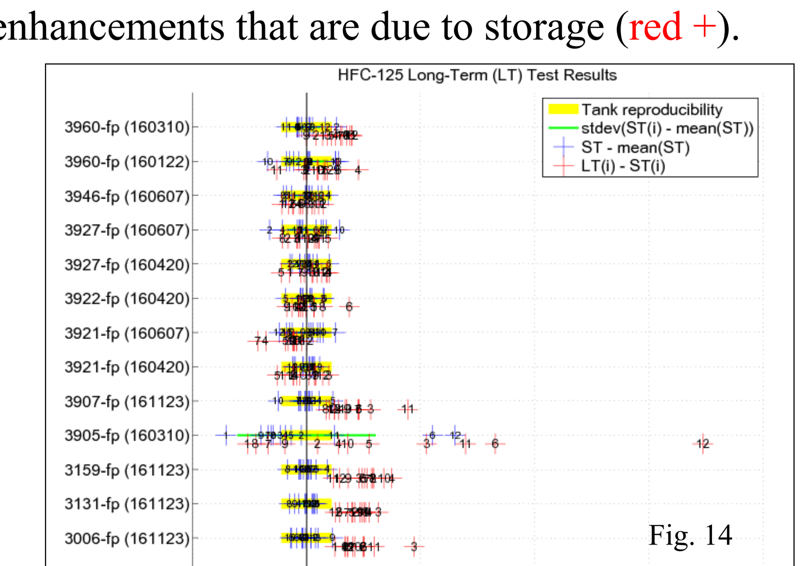


Fig. 14

Acknowledgments

We thank Jack Higgs and Thomas Legard for their continued help with BLD PFP testing, John Mund for his work with QA/QC flagging software and data management, and all the people involved in collecting the HATS and CCGG samples.