GMD's GC/MS Analytical System for Preconcentration of Environmentally Relevant Species (PERSEUS).

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GCWerks

What is PERSEUS?

Figure 1. PERSEUS-1 (PR1) is a system for analysis of 50+ trace substances in the ambient atmosphere, using cryogenic preconcentration to increase signal to noise levels for high precision measurements. Here a full compliment of seven programmable flask packages (PFPs) awaits automatic analysis. At a throughput of 65 samples per day (including standards, blanks, etc.), the twelve flasks of a PFP require ~5.5 hrs per package.

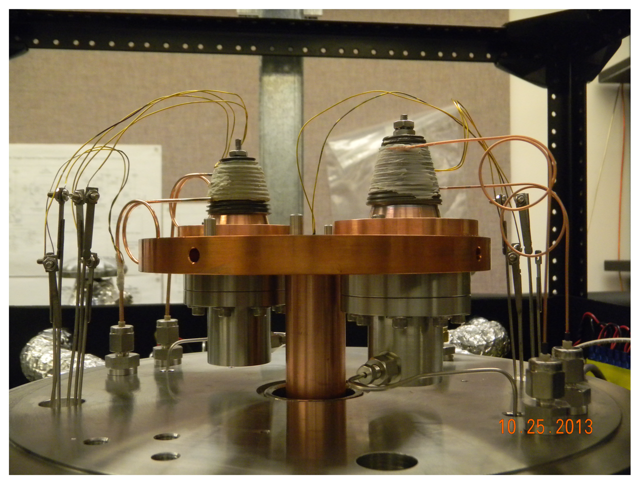


Figure 2. The cryogenic 'coldend' (patent pending) of PERSEUS allows two independent adsorbent traps to be cycled between -160°C and +100°C in under a minute for a fast analysis cycle time of 22 minutes. This device was developed with seed funds provided by a 2011 CIRES Innovative Research Proposal (IRP) to the author.

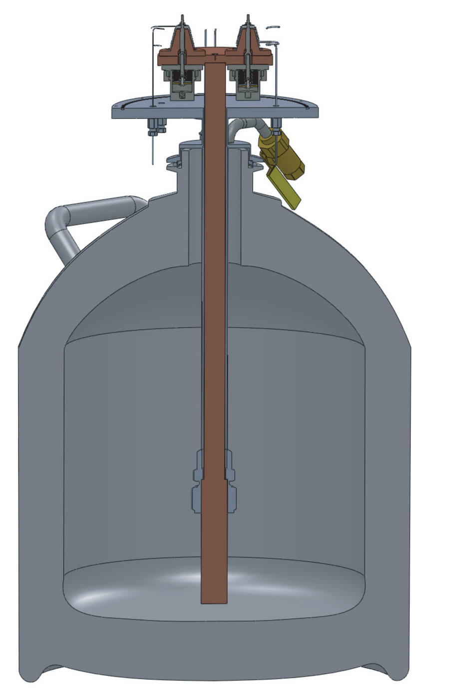


Figure 3. The cold end is cooled by conduction through a 1" O.D. x 26" long copper rod that has the lower 4" immersed in liquid nitrogen. The 35-L storage dewar keeps the liquid nitrogen at a working level for up to 5 days.

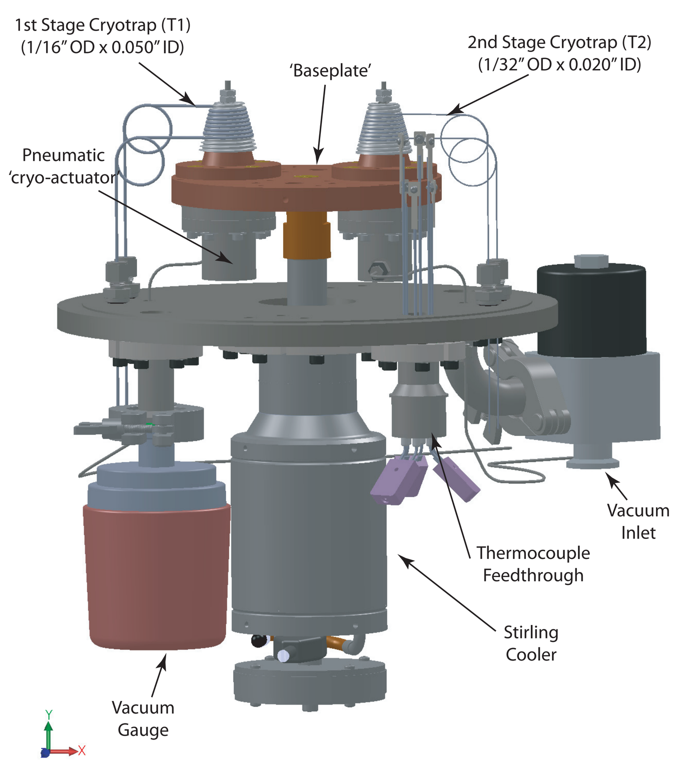
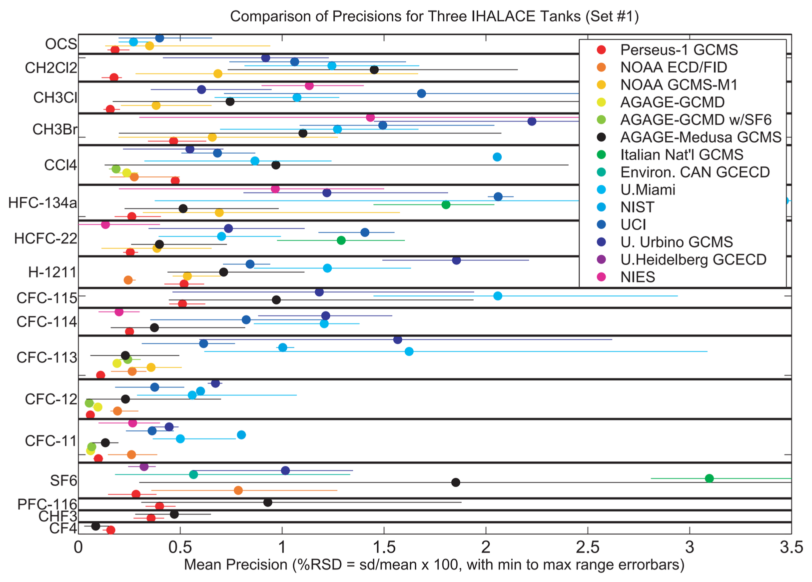


Figure 4. Work is currently underway to construct a second PERSEUS, PR2, for increased productivity and research experiments. The next version will utilize a Stirling Cooler in place of liquid nitrogen as the cold source.

Performance...

Table 1. PERSEUS analytes include greenhouse gases, ozone-depleting substances and/or pollutants involved in air quality. Analytes highlighted in yellow denote new compounds for routine PFP analyses by GCMS.

Class	Analyte	Formula	Abundance (ppt)	PR1 Reproducibility
PFCs	PFC-14	CF_4	83	0.2%
	PFC-116	C_2F_6	5	0.8%
	PFC-218	C_3F_8	0.6	2%
CFCs	CFC-11	CCl_3F	232	0.4%
	CFC-12	CCl_2F_2	520	0.1%
	CFC-13	$CClF_3$	3	2%
	CFC-113	CCl_2FCClF_2	72	0.2%
	CFC-114	$CClF_2CClF_2$	16	0.3%
	CFC-115	C_2ClF_5	9	0.3%
HCFCs	HCFC-124	$CHClFCF_3$	1.2	2%
	HCFC-133a	CH_2ClCF_3	0.5	1%
	HCFC-141b	CH_3CCl_2F	26	0.2%
	HCFC-142b	CH_3CClF_2	24	0.4%
	HCFC-21	$CHCl_2F$	0.6	23%
	HCFC-22	$CHClF_2$	247	0.2%
HFCs	HFC-125	CHF_2CF_3	21	0.1%
	HFC-134a	CH_2FCF_3	95	0.1%
	HFC-143a	CH_3CF_3	20	0.2%
	HFC-152a	CH_3CHF_2	10	0.7%
	HFC-23	CHF_3	29	1%
	HFC-32	CH_2F_2	13	7%
	HFC-227ea	CF_3CHFCF_3	1.3	2%
	HFC-236fa	$CF_3CH_2CF_3$	0.15	3%
	HFC-365mfc	$CH_3CF_2CH_2CF_3$	1	0.9%
Halons	H-1211	$CBrClF_2$	3.7	0.7%
	H-1301	$CBrF_3$	3.4	0.5%
	H-2402	$CBrF_2CBrF_2$	0.5	2%
Methyl halides	methyl bromide	CH_3Br	7	0.9%
	methyl chloride	CH_3Cl	500-600	0.3%
	methyl iodide	CH_3I	0.2	9%
Solvents	dichloromethane	CH_2Cl_2	63	0.4%
	chloroform	$CHCl_3$	15	0.6%
	carbon tetrachloride	CCl_4	83	3%
	methyl chloroform	CH_3CCl_3	3	8%
	trichloroethene, TCE	C_2HCl_3	0.2	50%
	prechloroethene, PCE	C_2Cl_4	3	9%
Hydrocarbons	acetylene	C_2H_2	100-600	1%
	ethane	C_2H_6	400-4000	0.2%
	propane	C_3H_8	20-3000	0.8%
	i-butane	$CH_3CH(CH_3)CH_3$	1-400	0.6%
	nC4H10	$CH_3CH_2CH_2CH3$	1-1000	0.4%
	iC5H12	$CH_3(CH_2)_3CH_3$	1-400	0.3%
	nC5H12	$CH_3CH(CH_3)CH_2CH_3$	1-300	0.5%
	n-hexane	$CH_3(CH_2)_4CH_3$	1-100	0.8%
	benzene	C_6H_6	1-200	5%
	toluene	C_7H_7	1-200	4%
Miscellaneous	nitrogen trifluoride	NF_3	1.6	2%
	dibromomethane	CH_2Br_2	1.2	5%
	bromoform	$CHBr_3$	0.5-4	2%
	bromochloromethane	CH_2BrCl	0.2	60%
	carbonyl sulfide	OCS	450-550	0.6%
	sulfur hexafluoride	SF_6	9.3	0.2%
	sulfuryl fluoride	SO_2F_2	2.3	0.6%



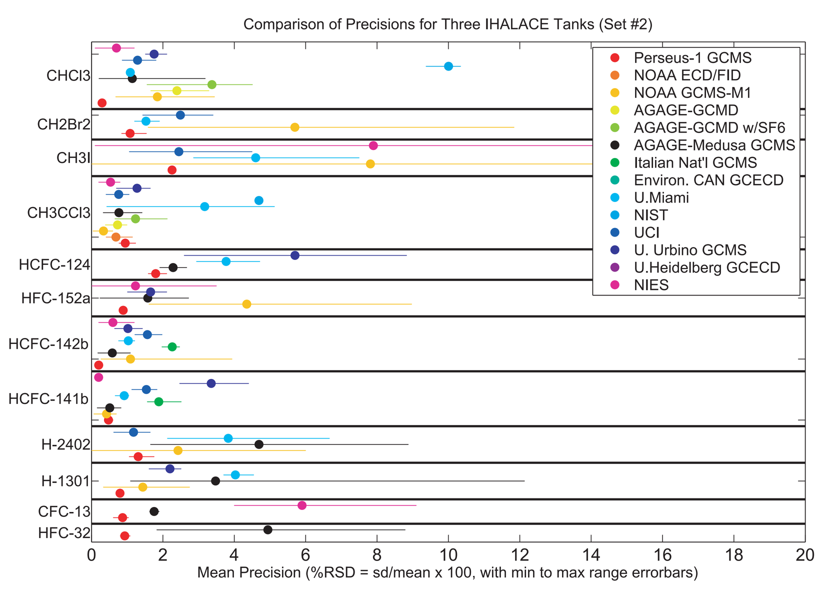


Figure 4. PERSEUS-1 repeatability (short-term precision) compared to other instruments. In 2014, *Hall et al.* published results from the ***International Halocarbons in Air Comparison*** (IHALACE), in which 19 laboratories and 27 different instruments analyzed at least three of six cylinders of whole air in 2006-2007 and reported their mole fractions and precisions. Eight years later, three of these extant cylinders of air were analyzed on PERSEUS-1. In the two figures above, the mean relative standard deviation of each lab's results are plotted, with errorbars that represent the range (best to worst) of precisions reported for the three cylinders. PERSEUS-1 (in red) frequently appears amongst the highest precision reported measurements.

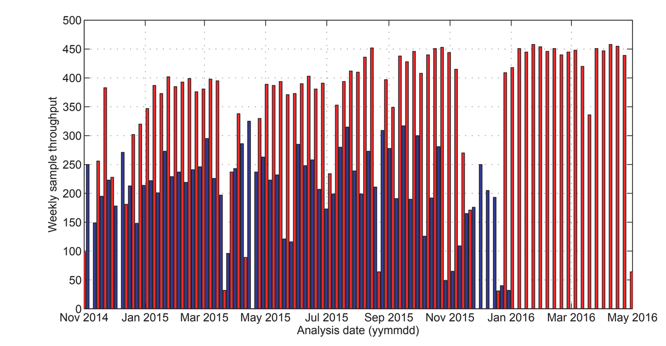


Figure 5. PERSEUS-1 has proven to be a robust, high sample throughput instrument. This time series shows weekly total sample throughput of PERSEUS-1 (red) and an older instrument GCMS-M2 (blue). Currently on PERSEUS-1, 458 analyses can be performed weekly (65 per day). PERSEUS-1 began measuring HATS flasks and a limited number of CCGG's programmable flask packages (PFPs) beginning October 2014. GCMS-M2 was the 'work-horse' instrument for analysis from 2007 until October 2015 when PERSEUS-1 took over that role. A Valco valve failure in mid-November 2015 in PERSEUS-1 stopped operations for ~4 weeks until replacement could be made.

Calibration...

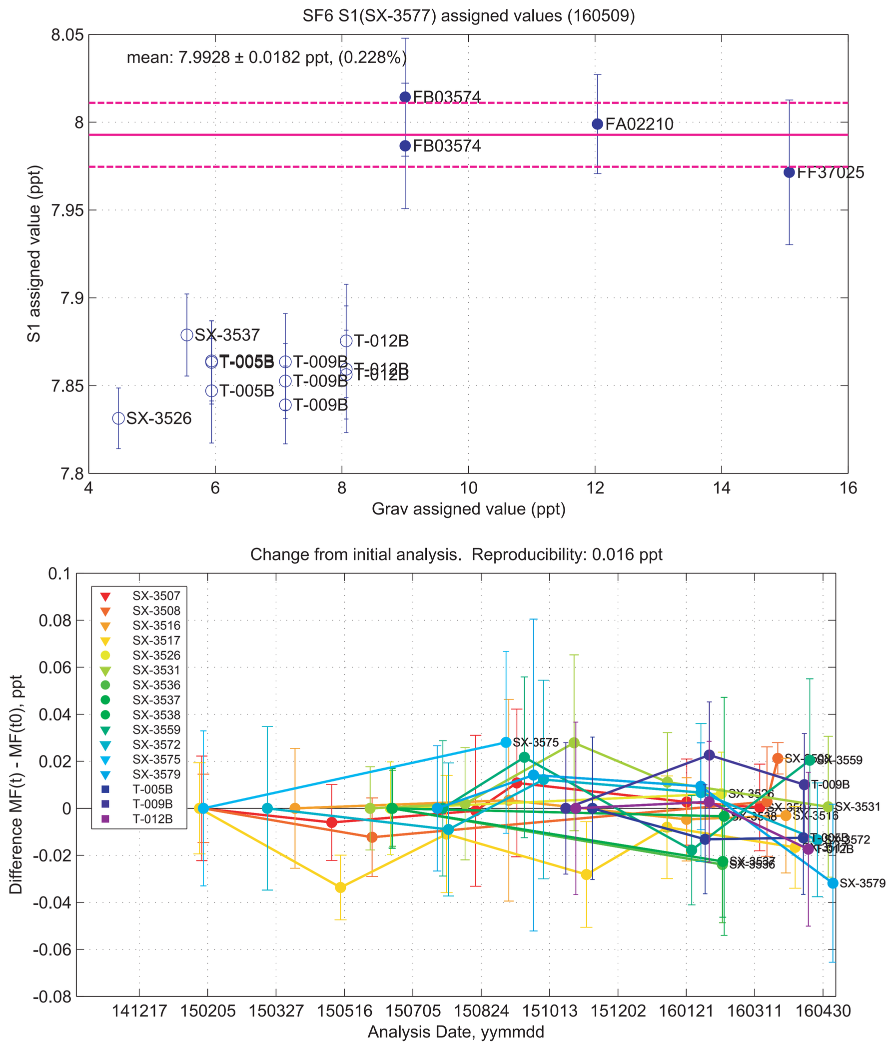


Figure 6. PERSEUS uses a hierarchy of standard gases to calibrate field samples. We begin with 'primaries' of high-accuracy, gravimetrically prepared mixtures of pure substances in synthetic "zero air". Primaries are used on PERSEUS to calibrate a long-term (~10 yrs) cylinder of whole air, the 'secondary'. Secondaries are used on PERSEUS to calibrate short-term (~1 yr working life) 'tertiaries'. Finally, tertiaries are analyzed daily on PERSEUS along with field samples to correct detector drift and to relate those measurements back to the primariy calibration scales. The top panel shows how SF6 primaries (solid dots) are used to assign the gravimetric scale to a secondary. Additional 'known' calibrated samples (open circles) from other labs may be also compared to NOAA calibrations. The bottom panel shows how archived samples of whole air are run weekly along with field samples to assess stability of calibrations over long time scales.

Intercomparisons...

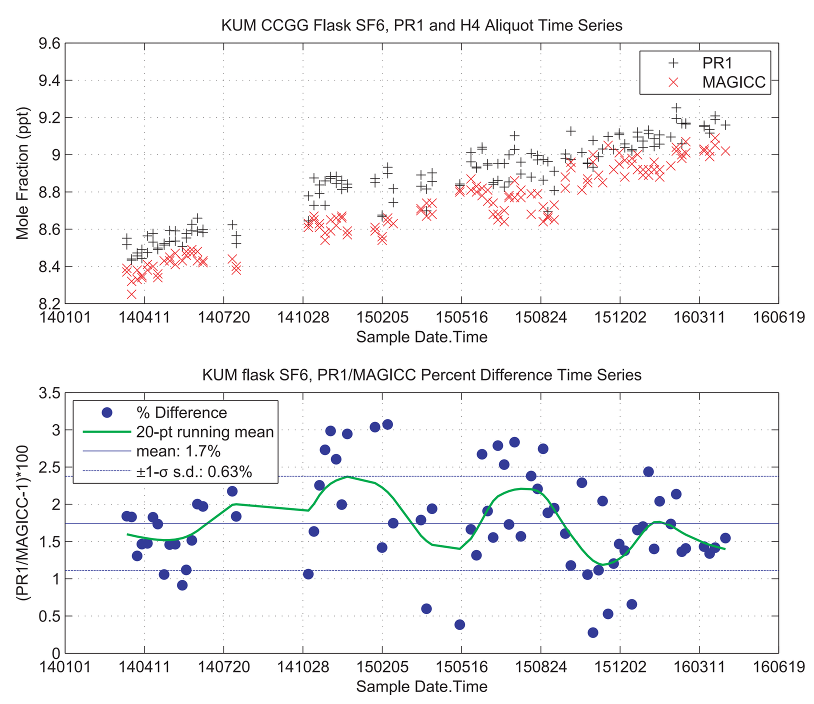


Figure 7. Same sample comparison: PERSEUS and MAGICC SF6. Samples collected at Cape Kumakahi, HI (KUM) as part of the CCGG Cooperative Network were analyzed on both instruments. Top panel shows individual analyses, while the bottom panel shows the ratio of matched points to access the level of agreement.

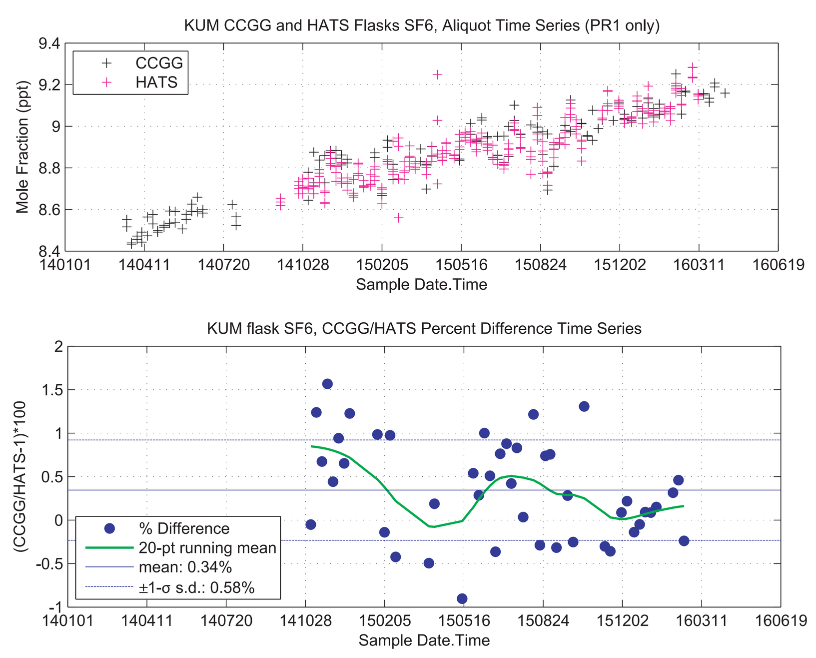


Figure 8. Another comparison of SF6, this time using the same instrument, PERSEUS-1, but with samples collected by two different methods: CCGG portable sample unit (PSU) and HATS pumping system. The PSU is currently capable of 'clean' sampling of about one-half of the PERSEUS-1 analyte suite.

New Applications...

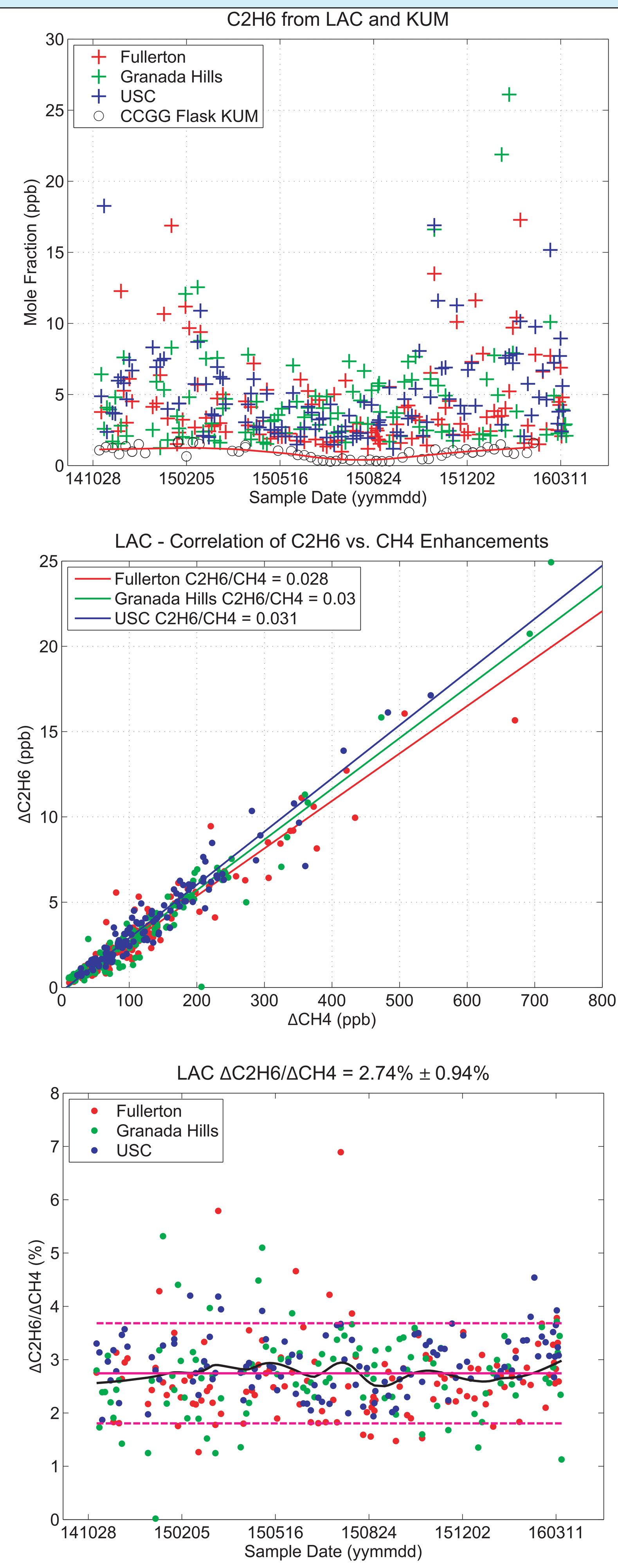


Figure 9. The increased capabilities of PERSEUS open up new possible applications. Here is a time series (top panel) of ethane analyses of CCGG programmable flask package (PFP) samples collected at three sites (colored plus signs) within the Los Angeles Network (LAC) of the Megacites Carbon Project. Note the seasonal pollution variations. These data are compared to a 'background' atmosphere proxy of Cape Kumakahi (KUM), HI, samples collected weekly by CCGG using portable sampling units (PSUs). The LAC ethane enhancements made be estimated by subtraction of the background from the LAC data. Similarly, a background and enhancements of methane may be estimated. The middle panel shows the correlation of ethane enhancements to methane enhancements. The bottom panel shows the temporal variation of individual enhancement ratios.

SUMMARY...

PERSEUS methodology delivers:

- High repeatability
  - Critical sample volume measured with high-precision Paroscientific quartz spiral manometer pressure readings of a precisely thermostated fixed volume.
  - Sample water content reduced to a consistent, non-interfering level.
  - Tertiary whole air standards run at least every two hours to track detector sensitivity drift.
- High long-term reproducibility
  - Secondary and tertiary suite of whole air standards compared frequently.
  - Analyte drift in the tertiary/secondary ratio precisely monitored and accounted for in calibration propagations.
  - Archived whole air samples analyzed weekly as 'target tanks' for assessing reproducibility.
- Wide range of analytes
  - 50+ analytes representing greenhouse gases (GHGs), ozone-depleting substance (ODSs) and/or pollutants involved in air quality.
  - Wide dynamic mole fraction range from 100's of part per quadrillion (ppq) up to 10's of part per billion (ppb).
  - Analytes of wide range of volatility.
- Mitigation of many potentially interfering substances from the sample.
  - Water removal
  - Bulk air components (mainly O_2, N_2, Ar, CO_2, CH_4) reduced to negligible levels.
- High sample throughput
  - 22 minutes analytical cycle time; 65 samples per day
  - Designed for 24/7/365 operation
  - Unattended operation for up to four days of sample analyses.
- Wide dynamic range of sample pressures, as low as 0.7 bar.
- Sample types include CCGG programmable flask packages (PFPs), CCGG glass flasks, and HATS glass & S.S. flasks.
- Easily accessible data through MySQL database.
- High-frequency (e.g., 1 Hz) acquisition of over 23 instrument diagnostics to ensure performance.
- Remote access for monitoring and controlling operations