Development of a new flask-air analysis system for the Global Greenhouse Gas Reference Network

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1. Introduction

A new flask-air analysis system (Magicc-3) has been developed for measurement of CO_2, CH_4, N_2O, CO, SF_6, and H_2 from discrete air samples collected as part of the NOAA ESRL GMD Global Greenhouse Gas Reference Network (GGRN). Magicc-3 uses laser spectroscopic instruments for CO_2, CH_4, N_2O, and CO along with gas chromatography for SF_6 and H_2. The new system offers several improvements over the current system (Magicc-1) which has been in use since 1997.

Key improvements:

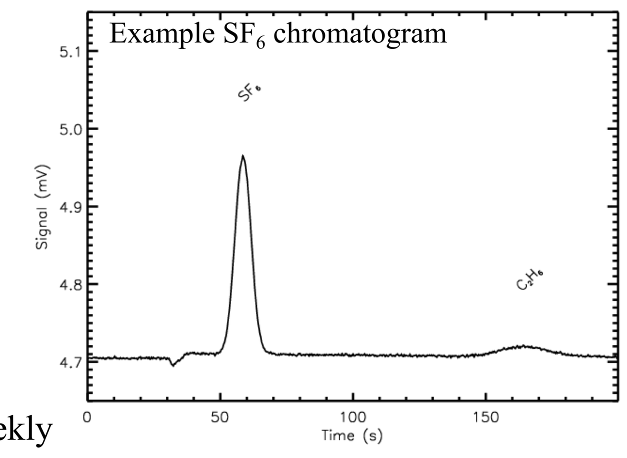
- **N_2O repeatability: 0.03 ppb** vs. 0.4 ppb on Magicc-1
- Sample gas usage: 325 mL vs. 525 mL on Magicc-1
- Measurement over larger mole fraction ranges
- Efficient operator interface and dual sample manifolds improve capacity

2. Instrumentation / Calibration

CO_2 / CH_4 - Picarro CRDS (G2301)
Picarro pulls gas through the system (~60 mL/min) under controlled pressure

N_2O / CO - Aerodyne QC-TILDAS
Stop flow measurement (150 mL cell at 50 Torr)

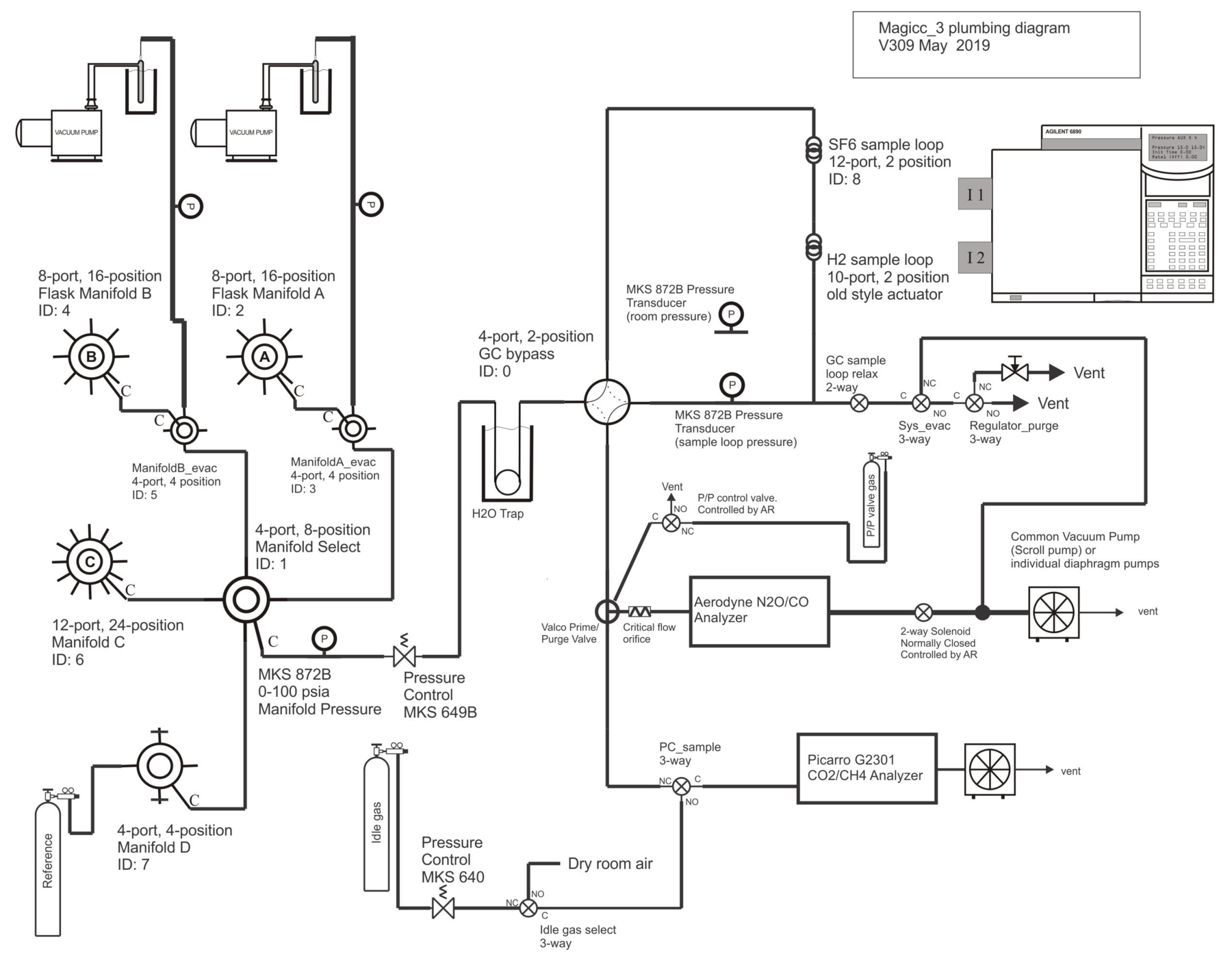
SF_6 / H_2 – Gas Chromatography (ECD / PDD)
New SF_6 chromatography
12-port injection valve heart cut O_2
Columns:
1) 1/8" OD x 0.25 m, Alumina F1, 60/80 mesh
2) 1/8" OD x 1.5 m, Alumina F1, 60/80 mesh
3) 1/8" OD x 0.3 m, 5A molecular sieve, 60/80 mesh
Used to separate SF_6 from C_2H_6
Carrier gas: Nitrogen Oven temp: 40 °C
Sample Loop: 5 mL Run time: 180 secs
Based on work at KRISS. Lim et al (2013)



Multi-point calibrations curves for all species
Off-line relative to a reference tank, approximately bi-weekly
Single set of 11 standards allows identical treatment of standards / samples
Dry air mole fraction ranges covered by Magicc-3 standards

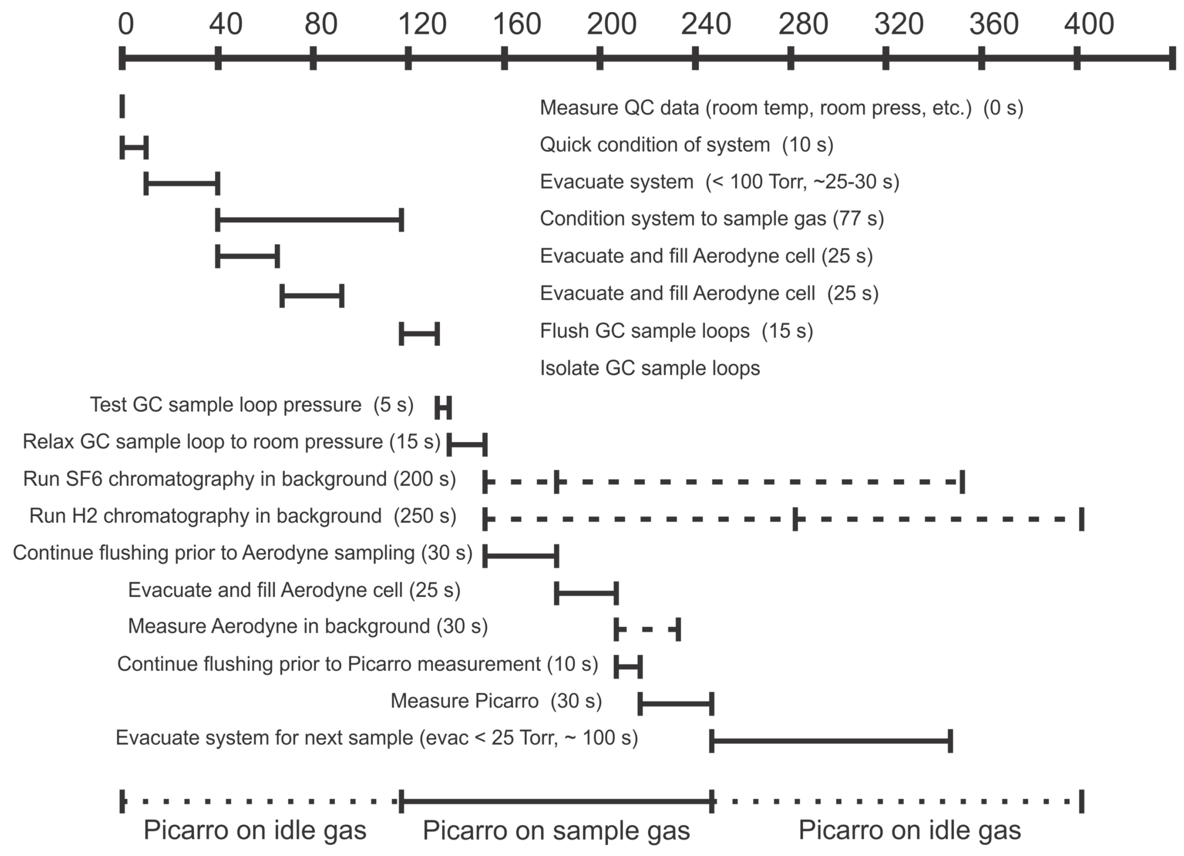
CO_2:	340 – 550 ppm	CH_4:	1500 – 4200 ppb
N_2O:	275 – 367 ppb	CO:	20 – 500 ppb
SF_6:	5 – 17 ppt	H_2:	200 – 600 ppb

3. Magicc-3 Plumbing Diagram

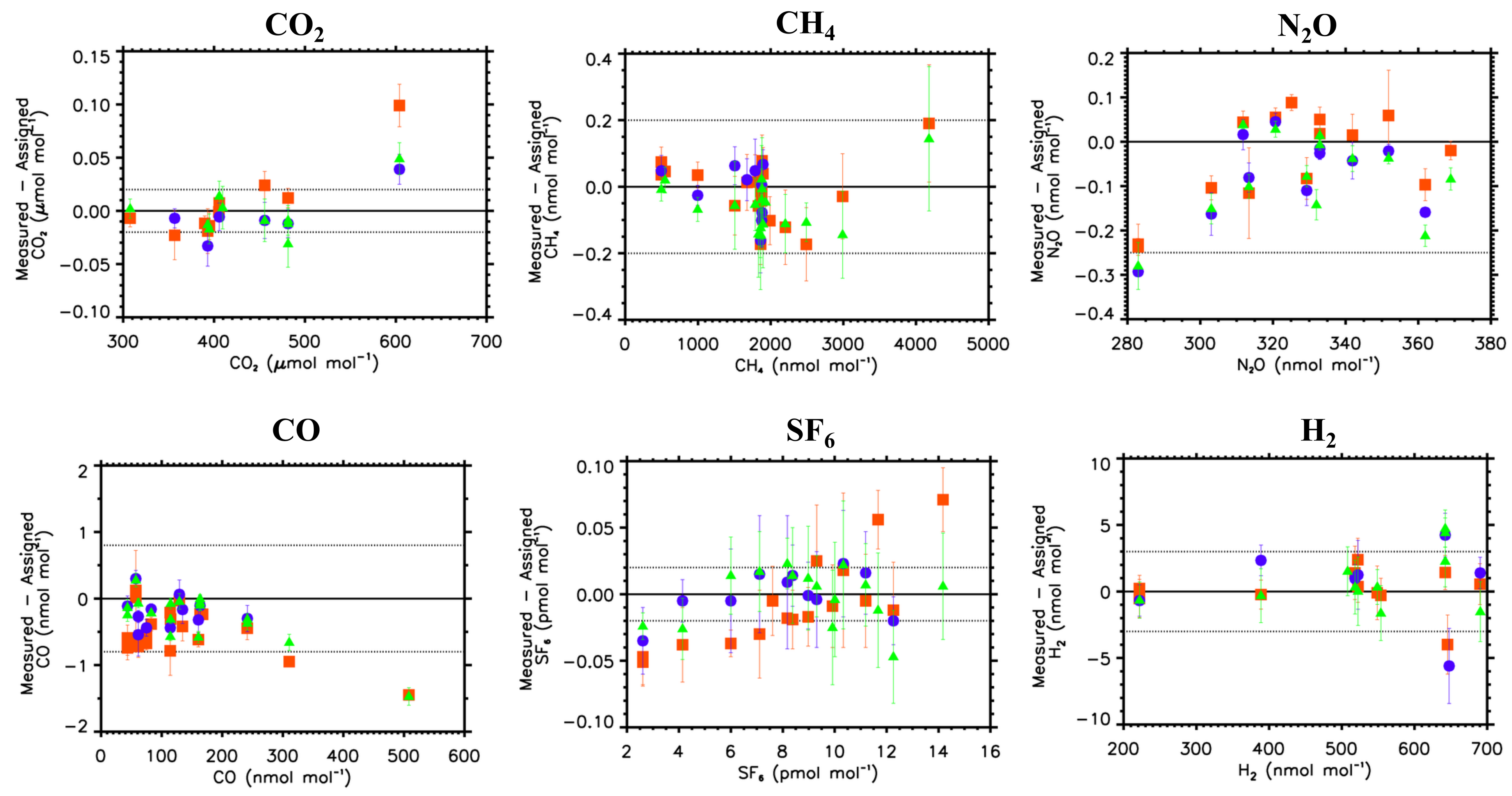


4. Magicc-3 Sample / Standard Measurement Sequence

7 minute cycle time, ~325 mL total gas usage

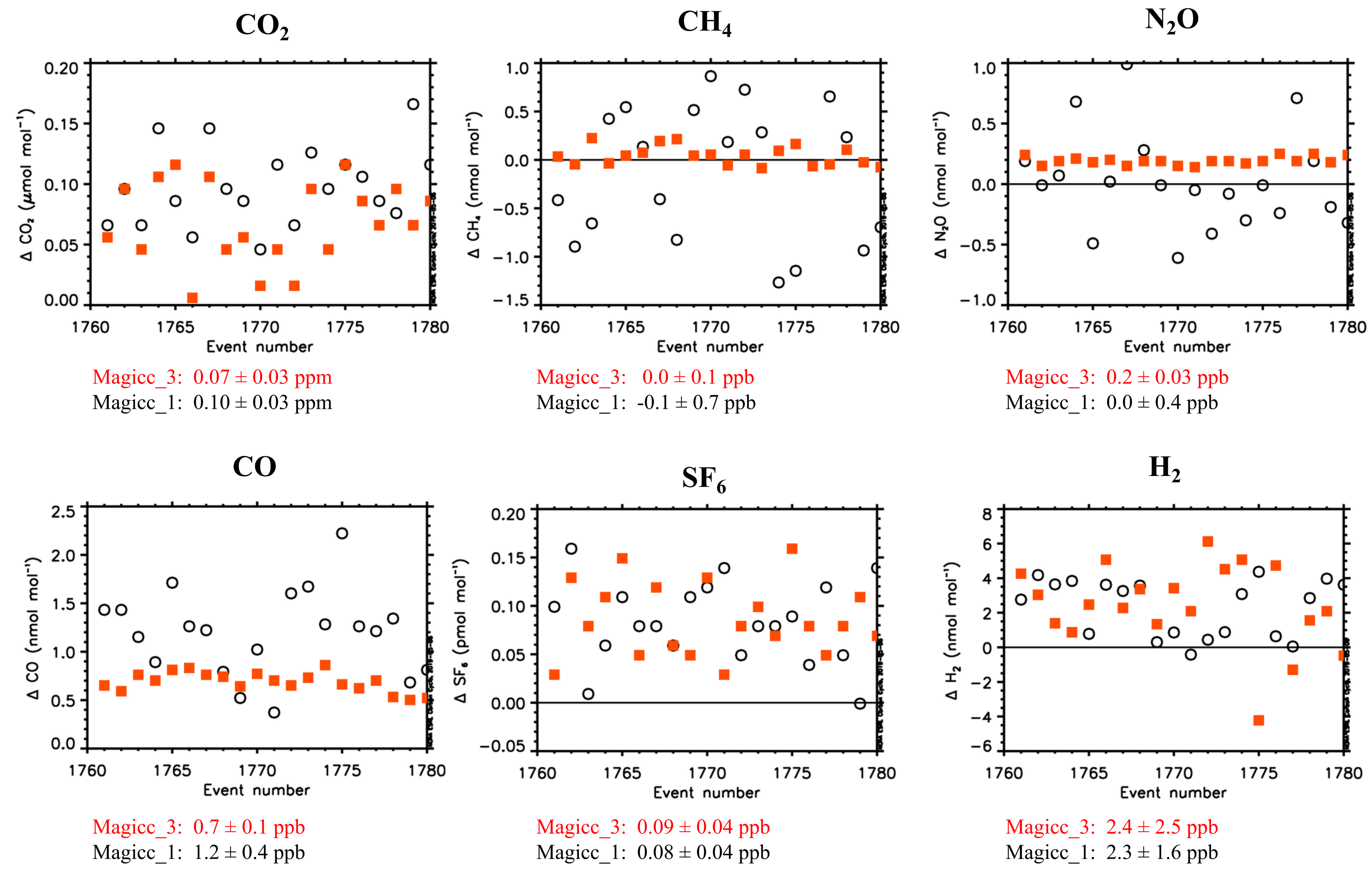


5. Target Tank Results for Different Gas Usage / Sample Volumes



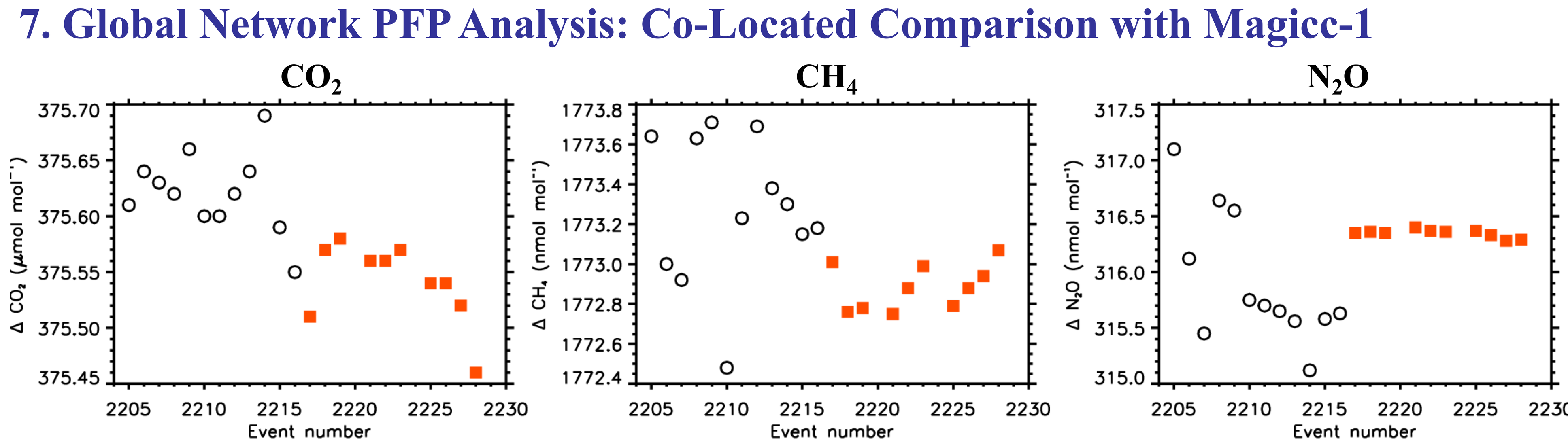
Calibrated target tanks are used to evaluate Magicc-3 over a range of mole fractions at three gas use scenarios (400, 360, and 325 mL from a 2 L network flask). Magicc-3 measurements minus the assigned values (error bars are standard deviations of 6 aliquots) are plotted versus mole fraction for each species. Results are generally within the ± 2-sigma reproducibility of the GGRN calibration systems (dashed lines) for all gas usage scenarios.

6. Global Network Flask Analysis: Same Air Comparison with Magicc-1



Flasks filled from a calibrated cylinder (test flasks) are used to compare Magicc-3 (red squares) to Magicc-1 (black circles). Flasks were measured first on Magicc-3 (using 360 mL of sample gas) and then on Magicc-1. Issues with the technique used to fill test flasks can cause offsets from the assigned values of the cylinder, especially for CO_2. The difference in the offsets for N_2O and CO may be related to assigned values of the test gas cylinder and / or the standards used to calibrate the analysis systems. This is under investigation.

7. Global Network PFP Analysis: Co-Located Comparison with Magicc-1



Two PFPs filled from a calibrated cylinder are used to compare Magicc-3 (red squares) to Magicc-1 (black circles). Known issues with filling a PFP from a cylinder lead to the apparent drift in both results for CO_2. A significant improvement in N_2O repeatability is observed.

8. Conclusions

Magicc-3 offers a significant improvement in N_2O (repeatability ~ ±0.03 ppb), CH_4, and CO measurements of discrete air samples (other species are comparable to Magicc-1) and can routinely measure samples over a wider mole fraction range for all species while using less sample gas. A slightly faster cycle time and the flexibility of the operator interface will improve the measurement capacity of the system.