White Paper

Matching Gas Chromatography Performance Using the Picarro Cavity Ring-Down Spectroscopy Analyzer and Sage Autosampler

PICARRO

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Key Findings

- **Sage-G2508 performs at par with traditional GC**
- **Enables multi-gas analysis (CO_2, N_2O, CH_4)**
- **Supports high throughput (≤150 vials/day)**

Introduction and Objectives

Atmospheric greenhouse gas (GHG) flux measurements from soils form a cornerstone of biogeochemical research, providing insight into carbon turnover, methanogenesis, nitrification, and denitrification processes in terrestrial environments. Gas chromatography (GC) has long been regarded as the reference method for discrete headspace analysis because of its precision, high throughput, and adaptability to a wide range of concentrations. Over the past decade, however, cavity ring-down spectroscopy (CRDS) has emerged as a powerful alternative due to its ability to simultaneously quantify multiple gases in real time with high sensitivity, exceptional stability, and minimal maintenance requirements.

The Picarro G2508 CRDS analyzer extends this capability by enabling direct measurement of CO_2, CH_4, and N_2O in discrete samples, allowing researchers to find simpler alternatives to complex and expensive GC workflows that require carrier gases, frequent calibration, and instrument tuning. Combined with the Picarro Sage autosampler, which automates analysis of up to 150 vials through a fully integrated software interface, the combined G2508-Sage system offers a high-efficiency, low-consumable alternative for analyzing large batches of gas samples.

The present study provides a direct intercomparison between the Sage-G2508 system and traditional GC analysis (Agilent, Model 7890B) coupled with a PAL 3 autosampler (Agilent Technologies). Samples of ambient air, certified GHG standards, and soil incubation samples were measured in three experiment sets, enabling an assessment of precision, linearity, and instrument-specific artifacts such as memory effects. The findings demonstrate the strengths and practical considerations associated with adopting CRDS-based workflows for soil GHG research in a laboratory setting.

Experimental Design

Experiment 1: Standards and Ambient Air Intercomparison

Five replicate measurements of three different certified GHG standards (Scott-Marrin Inc.) and ambient air samples were measured in both platforms. These measurements provided a baseline comparison between GC and Sage-G2508 performance under controlled, known concentration conditions. The standard gas had the following certified concentrations in air matrix:

- CH_4 = 10 ppm
- CO_2 = 1000 ppm
- N_2O = 9.9 ppm

Ambient air samples represented near-background concentrations.

Experiment 2: Dilution Series

A dilution series was generated by mixing the certified standards with ultra-high purity (UHP) zero air at 20%, 40%, 60%, 80%, and 90% standard concentration levels (Table 1). Three replicates (n = 3) were analyzed at each dilution step for both GC and Sage-G2508. The resulting concentrations after dilution spanned the following ranges:

- CH_4: ~1–10 ppm
- CO_2: ~100–1000 ppm
- N_2O: ~0.99–9.9 ppm

Dilution percentage (%) in zero air	CH_4 (ppm)	CO_2 (ppm)	N_2O (ppm)
90	1	100.8	0.99
80	2	201.6	1.98
60	4	403.2	3.96
40	6	604.8	5.94
20	8	806.4	7.92
0	10	1008	9.9

Table 1. *Dilutions with zero air of GHG certified standard.*

Experiment 3: Soil Incubation Headspace Intercomparison

Soil incubation experiments were conducted to generate a wide range of gas concentrations representative of real-world soil processes. Peat and sandy loam soils were incubated at field moisture capacity for 1–3 weeks. A total of 22 jars were analyzed, comprising four treatments with five replicates each and two additional jars representing extremely high concentration conditions. Each 60 mL syringe sample was split equally between 12 mL LabCo Exetainer vials for Sage analysis and 20 mL UC Berkeley vials for GC analysis.

Gas ranges included:

- CH_4: 2–10 ppm
- CO_2: 437–7,500 ppm, extending to 72,000 ppm
- N_2O: 0.33–20 ppm, >20 ppm, up to 561 ppm

Methodology

System Setup

The Picarro Sage autosampler was coupled directly to the G2508 CRDS analyzer. The system was installed and operated at UC Berkeley (Figure 1), with a full installation schematic shown in Figure 2.

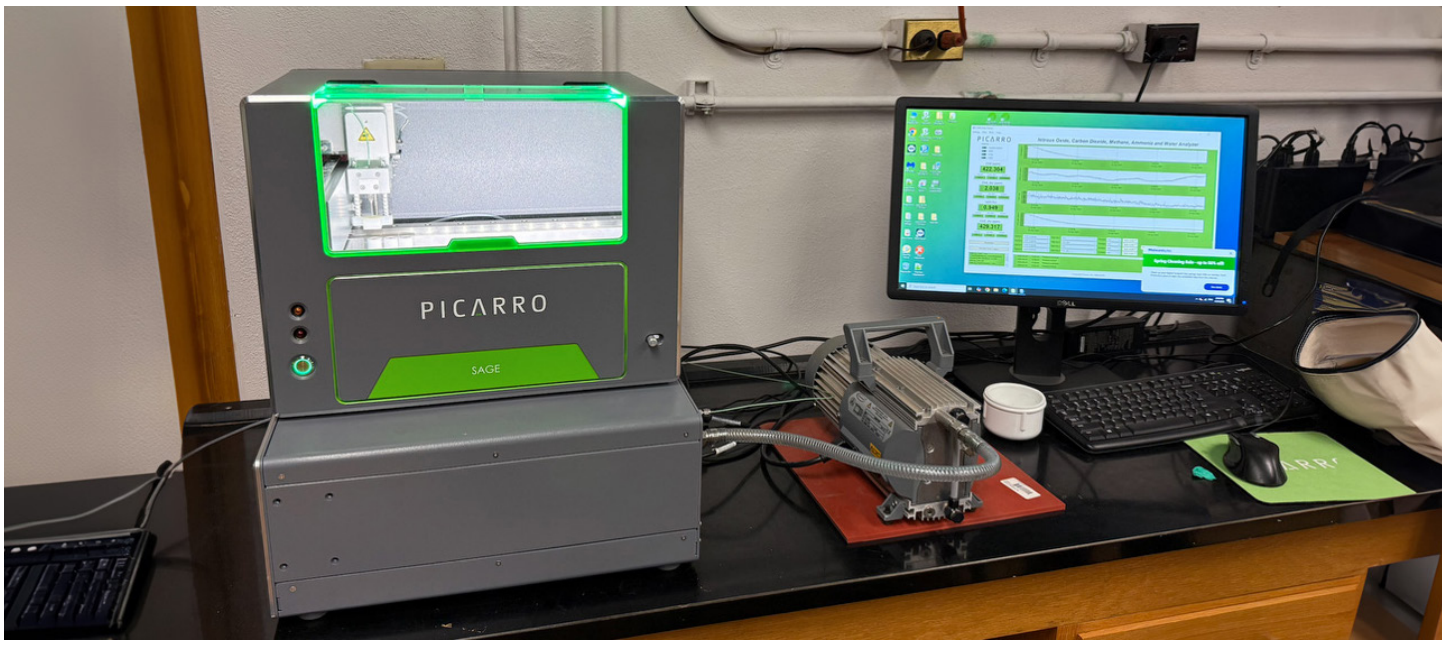

Figure 1. *The setup of the Sage gas autosampler and G2508 analyzer at UC Berkeley.*

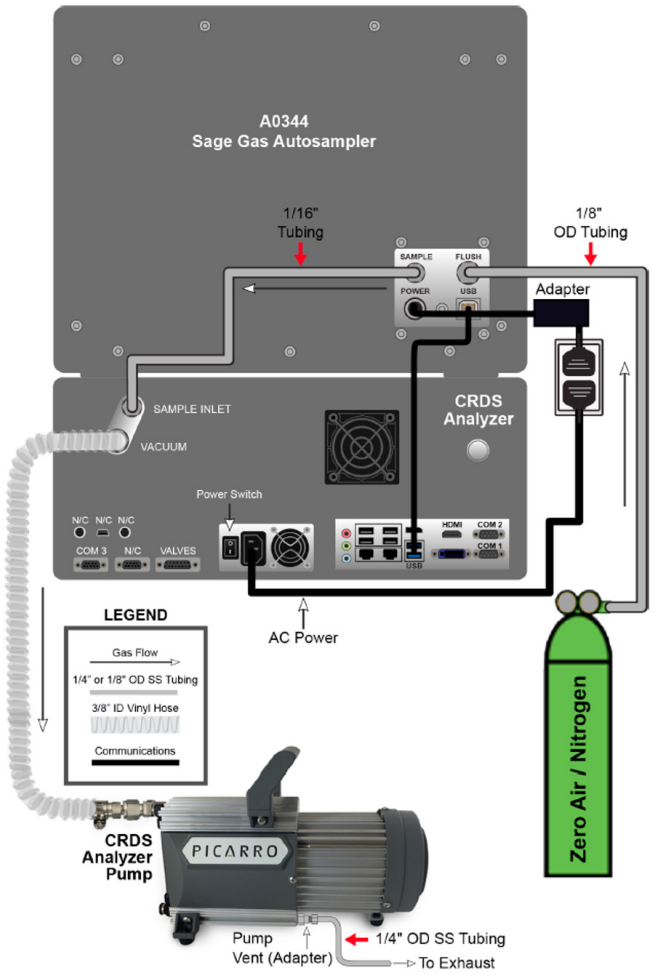

Figure 2. *The installation schematic for Picarro Sage-G2508 system.*

Vial Preparation

All vials were evacuated using the UC Berkeley manifold system capable of evacuating 10 vials simultaneously in approximately 5 minutes (Figure 3)*. Both Sage Exetainer vials and GC glass vials were evacuated using the same procedure to ensure consistency. Exetainer vials were sealed with doubly-wadded septa and analyzed shortly after filling to minimize leak-related drift. Glass vials were sealed with Teflon septa and metal crimps.

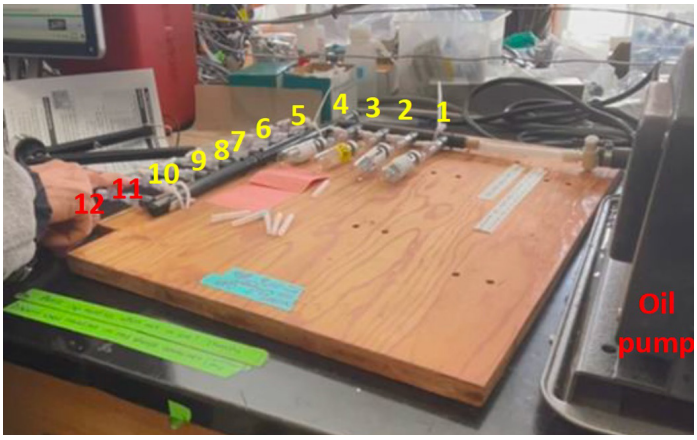

Figure 3. *UC Berkeley's vial evacuation system.*

**Users can also use Sage Sample Preparation Kit A0346 to automatically evacuate vials with Sage autosampler. Please refer to Sage User Manual for more information on evacuation techniques using A0346 Sample Preparation Kit.*

Sample Injection

Standard gases and ambient air were injected directly into evacuated vials using syringes. For soil incubations, a 60 mL headspace sample was withdrawn, and half the volume was transferred to Sage vials and half to GC vials. This parallel filling ensured direct comparison between the two platforms. A 30 mL sample volume for Sage exetainer vials was optimal for over-pressurizing the vials.

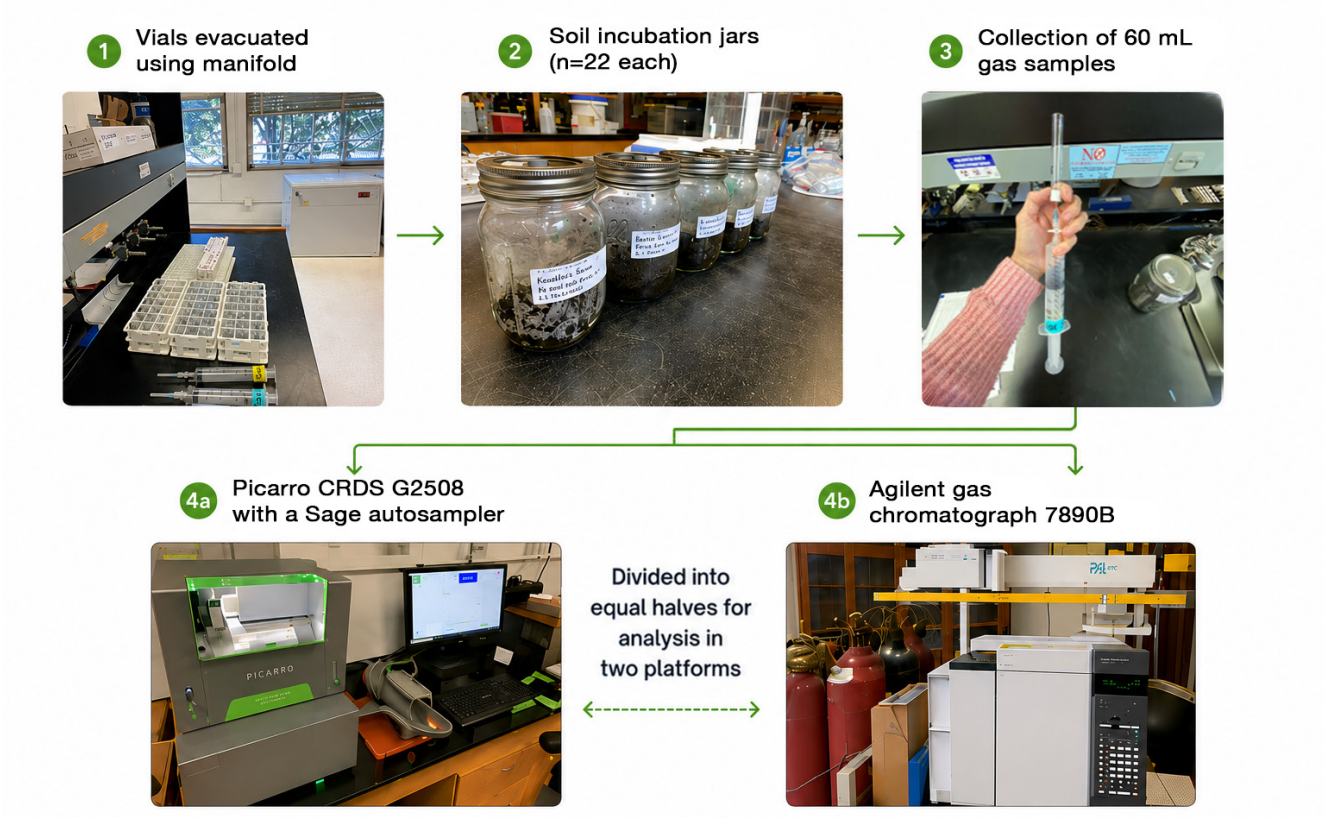

Figure 4. *Examples of incubation soil samples, whose headspace gas is extracted via a 60 mL syringe and vial filling method depicted in multiple steps.*

Analytical Platforms

Sage-G2508 System

The Sage autosampler automatically pierced each vial, flushed the internal pathways, and delivered the sample gas to the G2508 CRDS cavity, with automated vial handling and customizable analysis parameters managed through the integrated Sage software (Figure 5). Real-time concentration values were recorded directly.

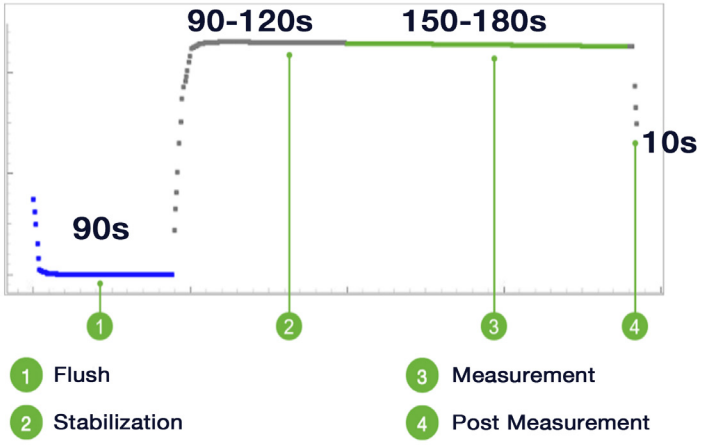

Figure 5. *Automated vial analysis workflow of the Sage-G2508 solution: The new software offers user-editable analysis parameters and real-time visualization.*

Gas Chromatography (Agilent 7890B)

GC measurements were conducted using standard peak area integration for CH_4, CO_2 and N_2O with appropriate detectors and calibration standards.

Results and Discussion

Linearity Between Two Systems

An overall strong linear agreement was observed between GC and Sage-G2508 measurement methods across all analytes. The three GHG analytes, CH_4, N_2O and CO_2, yielded R2>0.9 for all datasets that include measurement of certified standard gases, ambient air, dilution series of standard gases and soil incubation headspace samples (Figure 6).

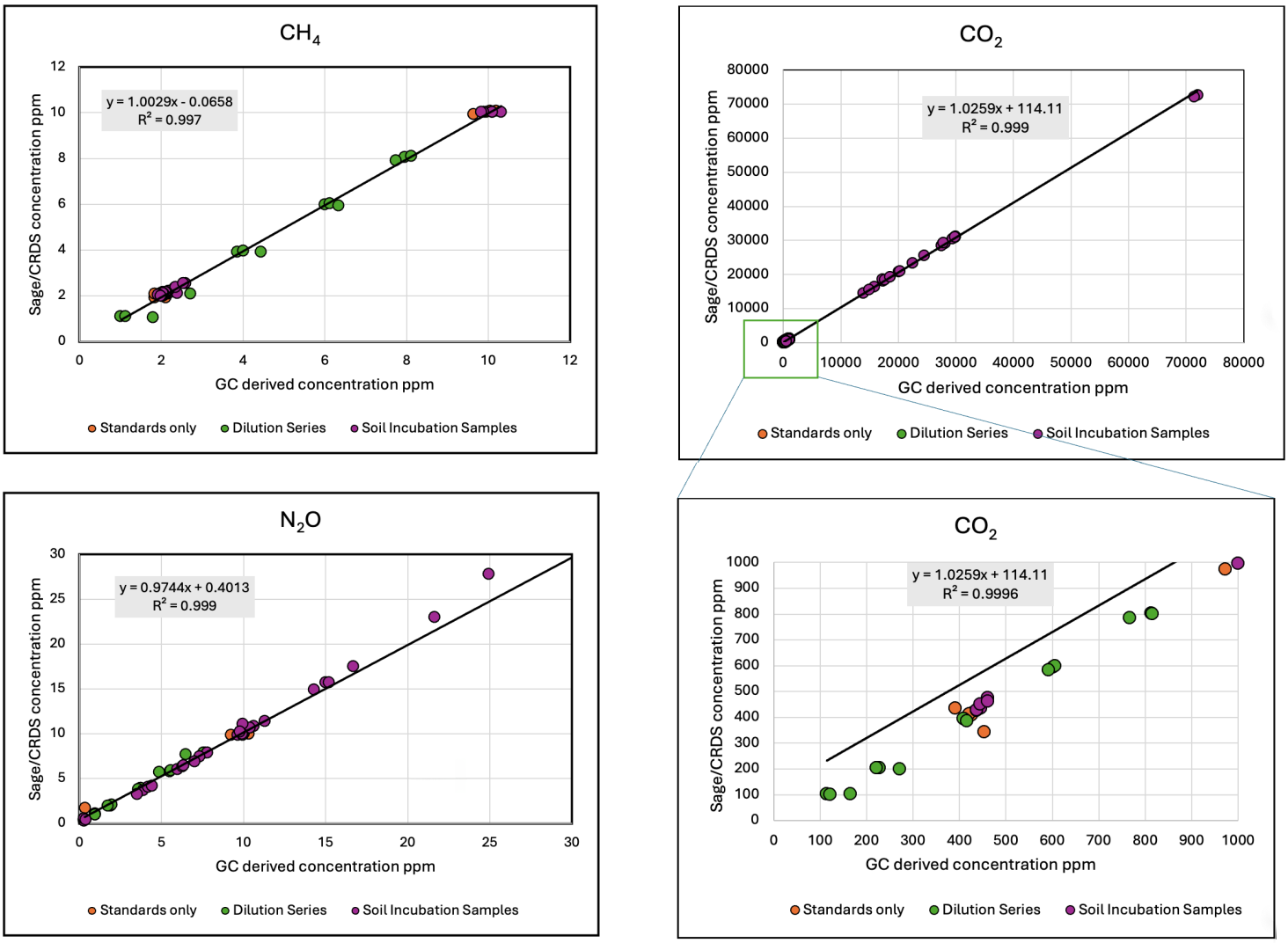

Figure 6. *1:1 comparison plot of GHG concentration of gas samples from three different experiments: standard gases, dilution series of standard gases, and soil incubation samples on Picarro Sage-G2508 system and GC (see Table 1 for details).*

Linearity varied based on sample types. Such variation is listed in Table 2. A higher agreement is observed in CH_4 compared to N_2O and CO_2. Experiment 1 showed lower level of agreement compared to Experiment 2 and 3 due to a few vials subject to contamination due to loosely tightened vial caps. CO_2 also had consistently lesser agreement than CH_4 or N_2O. The lower level of agreement for CO_2 could be explained by the fact that a lot of samples were outside the analyzer's guaranteed dynamic range.

R^2	CH_4	N_2O	CO_2
Experiment 1: Standard gases	0.999	0.991	0.981
Experiment 2: Dilution Series	0.989	0.988	0.995
Experiment 3: Soil Incubation	0.999	0.999	0.999

Table 2. *Coefficient of Determination (R2) for assessing linear agreement between GC and Sage-CRDS GHG concentration measurement methods.*

Data Reproducibility

Reproducibility was evaluated using parameters like standard deviation across replicate measurements of same sample and coefficient of variation (CV) calculated from the entire set of samples. Coefficient of variation is calculated as below:

CV = (standard deviation/mean)

Overall, both methods showed strong analytical precision, with CV generally below 5%. Variability was higher for ambient air samples than for standards with above-ambient concentrations. For dilution series, CV for GC was consistently higher than that for Sage, but that could also be attributed to non-consistent vial filling methods that inadvertently affected the GC measurements more than Sage.

Gas	Standard gas GC CV%	Standard gas Sage CV%	Ambient air GC CV%	Ambient air Sage CV%
CH_4	2.0	0.5	6.5	3.9
N_2O	2.4	0.8	3.5	4.4
CO_2	1.7	3.6	2.9	1.9

Table 3. *CV comparison between GC and Sage methods for standard gas and ambient air samples.*

For the dilution series experiment, standard deviation across true replicates can be used as a benchmark precision determination for Sage-CRDS method. The CV was <1% for the Sage-CRDS system and precision is displayed for the three compounds in Table 4.

Precision observed in Sage-CRDS system for dilution series experiment	Sage CH_4 concentration (ppm)	Sage N_2O concentration (ppm)	Sage CO_2 concentration (ppm)
Standard deviation across 3 replicates for 10% to 80% diluted standard gas samples (refer to target concentration in Table 1)	0.02	0.01	1.22
	0.02	0.04	2.08
	0.03	0.06	4.12
	0.04	0.08	7.85
	0.07	0.11	10.05
Coefficient of Variability	0.71	0.72	0.71

Table 4. *Standard deviation across replicates for Sage/CRDS method.*

Carryover Effects

Carry-over effects were primarily observed in the Sage-G2508 system following exposure to very high CO_2 and N_2O concentrations in the samples. For example, Figure 7 demonstrates a scenario where the same standard gas samples for CO_2 reported over-estimated values on the Sage after measuring high CO_2 containing soil incubation samples. Such temporary deviations in subsequent measurements of the standard gas samples were not observed in GC measurements. Extended flushing with zero air may help reduce carryover. While GC analysis showed minimal carry-over under comparable conditions, carry-over effects can be mitigated by adjusting flush time within the Sage sample analysis methods.

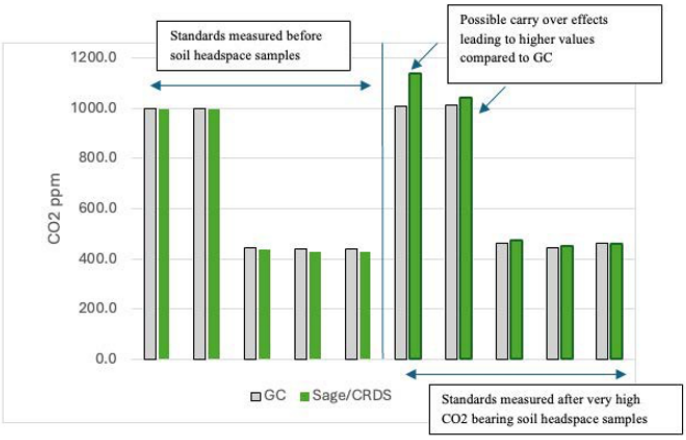

Figure 7. *Example of carry overeffect that affects Sage-CRDS system.*

Effects of Vial Integrity and Sample Volume

For the Sage-CRDS system, reproducibility was higher when sample volumes exceeded ~25 mL and vials were analyzed shortly after evacuation. Delayed analysis introduced deterioration in accuracy, particularly for CO_2 and N_2O. These observations reinforce the importance of consistent vial preparation and maintaining as little shelf storage time of filled vials as possible. and in some applications streamline, traditional GC workflows, particularly where high sample throughput and multi-gas capability are required.

Conclusions

This intercomparison study demonstrates that the Sage-G2508 system is a highly capable alternative to GC for discrete greenhouse gas analysis. In general, both methods maintained great reproducibility. Most differences in the Sage-G2508 system are largely attributable to carry-over effects following analysis of high-concentration samples.

Across standards, dilution series, and soil incubation samples, strong linear agreement was observed between the two platforms, with linear regression R2>0.9 between methods in all experiments. Methane measurements showed near-unity slopes across concentration ranges. In general, N_2O and CO_2 demonstrated robust agreement, although soil incubation samples with intermediate CO_2 and N_2O concentrations showed slight deviations toward higher values in the Sage-CRDS measurements relative to GC. These deviations may reflect concentration-dependent effects or transient carry-over effects potentially impacting Sage-G2508 system more than GC.

Memory effects in CO_2 and N_2O following high-concentration samples were the primary operational limitation identified in this study. Extended flushing with zero air reduced carryover and improved repeatability. Because some natural soil GHG fluxes in incubated soils may produce concentrations above the linear range of the Picarro G2508 CRDS, diluting samples with zero air in the evacuated vials may help minimize carry-over effects and improve the accuracy of the measured concentrations. With appropriate operational adjustments, the overall performance indicates that the Sage-G2508 system can reliably perform at par with, and in some applications streamline, traditional GC workflows, particularly where high sample throughput and multi-gas capability are required.

Recommendations for Best Performance

For reliable long-term operation of the Sage-G2508 system in soil gas applications:

- Thoroughly evacuate vials and fill them immediately prior to analysis whenever possible.
- Use sample volumes of at least 25–30 mL to maximize reproducibility and minimize vial-related variability.
- When analyzing sequences with high-concentration headspace samples:
  - Incorporate extended cavity flushing with zero air before returning to lower concentration measurements.
  - Consider diluting samples in the vials with zero air prior to analysis to reduce potential memory effects.
- Routinely verify instrument performance using certified standards to maintain consistency with historical GC datasets.
- Investigate intermediate concentration deviations and potential laser saturation effects to further refine operational parameters and expand the validated dynamic range of the system.

Acknowledgment

The authors would like to thank the University of California, Berkeley's Department of Environmental Science, Policy and Management for agreeing to collaborate on this methods' inter-comparison project. At Picarro Inc., this project would not have been successful without contributions from Petr Khromov, Ally Zhong, Magdalena Hofmann and Sohom Roy for software improvements, installation support and extensive technical reviews.

LIT CODE: 260623

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