



Recent developments within NOAA's AirCore atmospheric sampling program and insights from its long-term observational record over Boulder, Colorado

Bianca C. Baier¹, Colm Sweeney¹, Jack Higgs¹, Markus Jesswein^{2,1}, Jianghanyang Li^{2,1*}, Fred Moore^{2,1},
5 Tim Newberger^{2,1}, Pieter Tans^{1,+}, Sonja Wolter^{2,1}

¹NOAA Global Monitoring Laboratory, Boulder, Colorado, USA, 80305

²Cooperative Institute for Research in Environmental Sciences (CIRES), University of Colorado-Boulder, Boulder, Colorado, USA 80309

*Now at: Institute of Arctic and Alpine Research and Department of Atmospheric and Oceanic Sciences, University of
10 Colorado-Boulder, Boulder, Colorado 80309

⁺Now at: Institute of Arctic and Alpine Research, University of Colorado-Boulder, Boulder, Colorado 80309

Correspondence to: Bianca Baier (bianca.baier@noaa.gov)

Abstract

NOAA's AirCore atmospheric sampling program in Boulder, Colorado has provided one of the longest continuous
15 stratospheric records of calibrated carbon dioxide (CO₂), methane (CH₄), and carbon monoxide (CO) measurements in the
world from 2012 to present day. Further, the AirCore technology has been adopted by several institutions worldwide for
atmospheric vertical trace gas profiling. Over the past decade, this program has seen multiple technical improvements including
the development of smaller, more lightweight AirCores, which has allowed for new methodologies to routinely assess the
quality of vertical profile observations of trace gases. The development of new analytical techniques over the past decade,
20 along with new developments in methodological and analytical approaches to expand the vertical coverage and trace gases
concurrently analyzed in AirCore samples, expanded the AirCore profiling suite to additional species such as nitrous oxide
(N₂O). Disseminating these methodologies is essential for establishing new AirCore programs abroad and for maintaining
consistency and reproducibility with existing ones. Here, we highlight a 13-year observational record of CO₂, CH₄ and CO,
25 and a more recent record of N₂O (circa 2019) over Boulder, Colorado, from monthly profiling efforts within the NOAA
AirCore Program, examining trends in CO₂ and seasonal variability in all species. Same-string AirCore comparisons have
allowed for sampling system repeatability to be assessed throughout the atmospheric column from Boulder, Colorado, which
is typically less than 0.1 ppm, 2 ppb, 5 ppb, and 1 ppb for CO₂, CH₄, CO and N₂O, respectively, at pressure level intervals
commensurate with molecular diffusion length scales. These high-quality profiles uniquely capture both seasonal and transport
variability in atmospheric composition derived from changes in surface fluxes, long-range transport, potential vorticity
30 displacement and stratosphere-troposphere exchange, providing access to new understanding of stratospheric composition,
chemistry and dynamics. Other new aspects of the AirCore program described here include both additional trace gas species



that provide further insight into stratospheric transport time scales and a UAS-based platform for automated AirCore recovery and expansion of profiling capabilities to under-sampled regions.

1 Introduction

35 Accurately representing the distribution of greenhouse gases (GHGs) and other long-lived species throughout the atmosphere is critical for monitoring, understanding and predicting change in atmospheric composition, chemistry and transport from the surface to the stratosphere. Profile observations capture GHG variability throughout the atmospheric vertical column that reflects processes that occur on timescales ranging from diurnal to several years. Atmospheric profiles play a critical role in estimating carbon fluxes on regional to global scales through direct use in inverse models (Stephens et al., 2007; Yang et al., 40 2007; Crevoisier et al., 2010; Gatti et al., 2010; Zhang et al., 2014; Long et al., 2021) or indirect use of these observations to evaluate e.g. model vertical transport for flux estimation (Hall et al., 1999; Stephens et al., 2007; Boschetti et al., 2018; Saunio et al., 2025). Vertical profiles are also used for evaluating, bias-correcting and improving ground- and space-based remote sensing retrievals (Wunch et al., 2010; Deeter et al., 2014; Imasu et al., 2023; Laughner et al., 2023). Observations of long-lived trace gases such as CO₂ and nitrous oxide (N₂O) that extend into the stratosphere are particularly useful for monitoring 45 changes in both chemical and dynamical processes over time. Models have predicted that, with increasing GHGs and temperature, the Brewer-Dobson circulation (BDC) will intensify (Butchart et al., 2006; Li et al., 2008; Garcia and Randel, 2008). Routine observations of stratospheric GHGs allow for verification of this prediction from models, and an improved understanding of transport pathways of air into and within the stratosphere (Ray et al., 1999; Engel et al., 2009; Bönisch et al., 2011; Ray et al., 2010). Models must accurately depict troposphere-to-stratosphere transport in order to assess potential 50 feedbacks on surface weather and climate, air quality, stratospheric ozone recovery, water vapor concentrations and consequential changes to the earth's radiation budget. Equally important, accurate model transport in the stratosphere is critical for realistically simulating the effects of proposed climate intervention perturbations on the background atmosphere and quantifying uncertainties therein (e.g. Bednarz et al., 2023; Zhang et al., 2023).

55 Historically, flask sampling from both aircraft and balloons up to 28 km occurred in the 1930-1950s (Bischof, 1962; Keeling et al., 1968). It wasn't until the later 1990s that continuous, in situ measurements were conducted up to 20 km on research aircraft (Anderson et al., 1993; Boering et al., 1994; Tuck et al., 1997). It was also during the 1990s that vertical profiles extended further into the upper troposphere and lower stratosphere (30-35 km) using large volume balloons instrumented with in situ measurements (Pyle et al., 1994; Newman et al., 2002). NOAA's Global Greenhouse Gas Reference Network's 60 (GGGRN) aircraft program, conducting routine discrete flask sampling profiles up to ~8 km (Sweeney et al., 2015), was also realized in the late 1990s. By the early 2000s, in situ measurements on commercial aircraft started to provide additional coverage and expand routine profiling capabilities to altitudes of ~10-12 km (Brenninkmeijer et al., 2007; Machida et al., 2008, Matsueda et al., 2008; Thouret et al., 2022). Also at this time, satellites brought about the capability of routinely retrieving



atmospheric trace gas abundances with unprecedented global coverage, providing complementary spatial and temporal
 65 coverage to existing measurements (Yokota et al., 2009; Crisp et al., 2004). Satellites fundamentally cannot be directly
 calibrated and therefore must be frequently compared with calibrated in situ profiles, or models assimilating in situ profiles
 for bias-correcting trace gas retrievals (Emmons et al., 2004; Wunch et al., 2017, O'Dell et al., 2018). Satellites are also limited
 in vertical resolution, and sometimes unable to retrieve trace gas abundances through clouds (leaving significant gaps in
 tropical regions and potential fair-weather biases) or high latitudes (areas without sun for long periods of time). Logistical and
 70 operational costs have also prohibited routine in situ profiling on larger, more expensive platforms such as research aircraft
 and large volume balloons, resulting in sporadic observations of the upper troposphere and lower stratosphere since the 1990s
 (Krysztofiak et al., 2023; Ray et al., 2024; Schuck et al., 2025).

As a newer, complementary method for providing high-resolution, calibrated vertical atmospheric profiles for several gases
 75 such as CO₂, methane (CH₄), and carbon monoxide (CO) circa 2009, the AirCore atmospheric sampling system can be
 implemented routinely on small, low-cost weather balloons (Karion et al., 2010). AirCore sampling (Tans, 2009) relies on
 deploying a long, coiled tube into the atmosphere using a small balloon. The AirCore is prepped for flight by filling it with a
 dry, “fill gas” mixture with known mole fractions of species to be measured (Karion et al., 2010). The AirCore ascends on a
 balloon, and this gas passively evacuates through the open end of the tubing coil to equilibrate with decreasing ambient
 80 pressure. On descent after balloon burst or cutaway, air is passively collected in the AirCore as ambient pressure increases.
 Due to the long length and small diameter of the AirCore tubing, molecular diffusion and drag-induced (Taylor) dispersion
 have a relatively small impact on the air sample collected, preserving the variability within the sample over the storage time
 between landing and laboratory analysis (Karion et al., 2010, typically less than 4 hrs). If the pressure, temperature and altitude
 profile of the AirCore descent trajectory is also measured during flight, laboratory measurements can then be tied to the
 85 atmospheric pressure and altitude at which the sample air was collected using an evolving steady state fluid dynamics model.
 This model reproduces measured internal pressure gradients, which are used to estimate the exact amount of air ingested and
 airflow characteristics at any point throughout the flight, and is outlined in Tans (2022).

Since 2012, the NOAA Global Monitoring Laboratory's (NOAA/GML) AirCore Program has collected over a decade of
 90 routine vertical profile observations of CO₂, CH₄, CO – and, more recently, N₂O – with over 200 balloon flights. The AirCore
 technique, shared with international collaborators, has significantly contributed to remote sensing retrieval algorithm
 development and critical scaling (i.e. achieving compatibility with ground-based networks) of retrievals to World
 Meteorological Organization trace gas standard scales (Nalli et al., 2020; Mostafavipak et al., 2021; Laughner et al. 2023,
 2024; Martínez-Alonso et al., 2022; Parker et al., 2023; Chan Miller et al., 2024; Ortega et al., 2025); to the development of
 95 procedures and assessment of stratospheric age of air and its changes over time (Moore et al., 2014; Engel et al., 2017; Laube
 et al., 2020; Li et al., 2023; Ray et al., 2024); and to model evaluation of atmospheric composition (Peiro et al., 2021, 2022;
 Augusti-Panareda et al., 2023). This technology has been adopted by other, independent institutions or groups worldwide in



the following countries in addition to the United States: the Netherlands (University of Groningen); Finland (the Finnish Meteorological Institute); France (the Laboratoire de Météorologie Dynamique, École Polytechnique); Germany (Forschungszentrum Jülich's Institute of Energy and Climate Research and Goethe University Frankfurt) and China (Chinese Academy of Sciences) (Paul et al., 2016; Engel et al., 2017; Membrive et al., 2017; Laube et al., 2020; Wagenhäuser et al., 2021, 2023; Tans 2022; Yi et al., 2024). Like other long-term global measurement networks have demonstrated, it is critical that techniques and procedures be robust and consistent for AirCore profiling across this network in order to deliver high-quality, calibrated, compatible, atmospheric observations. In this work, we describe technical updates to the NOAA balloon-borne AirCore Program over the past decade that improve upon the quality and potential for compatibility across the AirCore global network for base measurements made monthly of CO₂, CH₄, CO, and N₂O. These updates include the development of smaller, more lightweight sampling systems, quality assurance procedures to routinely assess the AirCore repeatability, reproducibility and the altitude registration of vertical profiles and techniques that both expand the vertical coverage and suite of trace gases measured in the AirCore. In doing so, we describe standard practices, use of new tools and sensors onboard the AirCore sampling system and analytical techniques developed since first described in Karion et al. (2010). We also briefly highlight other directions that the NOAA AirCore Program has taken over the past decade that include quarterly measurements of additional species via gas chromatography (Li et al., 2023) and the development of a UAS-based platform as a return vehicle for AirCore samples (Takahashi et al., 2021). Finally, we examine trends in CO₂ over a 13-year NOAA AirCore record over Boulder, Colorado, and identify seasonal variability stemming from both emissions and dynamical characteristics in monthly profiles of base species CO₂, CH₄, CO and N₂O.

2 Methods

2.1 NOAA AirCore sampling system configurations

NOAA AirCores have gone through considerable configuration redevelopment since originally described in Karion et al., (2010) in an effort to increase sampling efficiency, robustness of AirCore operations, trueness of profile mole fractions and the accuracy of the profile altitude registration. Measures have been taken to a) reduce the total mass of each AirCore, b) capture variability in GHGs at relatively high resolution throughout the atmospheric column, c) increase passive air collection efficiency in AirCores at altitudes above 20 km above mean sea level (MSL) and d) routinely quality-check sampling systems and the modelled altitude registration of profiles.

NOAA/GML deploys AirCores at a monthly frequency in northeastern Colorado using new, second-generation configurations that enable two samplers to be flown on the same balloon string (Figure 1). With a total payload weight less than 5.44 kg (12 lbs), these balloons are exempted under U.S. Federal Aviation Administration's (FAA) Code of Federal Regulations (CFR) for Aeronautics and Space for unmanned balloons (14 CFR §101.3). Dual-AirCore balloon payloads allow for an assessment of the repeatability of samplers and the quality assurance of resulting profiles. Redundant samples are an important check for



130 the following potential sources of error: a) loss of sample from small leaks that is possible when these sealed systems warm and pressurize upon landing; b) artifacts due to the breakdown in coated surfaces of the AirCore tubing; and c) measurement errors during sample analysis.

The first of two second-generation sampling system designs is comprised of ~90 m of thin-walled (0.29 cm ID), 1/8" (0.31 cm
 135 OD) 304 stainless steel tubing for a total sample volume of approximately 600 mL and an average total mass of ~1.4 kg including valves, the foam protective housing and the connected payload string. Pairs of AirCores to be used for monthly flights are rotated from a suite of samplers to avoid the potential for biases produced with continuous use of a single sampling system. These 600 mL AirCores allow for measurements of trace gases at a calculated sampling altitude resolution between 75 m and 2000 m throughout the profile based on typical flight characteristics, diffusion during a four-hour storage time of the
 140 collected sample and the density of air. As AirCore tubing dimensions can be configured based on desired sampling resolution and scientific needs (Membrive et al., 2017; Baier et al., 2023), a second design and additional suite of larger volume, ~750 mL AirCores (here, AirCore configurations called "StratoCores") has been constructed with two diameters of 304 stainless steel tubing: a 27.9 m section of thin-walled 1/8" (0.31 cm OD, 0.29 cm ID) stratospheric portion, and a 20.9 m section of 1/4" (0.64 cm OD, 0.58 cm ID) tropospheric portion at the open end (~1.7 kg total). In both second-generation AirCore
 145 configurations, 304 stainless steel tubing is used as thin-walled tubing is not currently available in preferred, higher quality, 316 stainless steel. With larger diameter tubing at the inlet or open end of the sampler, StratoCores allow more air to be collected within the tubing at high altitudes (in this case, greater than ~18 km) than the single-dimension AirCores for the same flight profile and storage diffusion time, and has been demonstrated in previous literature (Karion et al., 2010; Membrive et al., 2017; Tans, 2022). The wide diameter inlet tubing design of the NOAA StratoCores significantly improves pressure
 150 equilibration of the tubing coil with the surrounding environment prior to and during descent. In addition, the StratoCore design is optimally flown on balloons that are equipped with a valve descent mechanism to slowly vent lifting gas from the balloon and allow for a float period and a slow initial descent before balloon cutaway, which allows for a slower turnaround from ascent to descent. With a lessened pressure buildup across the tubing coil, StratoCores have demonstrated more efficient air sampling at altitudes greater than ~25 km MSL (Section 2.3.2), which allows for a larger stratospheric portion of the profile
 155 to be compressed within the smaller diameter tubing at the "top" section of the AirCore. The AirCore tubing is internally coated with the Silconert 1000® (*Silcotek*) formulation to deter air sample-wall artifacts that could be otherwise present on bare stainless steel tubing. We chose this coating over other available formulations because it does not include organic components that could potentially oxidize in the sample air. Karion et al. (2010) has shown that this coating has a negligible impact on CO₂ and CH₄, with calibrated air within the tubing for both flow-through scenarios preserving the calibration tank
 160 value to within 0.04 ppm CO₂ and 0.2 ppb CH₄ and, after 13 h of storage, to within 0.07 ppm CO₂ and 0.4 ppb CH₄. Second-generation AirCores coated with Silconert 1000® similarly preserve CO₂ and CH₄ within this range after ~18 hours of storage (0.03 ppm CO₂, 0.4 ppb CH₄) in addition to CO (0.3 ppb) and N₂O (0.1 ppb). Experiments to-date using tubing coated with the Silconert 2000® have shown significant (more than 50 ppb) enhancements in CO, hypothesized to be due to oxidation of



organic compounds in the Silconert 2000® formulation by high concentrations of ozone in the stratosphere. Sample air is dried with coarse magnesium perchlorate ($\text{Mg}(\text{ClO}_4)_2$) granules prior to entering the AirCore to deter surface degradation in sample tubing over time. Desiccant granules are housed in either a short piece of 3/8" (0.95 cm) stainless steel tubing made with in-house threaded fittings or in Swagelok filter housings. Tubing coil temperature is monitored using five thermistors distributed around the coil and logged onboard the AirCore with GPS altitude, ambient temperature and pressure.

An important new addition to the AirCores is a differential pressure sensor (*All sensors 5-inch-D2-P4V-MINI*, Figure 2) that is routinely attached to the top, closed (stratospheric) end of the AirCore (after attaching, the AirCore "top valve" is opened, Figure 2). This sensor measures the pressure difference between the inside of the sampler and its surrounding environment. This difference is simulated with an evolving (with time and position in the tube) steady-state fill dynamics model, and ultimately used to register the AirCore sample with altitude. As such, measuring this quantity allows for a new, direct constraint on the AirCore fill dynamics model, which inherently makes some assumptions about the resistance of the tubing at the inlet (due to the valve and dryer tubing). To verify the fill dynamics model output, the differential pressure measurement is used to optimize the resistance of flow out of and back into the AirCore during flight and to more accurately model the collection of sample air, as demonstrated in Tans (2022). Because the differential pressure sensor is attached to the normally-closed, top end of the AirCore, it does not directly interfere with the flow path of the sample air, and the fill dynamics model can be validated for each flight given each sample's outflow and inflow conditions, which are dependent upon each individual flight's characteristics. We note that after the bottom valve of the AirCore is closed upon landing (Figure 2), the air sample's pressure will increase as the temperature of air within the coil increases. Because the differential pressure sensor is attached to the top AirCore valve (Figure 2), this configuration can present a possibility for leakage of stratospheric air out of a pressurizing AirCore through the differential pressure sensor, potentially leading to altitude registration errors. Thus, measures must be taken to ensure that both the top and bottom valve are closed immediately upon landing in this flight configuration. Others within the global AirCore network have developed an alternative model for registering the AirCore with altitude that makes the assumption of pressure equilibrium between the AirCore and surrounding air during balloon descent (Engel et al., 2017; Membrive et al., 2017; Wagenhauser et al., 2021). Wagenhauser et al. (2021) evaluate and correct this model's high bias in altitude registration by injecting a "tracer" gas into the AirCore inlet at known altitudes, with corrections ranging from ~ 1.2 km at 27 km and ~ 250 m below 20 km (which was specific to the multi-dimensional AirCore tubing coil used). The tracer gas in Wagenhauser et al. (2021) was spiked with a high mole fraction of CO, which can significantly bias resultant CO profiles. Therefore, if CO profile observations are of high scientific priority, one drawback to this technique is that it cannot be implemented for every flight. It should also be noted that CO diffusion occurs on different timescales than other trace gases measured within the tube (CH_4 , CO_2 , etc.).

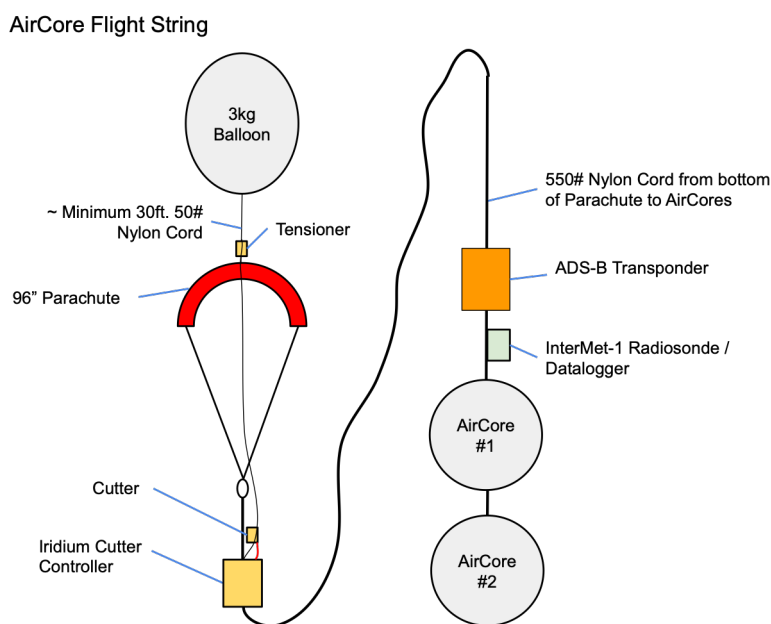


Figure 1. AirCore flight string schematic indicating several redundant GPS tracking devices (Iridium, ADS-B transponder, InterMet-1 Radiosonde) alongside a dual AirCore payload (adapted from Baier et al., 2023.)

2.2 AirCore analysis methodology

Below we describe updates to existing analytical methods using cavity ring-down spectrometry (CRDS, Picarro 2401-m and PI5310 systems) for measurement of the AirCore program's basic trace gases (CO_2 , CH_4 , CO , and N_2O) in AirCore samples collected on a monthly basis.

2.2.1 Analysis system configurations for AirCore samplers

For the majority of the AirCore profile record over northeastern Colorado, a Picarro CRDS system (G2401 series) is used to measure the AirCore sample using the apparatus shown in Figure 3a for CO_2 , CH_4 and CO . To decrease the potential for sample contamination by lab or ambient air during analysis, AirCore valves are flushed and purged with dry standard gas prior to pushing the sample air through the CRDS system. After purging, the AirCore is opened and the sample air is pushed through the CRDS system, starting with the stratospheric portion of the sample. The Picarro G2401 measurements have been shown in previous literature to provide extremely stable values over time, even in the absence of routine calibrations (Richardson et al., 2012; Karion et al., 2013). For AirCore analyses, calibrations of the Picarro CRDS systems are performed on an approximate yearly basis. A slope and intercept correction based on the system's most recent laboratory system calibration is applied to each AirCore sample analysis. In addition, a one-point offset correction using a gas calibration standard is applied to sample data during each AirCore analysis to account for a) any small drift of the Picarro system or b) inadequate flushing of tank regulators at the low flow rate used (30 standard cubic centimeters per minute (sccm)). Analysis of more than a decade of Picarro systems used in the NOAA AirCore Program supports literature findings (Richardson et al., 2012; Karion et al.,



2013) that Picarro G2401 measurements remain stable for AirCore trace gases analyzed over long periods of time. For example, when considering a Picarro system making measurements of the same calibration tank used over a duration of ten years (19 total calibrations performed during this time frame), the standard deviation of reported values is less than 0.05 ppm for CO₂, 0.25 ppb for CH₄, and 1.75 ppb for CO (Figs. S1-3). Due to the recent availability of Picarro-based CRDS analyzers for measurements of AirCore samples, N₂O measurements are not available for this historical analysis.

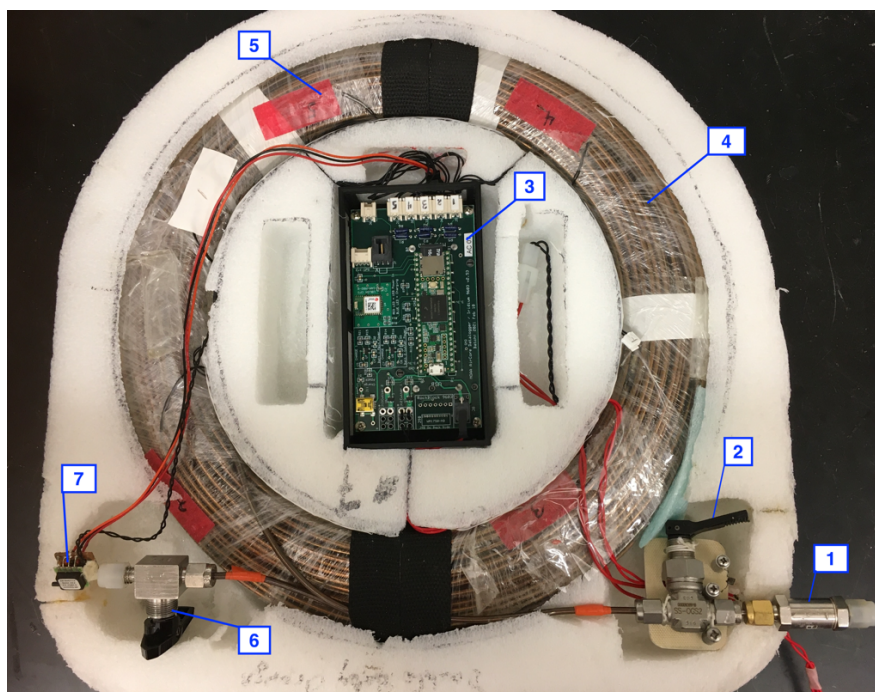


Figure 2. 600 mL AirCore sampler consisting of 1) magnesium perchlorate-filled dryer; 2) bottom valve, which is automatically closed after landing; 3) Arduino datalogger board which logs AirCore coil (4) temperatures from thermistors indicated by 5), in addition to ambient temperature, pressure, GPS location and differential pressure. (6) indicates the AirCore top valve, which remains open during flight to allow for the AirCore datalogger to record the differential pressure (7) between the inside of the AirCore and ambient air (adapted from Baier et al., 2023).

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While only analysis of CO₂, CH₄ and CO is discussed thus far, beginning in 2019, the NOAA/GML developed the capability to plumb two CRDS systems (Picarro G2401 and PI5310) in series to concurrently measure CO₂, CH₄, CO and N₂O, and this concept was shared and implemented within the global AirCore community (e.g. Tong et al., 2022, Figure 3b). In addition to analysis by CRDS, others have demonstrated the utility of AirCores for measurement of additional long-lived trace gases in the upper troposphere and lower stratosphere via mass spectroscopy, gas chromatography, and accelerator mass spectrometry (Paul et al., 2016; Laube et al., 2020; Li et al., 2023).

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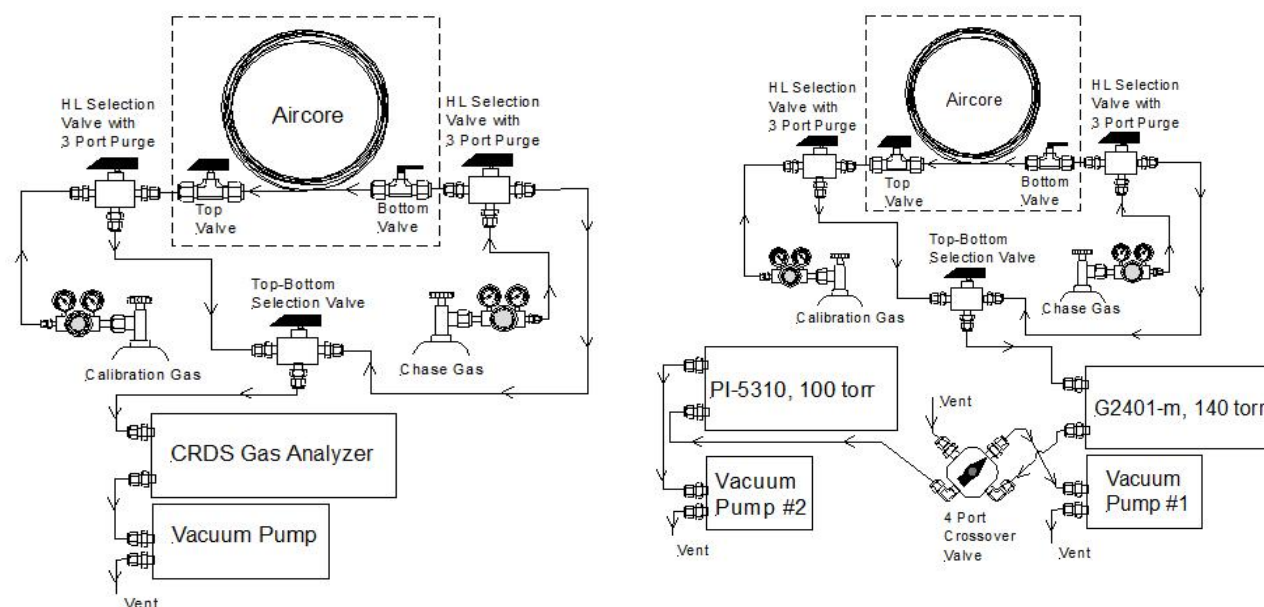


Figure 3 Left) Schematic of analysis apparatus used to prepare, purge and analyze AirCore samples prior to 2019. AirCore components contained within the dotted line are in the flight package; other components are for post-flight sample analysis. Swagelok “HL flow path” three-way ball valves allow for simultaneous flushing and purging of both bottom and top valves on the AirCore with dry air prior to analysis. Air samples are analyzed from top to bottom at a 30 sccm flow rate, with the CRDS gas analyzer (here, a Picarro G2401 series) operating in inlet valve control mode at a 140-torr cavity pressure. **Figure 3 Right)** shows the “dual-Picarro” setup used to analyze AirCore samples for CO₂, CH₄, CO, and N₂O simultaneously using a 4-port crossover valve that connects the two analyzers. Air samples for this analysis setup are analyzed again, from top to bottom at a 30 sccm flow rate with the G2401 operating at its factory setting of 140 torr in inlet valve control mode and the PI5310 operating at its factory setting of 100 torr in outlet valve control mode (inlet valve is not available for the PI5310 configuration).

2.2.2 Fill gas mixing correction and uncertainties

The AirCore fill gas is a mixture of air with tropospheric levels of all measured species, but spiked with approximately 2 ppm of CO to differentiate the topmost (stratospheric) air sampled by the AirCore during analysis. While higher levels of CO have been used to spike fill gas (up to 10 ppm), we caution the risk of saturating the CRDS analyzer CO channel; 2 ppm CO was settled on as a maximum level to maintain sufficiently fast recovery of the analyzer from these high values. This same gas mixture (“chase gas”) is used to push the AirCore sample through the CRDS to similarly signal the bottommost (atmospheric boundary layer) AirCore sample. As end-member mixing occurs between the AirCore sample and the fill and chase gas, it is possible to correct for this mixing post-analysis. Below the use of two different fill gases for AirCore flights is demonstrated based on the analyzed species of interest, along with corrections to resultant profiles due to fill gas mixing and uncertainties.



Based on the routine flights described above and approximate 30 km altitudes reached therein, sampling systems generally evacuate all but ~ 1% of their total volume of fill gas just prior to sample collection in the stratosphere on balloon descent. After payload landing, AirCores are automatically triggered to close, preserving the air sample for laboratory analysis. At 20°C and with a four-hour average storage time, we calculate below that a CO₂ molecule will have an average root-mean-square diffusion distance of about 0.5 m in each direction within the tubing coil at the start of sample analysis. The topmost AirCore sample collected in the stratosphere mixes with the fill gas. While the bottommost AirCore sample collected mixes with the chase gas upon analysis, the mixing time is only the length of time (20-30 minutes) that it takes to conduct the AirCore analysis (Figure 4). We estimate how much of the AirCore sample has been mixed by calculating the fraction of CO-enhanced fill gas in each AirCore sample collected and use a simple mixing equation to correct CO₂ and CH₄ measurements affected by mixing during sample storage and analysis.

Equation 1 is used as a simple model to estimate the amount of fill gas present in an AirCore sample:

$$X_{std} * f_{fill} + X_{sam} * (1 - f_{fill}) = X_{meas} \quad , \quad (1)$$

where X_{meas} is the trace gas mole fraction of CO₂ or CH₄ measured by the CRDS, X_{std} is the mole fraction of CO₂ of CH₄ contained in the original fill gas cylinder, X_{sam} is the sample mole fraction of these trace gases collected in the AirCore and f_{fill} is the fraction of fill gas contained in the mixture. If we assume f_{sam} is the fraction of sample gas in this mixture, then

$$f_{sam} = 1 - f_{fill} \quad , \quad (2)$$

and we can rearrange and solve for the sample gas mole fraction, X_{sam} :

$$X_{sam} = \frac{X_{meas} - X_{std}}{f_{sam}} + X_{std} \quad . \quad (3)$$

We use the assumption that when $f_{sam} = 1$, the amount of CO in sampled air is equal to the minimum amount of CO measured in the stratospheric portion of the AirCore sample, CO_{min} . Using Eq. (2) and replacing X_{meas} and X_{std} with CO_{meas} and CO_{std} , we can define f_{sam} from the mole fraction of enhanced CO in the fill gas at any point as:

$$f_{sam} = \frac{CO_{std} - CO_{meas}}{CO_{std} - CO_{min}} \quad . \quad (4)$$



Equations. (3) and (4) are used to provide corrected AirCore sample mole fractions for the topmost stratospheric samples and bottommost surface samples for e.g. CO₂ and CH₄ as shown in Figure 4. Simplifying Eq. (4) using ΔCO as $CO_{std} - CO_{meas}$ and $\Delta CO_{min} = CO_{std} - CO_{min}$, f_{sam} can be simplified to:

$$f_{sam} = \frac{\Delta CO}{\Delta CO_{min}}. \quad (5)$$

We can then calculate the uncertainty in these corrected profile sample mole fractions. First, we write the uncertainty in f_{sam} in from Eq. (5) as $u_{f_{sam}}$:

$$u_{f_{sam}} = \sqrt{\left(\frac{\partial f_{sam}}{\partial \Delta CO} u_{\Delta CO}\right)^2 + \left(\frac{\partial f_{sam}}{\partial \Delta CO_{min}} u_{\Delta CO_{min}}\right)^2},$$

which can be simplified to:

$$u_{f_{sam}} = \sqrt{\left(\frac{1}{\Delta CO_{min}}\right)^2 u_{\Delta CO}^2 + \left(-\frac{\Delta CO}{\Delta CO_{min}^2}\right)^2 u_{\Delta CO_{min}}^2}. \quad (6)$$

Using Eqs. (3) and (6), the uncertainty in X_{sam} , $u_{X_{sam}}$, follows as:

$$u_{X_{sam}} = \sqrt{\left(\frac{u_{X_{meas}}}{f_{sam}}\right)^2 + \left(-\frac{1}{f_{sam}} + 1\right)^2 u_{X_{std}}^2 + \left(\frac{X_{std} - X_{meas}}{f_{sam}^2}\right)^2 u_{f_{sam}}^2}. \quad (7)$$

Here, Eq. (7) refers to the uncertainty in the “fill gas-corrected” AirCore trace gas mole fraction, which is depicted in Figure 4 in red at the top and bottom of the AirCore measurement. While f_{sam} is calculated, X_{std} and X_{meas} are defined as the calibration standard and measured mole fraction values of gas ‘X’ being corrected for fill gas mixing (here, CO₂ or CH₄), $u_{X_{std}}$ is the calibration tank measurement error of gas ‘X’, and $u_{X_{meas}}$ is the precision of trace gas measurements over a five-minute calibration period conducted just prior to AirCore sample analysis. CO measurements contaminated by fill gas and used for correcting CO₂ and CH₄ at the top and bottom portions of the AirCore sample are discarded, truncating the resultant CO mole fraction profile (Figure 4, green trace).

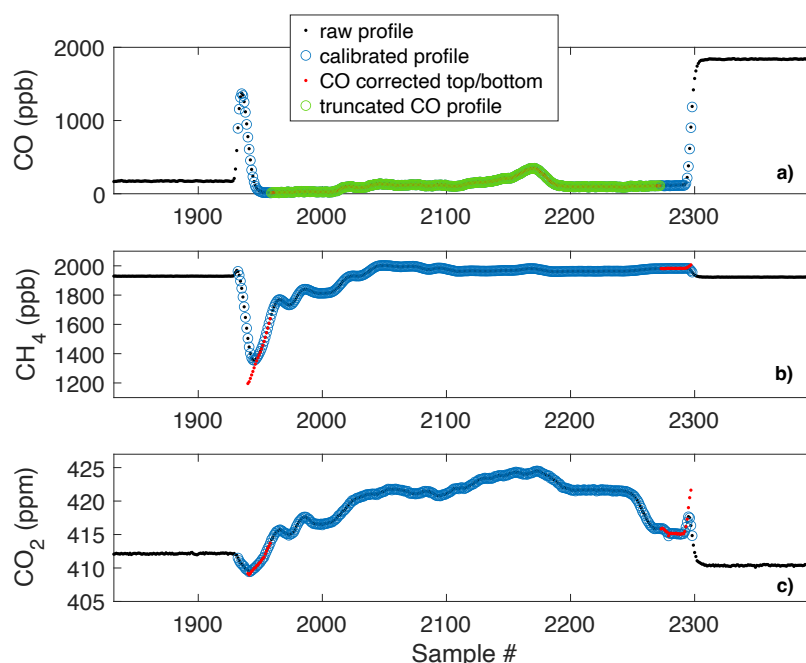


Figure 4. CO a), CH₄ b) and CO₂ c) measurements from AirCore samples from a balloon flight on June 14, 2023. Raw, uncalibrated measurements for all species are shown in black. Blue open circles indicate calibrated measurements. For CO in a), green open circles represented the final, truncated CO time trace of measurements after discarding those that contain remaining fill gas or mixed chase gas. Red circles in b) and c) represent fill/chase gas-corrected portions of the top (stratosphere, sample numbers 1900-2000) and bottom (troposphere, sample numbers 2250-2300) profiles. ‘Sample #’ refers to each CRDS measurement in time-ascending order during AirCore analysis.

2.2.3 Use and testing of ¹³CO₂ fill gas

It is important to note that more recent fill gas CO mole fractions have ranged between 1-2 ppm CO as higher mole fractions provide a larger correction on corrected stratospheric levels of CO₂, CH₄ and N₂O and result in truncation of a large portion of the CO profile above ~18 km MSL. Also, ideally, fill gas mole fractions of AirCore trace gases would be as close to stratospheric values as possible. With this in mind, the carbon-13 CO₂ absorption line (¹³CO₂) reported by Picarro’s PI5310 mid-infrared N₂O and CO CRDS allows for the use of ¹³C-labelled CO₂ enhanced fill gas, allowing the full CO profile to be measured with no truncation. By plumbing a PI5310 in series with a G2401 CRDS and maintaining a constant volumetric flow rate for the dual-analyzer system (Fig. 3b), it is possible to distinguish the top and bottom of the AirCore by altering the ¹³CO₂:¹²CO₂ (¹³C/¹²C) ratio in a fill/chase gas mixture to be significantly different from ambient air. Here, pure ¹³CO₂ (*Sigma Aldrich*) is used to create a fill gas mixture that has a ¹³C/¹²C signature (~3.6%) that is significantly different from ambient tropospheric or stratospheric air (~1.1%). In Figure 5a, the AirCore ¹³C/¹²C is measured by the dual-Picarro PI5310-G2401 system, showing ~1% remaining fill gas in the sample as seen between sample numbers 3000 and 3100. The ¹³C/¹²C is then used to determine the fraction of fill gas remaining in the AirCore, and subsequently correct the top and bottom air sample measurements for deriving near-total-column CO₂, CH₄, CO, and N₂O profiles with uncertainties using Eqs. (3)-(7). For the

first time, extended AirCore CO profiles are demonstrated, extending CO measured from AirCores approximately 5-6 km into
 305 the stratosphere with good agreement to previous fill gas usage methods (Fig. 5b). This demonstration on June 14, 2023 shown
 in Fig. 5 can be extremely valuable for estimating stratospheric CO abundances, but also ongoing work to evaluate total-
 column CO retrieved from satellites (e.g. Deeter et al., 2014; Martínez-Alonso et al., 2022), validating stratospheric oxidation
 chemistry (Fu and Dong, 2026) and ensuring compatibility between satellite records for routine atmospheric composition
 monitoring (Salawitch et al., 2025).

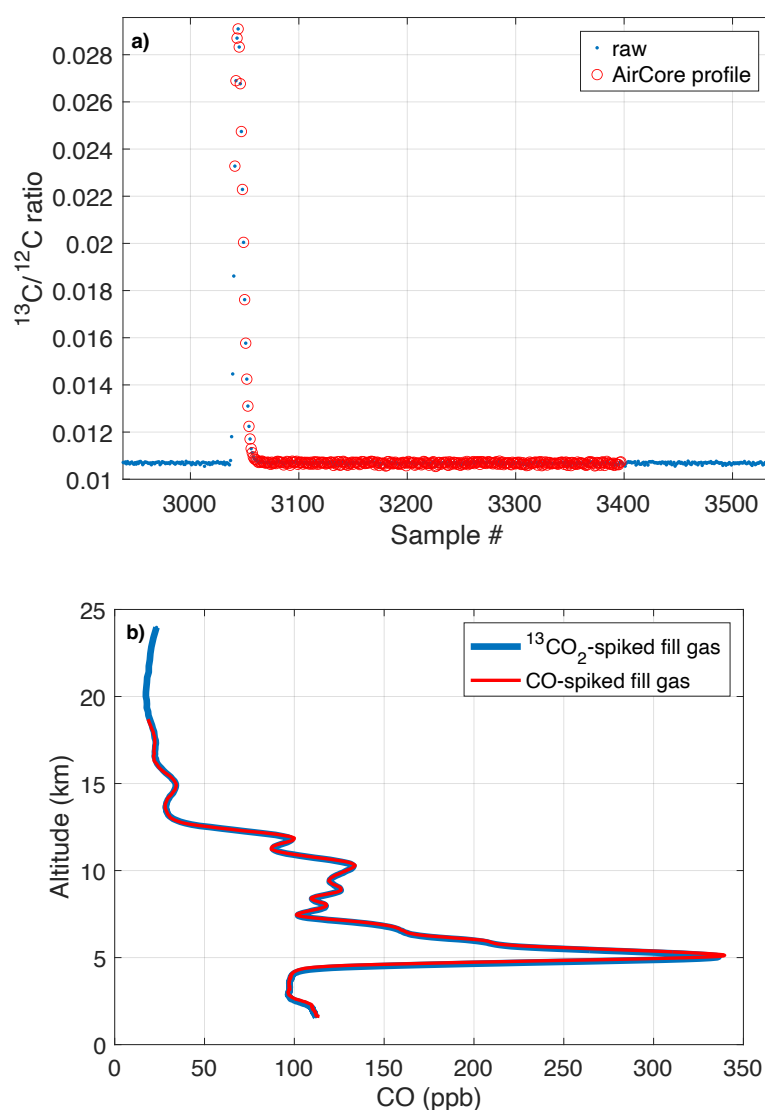


Fig. 5. Test flight on June 14, 2023 with $^{13}\text{CO}_2$ -spiked fill gas. a) shows the $^{13}\text{C}:^{12}\text{C}$ ratio in the fill gas remaining inside of the AirCore between sample numbers 3000 and 3100 and of sample air after number 3100; b)



shows the resultant extension of the CO profile obtained when using $^{13}\text{CO}_2$ -spiked fill gas in blue versus with regular CO-spiked fill gas in red.

310 2.3 Uncertainty analysis for AirCore profiles

2.3.1. Mole fraction uncertainty

For AirCore analyses, the Picarro G2401 CRDS is operated at a cavity pressure of 140 torr, resulting in a cell volume of approximately 6.4 cm^3 , and a typical measurement precision of less than 0.05 ppm for CO_2 , 0.4 ppb for CH_4 and less than 5 ppb for CO. The G2401 is operated in “inlet” valve mode, which enables control of cavity pressure using the inlet valve, to
 315 prevent pressure changes during AirCore analysis from affecting the mass flow rate of sample air during analysis. The cavity pressure standard deviation of the CRDS system is reduced as much as possible during AirCore analysis to optimize the precision in the abovementioned trace gas species. The PI5310 CRDS, operated at 100 torr with a cell volume of approximately 4.6 cm^3 , results in precisions for CO and N_2O of $<0.25 \text{ ppb}$ using a similar cavity pressure optimization approach. The fill gas mixing error described above takes into account the measurement precision ($u_{x_{meas}}$) in Eq. (7).

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The overall mole fraction uncertainty for sample air not affected by fill gas mixing is calculated by propagating in quadrature the measurement precision of the analyzer with a calculation of the average yearly calibration tank drift for a given trace gas. For gases CO_2 , CH_4 and N_2O , the mole fraction uncertainty is dominated by the precision of each measurement (with a measurement interval of $\sim 2.4\text{-}3 \text{ s}$) of the CRDS analyzer. We note that, with the cell volumes of 6.4 cm^3 and 4.6 cm^3 of the
 325 G2401 and PI5310 analyzers above, a flow rate of $0.25 \text{ cm}^3\text{s}^{-1}$, and a measurement interval of $2.4\text{-}3\text{s}$, it is possible to obtain multiple overlapping measurements of each cell volume. In addition, it is known that CO can exhibit growth in high-pressure aluminum cylinders (Novelli et al., 1991), with CO growth dependent on the size of the cylinder, or surface to volume ratio. Oftentimes for field deployments, it is logistically more advantageous to use smaller cylinders, which exhibit faster CO growth. Thus, for some AirCore profiles, tank drift carries a larger overall weight in the CO mole fraction uncertainty when using a
 330 CRDS with a CO precision less than $\sim 1 \text{ ppb}$.

2.3.2 Altitude registration kernel

The AirCore mole fraction measurements are registered with altitude using an evolving steady-state fill dynamics model described in detail in Tans (2022). The diffusion length scale of each air parcel sampled by the AirCore is calculated in total from AirCore descent and fill, storage and transport to the laboratory for analysis and during analysis. Eq. (8) is used to
 335 calculated the effective diffusive coefficient (D_{eff}), taking into account both Taylor dispersion and molecular diffusion in the longitudinal direction:

$$D_{eff} = D + \frac{a^2 \overline{V^2}}{48D}, \quad (8)$$



340 where D is the molecular diffusivity, a is the tube radius and V is the average velocity of the sample gas throughout AirCore sampling, storage and analysis. Diffusivities for CO_2 , CH_4 , CO and N_2O in air at 20°C and 1000 hPa are derived from Massman et al. (1998). The average temperature of the AirCore coil measured by the five thermistors in Fig. 2, and the history of each measurement's temperature and pressure all factor into calculated D_{eff} for each molecular species analyzed to obtain a one-directional root-mean-square diffusion distance and the pressure change associated with this distance in the AirCore for each measurement. The root-mean-square distance of molecular travel is defined in Eq. (9):

$$x_{\text{rms}} = (2D_{\text{eff}}t)^{0.5}, \quad (9)$$

where D_{eff} is defined in Eq. (8) for a molecule in surrounding gas and t is the time over which diffusion or travel takes place. The total amount of spreading is twice the x_{rms} as diffusion occurs in two directions and is assumed to be Gaussian. Because an air parcel's concentration (C) over time and distance can be defined by the 1-D diffusion equation:

$$\frac{\partial C}{\partial t} = D_{\text{eff}} \frac{\partial^2 C}{\partial x^2}, \quad (10)$$

355 and the solution to Eq. (10) is of the form of a normal (Gaussian) distribution, $f(x) = \frac{1}{\sigma\sqrt{2\pi}} \exp(-\frac{(x-\mu)^2}{2\sigma^2})$ shown in Eq. (11):

$$C(x, t) = \frac{M}{\sqrt{4\pi D_{\text{eff}}t}} \exp(-\frac{x^2}{4D_{\text{eff}}t}), \quad (11)$$

it follows that the variance, σ , of this normal distribution can be described as:

$$360 \quad \sigma = (2D_{\text{eff}}t)^{0.5}, \quad (12)$$

assuming that diffusion is random and the mean position $\mu = 0$. Thus, Eq. (12) denotes that the root-mean-square distance of molecular travel describes the representativeness “kernel” around each parcel's defined altitude registration in the AirCore at the 1σ , or $\sim 68\%$ confidence level. In general, a four-hour storage time for a flight to approximately 30 km MSL results in a x_{rms} of $\sim 0.5\text{ m}$ within the AirCore tubing coil. Accounting for diffusion acting in both directions, this fraction of tubing (1 m) across 90 m total tubing length results in an effective altitude kernel of the tubing coil in the atmosphere of approximately 9.5 hPa over Boulder, Colorado (Karion et al., 2010). This resolution roughly translates to an altitude kernel of less than 100 m in the atmospheric boundary layer and to less than 2 km below 30 km (Figure 6), depending on whether a dual-dimension StratoCore or a single-dimension AirCore is used (see Section 2.1 above) and can be used to distinguish the total degrees of freedom of the AirCore sample after a known storage time.

2.4 Monthly detrended profiles and HYSPLIT back trajectories

To examine variability in AirCore observations across the 13-year record, profiles are interpolated onto a common pressure vertical coordinate and averaged into 10 hPa bins. Only balloon flights from northeastern Colorado are included in this analysis, and if multiple AirCore profiles were collected on the same balloon flight, these profiles are averaged together, given that the differences between profiles is small (see Section 3.1.1). Flask surface measurements from Mauna Loa, Hawaii (MLO) are used to represent clean, background air for deriving trends in CO₂, CH₄, CO and N₂O that can be subtracted from AirCore trace gas profiles to isolate seasonal variability for these species throughout the atmospheric vertical column. MLO provides access to air that is representative of a large portion of the mid-troposphere in the Northern Hemisphere. A third-order multi-year polynomial seasonal fit (Thoning et al., 1989) to the MLO flask surface sample trace gas data from the NOAA GGGRN time series spanning the AirCore record time frame (NOAA/GML, 2025) was calculated with residuals fit to a sinusoidal parameter with four degrees of freedom for AirCore trace gas species to determine their surface trends over time. Each MLO species' trend at the time of each AirCore flight over the 13-year record was then subtracted from the AirCore profiles to detrend them. Detrended profiles were binned into monthly medians to examine seasonal variability throughout the AirCore trace gas record over Boulder, Colorado.

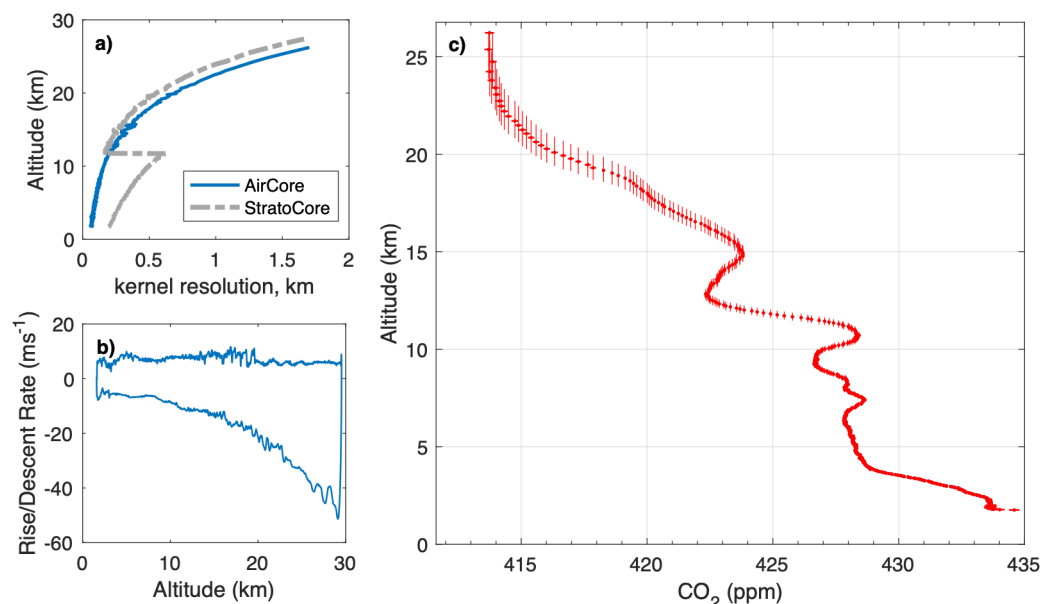


Figure 6. a) Vertical resolution for AirCore (blue) flown to 29 km MSL on March 5, 2025 with approximately two hours of storage time between landing and analysis, and calculated hypothetical StratoCore vertical resolution for the same flight characteristics. The ascent (positive) and descent (negative) rate of the balloon flight is shown in b). The resultant AirCore profile is shown in c) with horizontal and vertical error bars indicating measurement uncertainty and the altitude registration kernel, respectively.



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We also utilize the HYSPLIT model (Stein et al., 2015) to explain springtime CO profile variability over Boulder, Colorado. Particle back trajectories are initialized with 500 particles in the upper troposphere (8500 m, ~300-350 hPa) and run backwards for 10 days total from northeastern Colorado on all available springtime flight days between March and May. The model was driven by the National Centers for Environmental Prediction (NCEP) Global Data Assimilation System (GDAS) 1-degree meteorology. Summed footprints (cumulative surface influence) from these back trajectories are shown in Fig. S6.

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3. Results and Discussion

3.1 Validation of AirCore sampling techniques

3.1.1 Dual-profile comparisons

The use of second-generation, lightweight AirCore designs allows for the capability to assess the repeatability of AirCore samplers flown on the same balloon string. In Fig. 7, AirCores of identical design are compared to calculate the CO₂, CH₄, CO and N₂O difference as a function of pressure for all flights available (Boulder, Colorado and elsewhere, N=50 pairs for CO₂, CH₄, CO since 2016; N= 17 pairs for N₂O since 2019). CO₂, CH₄, CO and N₂O differences between AirCores are typically below 0.1 ppm, 2 ppb, 5 ppb, and 1 ppb, respectively. Larger differences (e.g. less than 0.5 ppm CO₂, 15 ppb CH₄, and 4 ppb N₂O) are observed in the lowermost troposphere and at the topmost portion of the AirCore profiles within the stratosphere where mole fractions are more variable and where large gradients exist in CH₄ and N₂O, amplifying differences in diffusion between AirCores that experience at least an hour-long difference in laboratory analysis time periods. Larger differences at the topmost (stratospheric) portion of the AirCore profiles could also be due to slight differences in high-CO fill gas mixing corrections to trace gas mole fractions. Overall, there is high repeatability between NOAA AirCore sampling systems flown on the same balloon string and mole fraction plots for dual-AirCore strings show compact correlations between expected species such as CO₂ and CH₄. Therefore, when examining the AirCore dataset, we can be confident that variability seen in trace gas profiles beyond the relatively small differences seen in Fig. 7 is a result of true atmospheric variability, and not due to sampling or analysis artifacts.

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3.1.2 Dual-flight comparisons

Dual-AirCore flight comparisons (i.e. two balloons with two different AirCores on each balloon string) have been conducted to inform sampling strategies and evaluate the reproducibility and tropospheric variability seen between balloon profiles launched in quick succession (< 30 minutes apart). Figure 8 shows an example case for a flight on July 14, 2017 in Lamont, OK where two dual-AirCore flight strings were launched 20 minutes apart. While only slight differences between the profiles are seen above 5 km MSL, significant differences in the CO₂ and CO profiles are seen below this altitude due to higher relative tropospheric variability (e.g. due to local sources, sinks and transport) in the landing regions of each balloon payload. While

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the use of successive flights can provide information on small-scale variability between the AirCore profiles, they can also be used for evaluating the reproducibility of AirCore sampling systems when considering trace gas mole fraction variability on larger spatial and temporal scales. AirCore global network groups in the past have evaluated AirCore reproducibility in the stratosphere in this way (Baier et al., 2023).

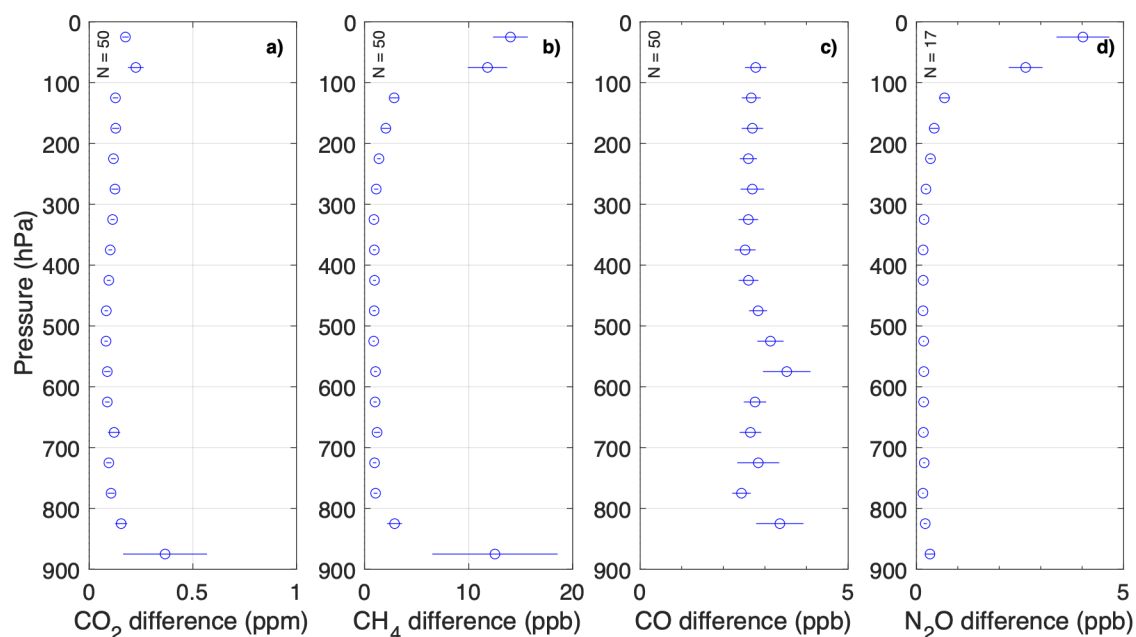


Figure 7. Trace gas species differences computed from all dual-AirCore flight strings in 50 hPa pressure bins for NOAA AirCore flights in Boulder, Colorado between 2012 and 2025 for a) CO₂, b) CH₄, c) CO and d) N₂O. Error bars are expressed as standard errors calculated based on the number of available AirCore profile comparisons in each pressure bin. Note that the sample comparison number (N) differ for CO₂, CH₄ and CO relative to N₂O because routine N₂O measurements in AirCores began in 2019.

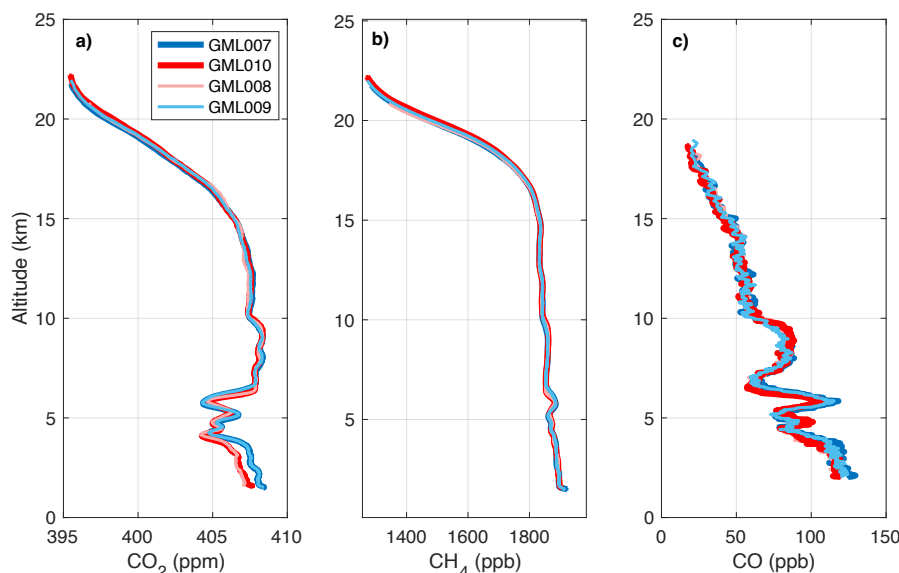


Figure 8. Successive dual-AirCore balloon launches of two flight strings on July 14, 2017 and resultant profiles of a) CO₂, b) CH₄ and c) CO. GML008 and GML010 are launched on the same balloon string approximately 20 minutes after GML007 and GML009.

3.2 Over a decade of AirCore sampling above Boulder, Colorado

3.2.1 Historical flight sample density and sampling strategies

NOAA's AirCore program began routine flights in 2012, originally aimed at evaluating remote sensing retrievals of trace gases such as CO₂, CO and CH₄ (Karion et al., 2010; Hedelius et al., 2019; Pak et al., 2023; Laughner et al., 2023) with a goal of maintaining a low-cost monthly sampling program to monitor and assess changes in these gases and other, long-lived species throughout the troposphere and stratosphere (Karion et al., 2010). Figure 9 indicates flight numbers across the development and progression toward routine, monthly flights from Boulder, Colorado (40.02°N, 105.27°W) from 2012 through 2025, though it should be noted that field campaign flights were also conducted during this time frame outside of Boulder, Colorado. NOAA's ability to maintain a relatively high frequency of flights per year is a result of years of diligent and routine communication of balloon trajectories with air traffic control units and the fact that most trajectories indicate landing points in regions within northeastern Colorado that are of low population and that contain few ground obstacles that would prohibit recovery of the AirCores. In addition, the use of a lightweight Automatic Dependent Surveillance-Broadcast (ADS-B) transponder (Fig. 1) on each flight ensures that AirCore balloon payloads are visible by non-participating aircraft and air traffic control units throughout the entirety of the flight.

NOAA second-generation, 600 mL AirCores are flown at a monthly frequency to capture high resolution trace gas vertical profiles throughout the near-total atmospheric column. In addition to monthly flights, circa 2019, NOAA StratoCores have



been flown at a quarterly frequency. Because two samplers are flown on a single balloon string, one can be analyzed for other long-lived stratospheric age tracers such as N₂O, sulfur hexafluoride (SF₆) and ozone-depleting substances via GC-ECD (Li et al., 2023) while the other is concurrently analyzed via CRDS for CO₂, CH₄, CO and N₂O.

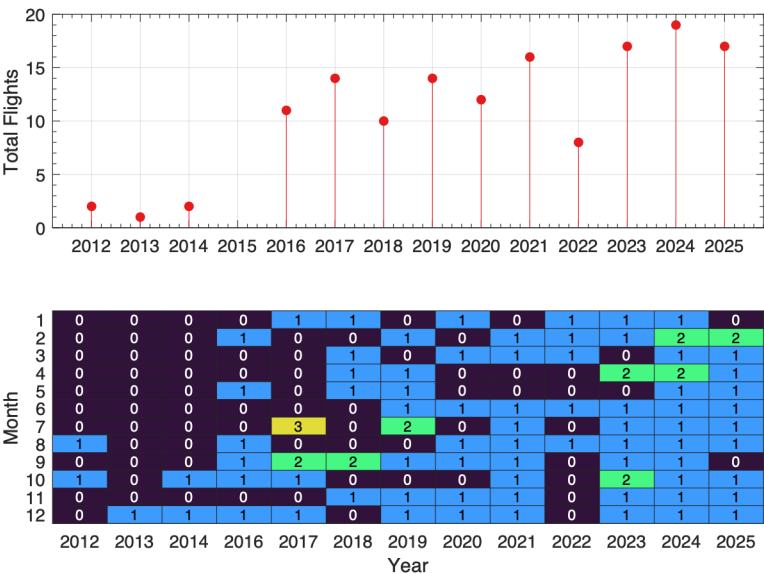


Figure 9. Top) Total number of yearly and bottom) monthly NOAA AirCore flights performed from Boulder, Colorado only (i.e. additional campaign flights from elsewhere are not included here). Although AirCores were launched in other regions, no Boulder flights were conducted in 2015.

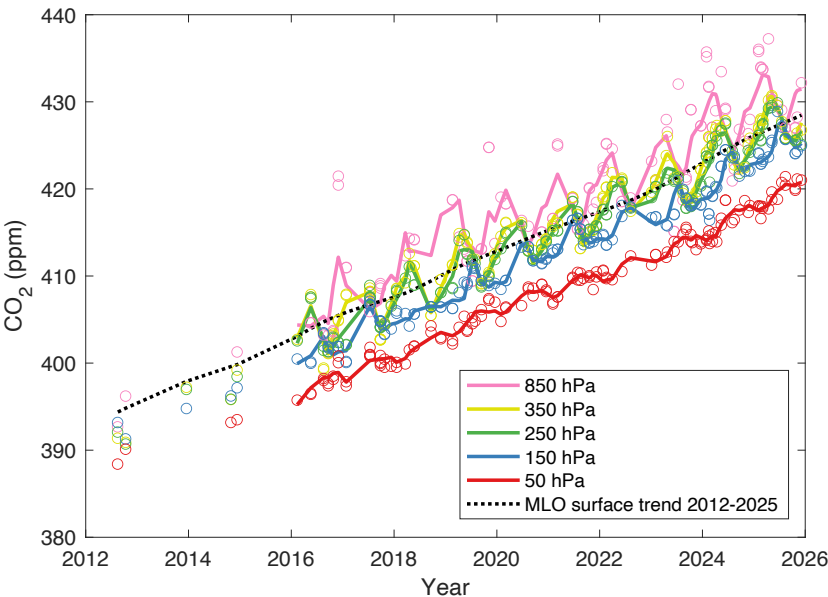


Figure 10. Time trend of CO₂ measured in NOAA AirCores launched from Boulder, Colorado from 2012 through 2025. AirCore data (individual points) are averaged in 100 hPa pressure bins, centered at the average of each bin and plotted for pressure levels at 850, 350, 250, 150, and 50 hPa levels. Smooth-curve fits (Thoning et al., 1989) of binned data in each pressure level are shown in corresponding solid lines. The trend in NOAA surface flask data from 2012 to 2025 at MLO is shown in the black dotted line.



3.2.2 AirCore CO₂ trend from 2012-2025

AirCore profile data uniquely capture the long-term global growth of trace gases in the troposphere, in addition to their seasonal cycles and the propagation of these signals into the upper troposphere and lower stratosphere. As an example, Fig. 10 shows AirCore profile CO₂ data at various atmospheric pressure levels over time from 2012 through 2025 in Boulder, Colorado alongside smoothed curve fits to these data for each pressure level. Here, the decrease in CO₂ moving from tropospheric levels to stratospheric ones is seen, highlighting the surface seasonal cycle of CO₂ and the modulation of this signal and decrease in amplitude with decreasing pressure levels in the atmosphere. The phase shift or time lag in the CO₂ seasonal cycle with decreasing pressure levels is also visualized here. Finally, Fig. 10 shows the trend (linear fit $\pm$ standard error) of AirCore profile CO₂ over time as 2.42 ± 0.05 ppm yr⁻¹ to 2.69 ± 0.14 ppm yr⁻¹ between 2012 and 2025 at all levels, which agrees with the average surface NOAA marine boundary layer CO₂ growth rate at MLO between 2012 and 2025 of 2.55 ± 0.11 ppm yr⁻¹ within calculated uncertainties (NOAA/GML, 2025). Trends of CO, CH₄ and N₂O also are in general agreement with the average MLO growth rates of these species, respectively (see Fig. S4). Historically, there exists a dearth of in situ stratospheric data collected from the mid-1970s to present day (Engel et al., 2009; Schuck et al., 2025; Ray et al., 2026). Some of the only observations available include high-altitude aircraft and large-balloon campaign in situ and flask data collected globally, but collection occurred in a sporadic manner due to the campaign-style nature of funded observations. Thus, large gaps in historical stratospheric observations exist, and have become more frequent in the past few decades, highlighting the utility of the NOAA AirCore Program for filling gaps in stratospheric observational records or for calculating robust trends, even if from a single mid-latitude site as Boulder, Colorado. As such, Fig. 10 also highlights the seasonality and variability captured in profile data such as the NOAA AirCore CO₂ record over time with a low-cost, routine balloon program. Several other global AirCore sites have enabled more recent routine profiling in the countries of Finland, France (CNES, 2018) and Germany (Degen et al., 2025).

3.2.3 Seasonal variability in AirCore profiles from 2012-2025

Because the NOAA AirCore trace gas growth rates between 2012 and 2025 agree with MLO growth rates, and monthly profiles have been obtained across several years within the NOAA AirCore record (Fig. 9), seasonal profile data can be detrended with the MLO flask surface sample trace gas data (Section 2.4). Figure 11 shows monthly median AirCore CO₂, CH₄, CO and N₂O throughout the troposphere and lower stratosphere for the 13-year data record. In all species, monthly profiles indicate relatively coherent variability above 380 K potential temperature as expected, due to the long lifetimes of species in the stratosphere and slower mixing and circulation processes. The region of the stratosphere above 380 K potential temperature is known and referred to here as the “overworld”, where isentropes lie entirely within the stratosphere (Holton et al., 1995).

For CO₂, the seasonal cycle over Boulder, Colorado shows a short, relatively weak drawdown period evident in June and July average monthly profiles, similar to that shown in NOAA GGGRN aircraft network profiles from northeastern Colorado in



475 Sweeney et al. (2015) (Fig. 11a). Surface CO₂ respiration and emissions between January and May are clearly seen in Fig. 12a, along with the upward propagation of the surface CO₂ seasonal cycle to roughly ~100 hPa. Because this 13-year AirCore profile record over Boulder, Colorado spans a large equivalent latitude range, the “tape recorder” effect (Mote et al., 1996) likely to be seen at higher, stratospheric altitudes above Boulder, Colorado only may be less evident in Figure 12a, though this is one phenomenon that can be visualized with the AirCore dataset upon further analysis. The standard deviation across binned
 480 monthly detrended profiles from 2012-2025 indicates that the trace gases are relatively well-mixed vertically throughout the atmosphere, with the exception of near-surface levels, which are expected to vary largely within monthly profiles taken each year due to differing AirCore landing conditions (Figure S6a).

Monthly average CH₄ profiles show little variability throughout the lower troposphere, with the exception of periodic positive
 485 excursions from the MLO trend attributable to local surface emissions (Fig. 11b, Fig. 12c). Figures 11b and 12c show clear CH₄ depletion relative to MLO in the upper troposphere and lower stratosphere, and extending above the 380K level in the winter and spring. High variability of > 200 ppb within monthly profiles throughout the 13-year record is also seen above the upper troposphere and into the stratospheric overworld (e.g. above 200 hPa, Figure S6c) due to large troposphere to stratosphere gradients, with the highest variability observed above 100 hPa in April. The seasonality in the strength of the
 490 Brewer-Dobson Circulation (BDC) is known to dominate the seasonal cycle of long-lived trace gases in the lower stratosphere (Strahan et al., 1999; Hegglin et al., 2006). The monthly variability in CH₄ surrounding 380K potential temperature is likely attributed to exchange of this lower stratospheric air with the air in the upper troposphere; a mechanism which is strongest in the midlatitudes and associated with synoptic-scale storms (Holton et al., 1995). Stratosphere-troposphere exchange (STE) or the exchange of air masses back and forth between the stratosphere and the troposphere in either direction, and similar
 495 variability of other long-lived stratospheric tracers in the upper troposphere and lower stratosphere (UT/LS) has been observed previously from aircraft (Hegglin et al., 2006; Bisht et al., 2021). Hegglin et al., (2006) note that while the strength of the BDC has a maximum in midwinter, minimum values of stratospherically-depleted species were seen in the springtime in the UT/LS due to the transport time between lower altitudes and the 380K isentrope. Net STE is also highest during winter and early spring (Stohl et al., 2003; Gettelman et al., 2011), with Lagrangian models indicating that a higher frequency of rapid deep
 500 intrusions may occur in the springtime, suggesting that more depleted CH₄ seen between March and May in Fig. 12c may be due to mixing down of lower CH₄ from the stratospheric overworld to the UT/LS from these types of STE events. Due to the routine nature of sampling, AirCore profiles may also be able to capture influence of interhemispheric exchange, the quasi-biennial oscillation (QBO) and the N. American Monsoon in the northern hemisphere midlatitudes (Hamilton and Fan, 2000; Randel et al., 2001; Park et al., 2004; Ray et al., 2020; Ruiz et al., 2021; Ruiz and Prather, 2022), with further disentanglement
 505 of these features to be analyzed in future work.

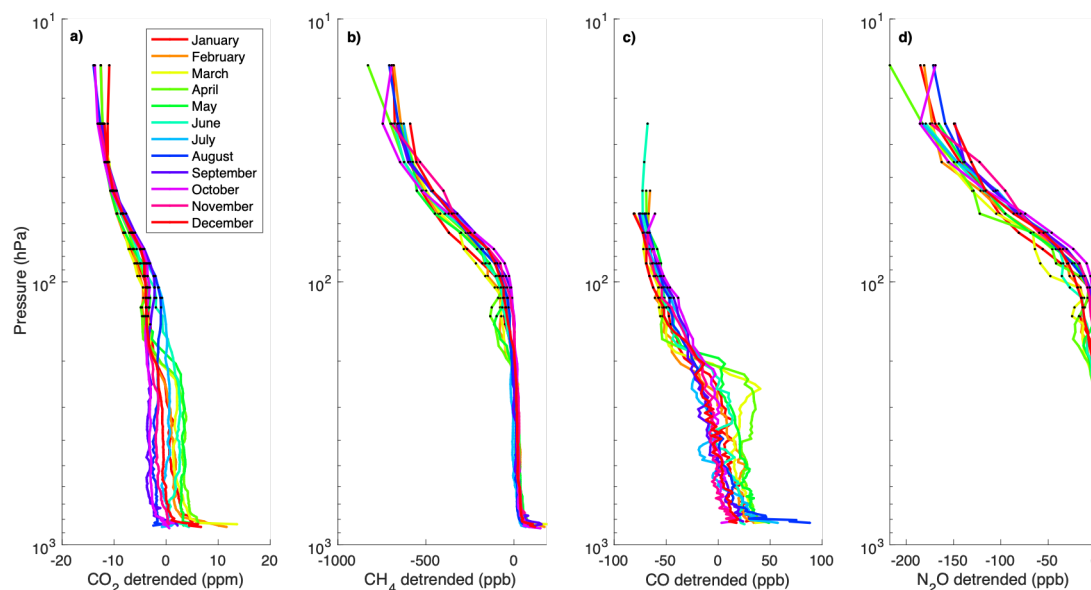


Figure 11. Median monthly detrended CO_2 (a), CH_4 (b), CO (c) and N_2O (d) from 2012-2025 over Boulder, Colorado (N_2O data from 2019-2025). Profiles are interpolated onto a common pressure coordinate and averaged in 10 hPa bins before detrending and taking monthly medians. Profiles are colored by month and black dots represent binned data above 380 K potential temperature, a threshold indicating that air is contained within the stratospheric overworld. Note that CO data primarily extend only to ~30 hPa due to profiles being truncated by CO fill gas contamination. Because monthly N_2O (d) profiling began in 2019, monthly averages contain fewer profiles ($N=55$) than for other trace gases ($N=143$).

Even though profiles of CO over Boulder are truncated due to remaining high- CO fill gas in the AirCores (Fig. 4), local CO biogenic and anthropogenic emissions are evident throughout the troposphere as indicated by enhancements of CO relative to MLO at the surface (Figs. 11c and 12b). Notable enhancements in CO in the upper troposphere (200-400 hPa) are also
 510 observed, especially during the months of March, April and May that are likely from long-range transport of fossil fuel or biomass burning emissions sourced from other regions. The standard deviation of March, April and May profiles in this atmospheric layer is 20-40 ppb CO but is relatively well-mixed throughout the 200-400 hPa layer (Fig. S6b), indicating that there is some variability in CO enhancements seen in this part of the upper troposphere, but that springtime enhancements are relatively common throughout the 13-year CO time series. Outflow of emissions from Asia have been known to partially
 515 impact upper tropospheric CO abundances in the western U.S. (Liang et al., 2004; Jiang et al., 2007) and this influence is also consistent with NOAA GGGRN aircraft CO profiles (Sweeney et al., 2015). Springtime (March-May) cumulative HYSPLIT particle back trajectories initialized in the middle of this layer (~300-350 hPa) show surface influence from the Asian continent or over the western Pacific, indicating that these upper tropospheric CO enhancements are likely influenced by Asian outflow (Fig. S7). While it is not evident in monthly median detrended profiles shown in Figs. 11c and 12b, biomass burning plume
 520 enhancements in CO over Boulder are routinely captured in AirCore samples throughout the year in the UT/LS; large variability is seen throughout August and September months from the surface to the upper troposphere (Figure S6b).



Oftentimes, remote sensing instrumentation cannot retrieve these relatively thin plumes due to instrument sensitivity or limited degrees of freedom in retrievals (Gurganus et al., 2025).

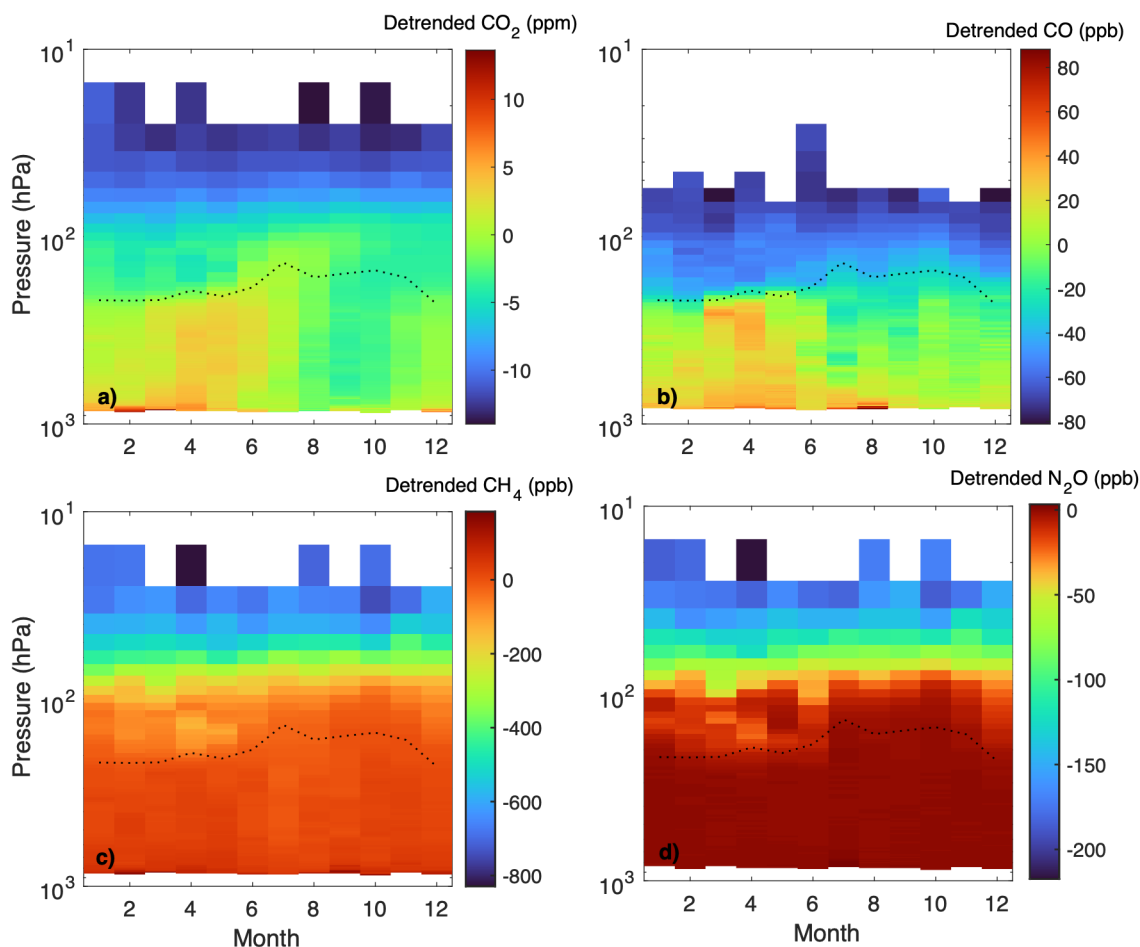


Figure 12. Detrended and binned CO_2 (a), CO (b), CH_4 (c) monthly median mole fractions as a function of pressure from 2012-2025 over Boulder, Colorado. d) N_2O data detrended and binned medians are from AirCore flights since 2019 only. The dotted black line in each subplot is the average monthly calculated tropopause pressure altitude from each flight's radiosonde temperature and pressure based on the standard World Meteorological Organization (WMO) definition (WMO, 1957).

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Finally, AirCore N_2O profiles over Boulder show low enhancements in the troposphere relative to MLO surface N_2O with expected low variability (< 1 ppb) throughout the troposphere (Fig. 11d, Fig. 12d). Similar covariation with CH_4 is seen in the



UT/LS and above 380K potential temperature in the winter and spring with depleted N₂O, again likely due to STE events.

530 Within-month variability in the UT/LS mirrors that of CH₄ due to large troposphere to stratosphere gradients in N₂O; like CH₄, the highest variability in the N₂O record (> 200 ppb) seasonally is seen in April above 100 hPa (Figure S6d). While the AirCore N₂O record does not span the full 13 year record shown for CO₂, CH₄ and CO, but begins in 2019, annual N₂O variability throughout the atmospheric column shown in Figs. 11d and 12d is likely to be similar to that for 2012-2025 given that the differences in the standard deviation of in CO₂, CH₄ and CO (1 σ) between these two time periods are also small (Fig. S6d).

535 The current AirCore record of CO₂, CH₄, CO and N₂O remains a globally unique dataset that captures seasonal variability of these trace gases in the UT/LS as satellite retrievals often a) do not extend into the UT/LS; b) have too low precision and vertical resolution or c) retrieve column abundances rather than vertical profiles, preventing them from sufficiently resolving the features seen in Figs. 11 and 12.

3.2.4 Future NOAA AirCore datasets and directions

540 The NOAA AirCore dataset described here for base species CO₂, CH₄, CO and N₂O allows for coordinated analyses of several long-lived tracers throughout the troposphere and stratosphere that can help to identify emissions and transport processes on length scales from days to decades. For example, CO:CO₂ ratios can be examined to identify long-range transport of biomass burning plumes within the troposphere (Andreae et al., 1994; Jost et al., 2004; Hooghiem et al., 2020). Given that the AirCore dataset from launches conducted over Boulder, Colorado span a wide range of equivalent latitudes, Ray et al. (2024) use these

545 data to show that a coordinated dataset of vertical profiles of CO₂, CH₄, SF₆ and N₂O can allow for new methods to be developed to estimate time scales of transport between surface emissions of species and when these emissions enter the stratosphere. The fact that all of these species can be measurement by AirCore on the same balloon string provides a correlated dataset for robust scientific analysis. Stratospheric mean age of air (AoA) is commonly used to quantify transport timescales and has applications to the upper troposphere, lowermost stratosphere and stratospheric overworld. Further, because of the

550 routine nature of sampling within NOAA's AirCore Program, seasonal variability in AirCore-derived AoA from CO₂ and sulfur hexafluoride (SF₆) can be examined in ways that are not possible with sporadic, campaign-based aircraft of large-balloon deployments, opening avenues for new understanding in stratospheric circulation using these data alongside models (Ray et al., 2026).

555 As mentioned above, new analytical methods have been developed concurrently within the NOAA AirCore Program since 2019 to measure AirCore samples via gas chromatography for long-lived, photolytically unique stratospheric species such as SF₆, CFCs and halogenated compounds (Moore et al., 2014; Li et al., 2023). Long-lived trace gas profiles such as those from the AirCore in the southern hemisphere and tropical regions is severely lacking. In particular, carbon reservoirs in the tropics have high impact on the global carbon cycle and this latitude band is where air primarily enters the stratosphere through the

560 BDC, yet routine profile or vertical column observations are extremely sparse and only executed through sporadic campaigns (Krysztofiak et al., 2023; Ray et al., 2024; Schuck et al., 2025). Future sampling goals include expanding AirCore



measurements of these long-lived stratospheric trace gases to provide increased latitudinal coverage for examining the vertical distribution of GHGs, troposphere to stratosphere transport and exchange and changes in the BDC due to changes in the large-scale distribution of surface temperature. In particular, trace gases with varying stratospheric photochemical lifetimes as measured by GC-ECD can be used to assess changes in mass flux and stratospheric transport in both models and measurements at various altitudes within the stratosphere over time (Volk et al., 1996) and can uniquely distinguish the strength and depth of the BDC and changes therein.

The landscape and low variability of terrain in eastern Colorado is particularly conducive for recovery of NOAA AirCores relative to other areas within the U.S. or abroad where a higher density of trees and bodies of water are present. To expand AirCore operations to other latitude bands, recovery of AirCore sampling systems must be enhanced for quick analysis of samples. To this end, the custom, NOAA High-altitude Operational Returning Uncrewed System (HORUS) has been developed within the AirCore Program, which has the capability of housing a comprehensive onboard measurement suite of atmospheric constituents, including the AirCore, for simultaneous atmospheric observing of ozone, aerosols and trace gases on the same platform (Takahashi et al., 2021).

The AirCore adds unique and useful information relevant for urban and national carbon management (Parazoo et al., 2026). In addition, as satellites providing global-scale monitoring of trace gases near end-of-life or are discontinued, the scientific community will lose observational capabilities for trace gas monitoring over large swaths of the globe, providing significant challenges for understanding atmospheric composition and impacts thereof with a changing climate (Salawitch et al., 2025). Sustained, routine observations from the NOAA AirCore program and other, global AirCore programs will prove to be a critical dataset for bridging data gaps between satellite retrievals, especially in the stratosphere.

4. Conclusions

Updates have been implemented within NOAA's AirCore Program to improve several aspects of the AirCore sampling systems themselves and robustness and accuracy of profile measurements of these air samples since first described in Karion et al. (2010). Added quality assurance steps in current techniques and practices include routinely assessing the repeatability between samplers with flights of two AirCores on the same balloon string, in addition to quality checks on the altitude registration of vertical profiles. We describe the use of a new, dual-Picarro CRDS analysis system that has added both new opportunities for fill gas development and extension of AirCore CO profiles to ~ 25 km MSL, alongside new gases measured in AirCore air samples such as N₂O.

Routine AirCore profiles to ~ 25 km MSL capture seasonal variability throughout the atmospheric vertical column at high resolution and low cost relative to other observational techniques. With these seasonal data, we can identify relevant



dynamical processes in the stratosphere and temporal structure of these processes. The results for a suite of trace gases
595 measured in AirCores since 2012 over Boulder, Colorado reproduce trace gas trends measured at NOAA GGRN marine
boundary layer background sites such as Mauna Loa, Hawaii, and they capture variability in atmospheric composition from
surface fluxes, long-range transport and emissions and stratosphere-troposphere exchange. While this stratospheric mid-
latitude northern hemisphere profile record in Boulder, Colorado combines influence of transport from a multitude of
equivalent latitudes, direct AirCore profiling in areas such as the tropics and within the polar vortex can more sufficiently
600 examine stratospheric dynamics and changes driven by climate variability by capturing air entering the stratosphere or that
within the polar vortex with mesospheric influence. Ongoing efforts include expansion of observations, including
observations of additional species measured by GC-ECD, to these unique regions.

Finally, given that the AirCore technique has been adopted at several institutes worldwide, it is important that techniques
605 within this AirCore global network are consistent for comparability between model and satellite evaluation applications by
end users. Maintaining collaborative efforts is essential to establishing (and developing new) robust AirCore methodologies
and reproducibility within this network. The AirCore offers the most low-cost and effective method for making remote sensing
retrievals compatible with calibrated measurements, and it can bridge gaps in trace gas satellite retrievals as many platforms
are decommissioned or near end-of-life.

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Data Availability.

All NOAA AirCore profile data presented in this study are available for public use at <https://gml.noaa.gov/ccgg/arc/?id=144>
(Baier et al., 2021).

615 *Author Contributions.*

BB contributed to the development of methodologies, laboratory experiments, data collection and analysis and processing of
data, and writing of the manuscript. CS contributed to the development of methodologies, data collection, analysis and
processing of the data, reviewing and editing of the paper. JL contributed to the development of methodologies, laboratory
experiments, data collection, analysis and processing of the data, reviewing and editing of the paper. TN contributed to the
620 development of methodologies, laboratory experiments, data collection and reviewing of the paper. JH and SW both
contributed to the development of methodologies, laboratory experiment and data collection. MJ contributed to the data
collection, reviewing and editing of the paper. FM contributed to the analysis of the data, in addition to reviewing and editing
of the paper. PT contributed to the development of ideas within and reviewing and editing of the paper.

625 *Competing Interests.*

The authors declare that they have no conflict of interest.



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 Eqs. (10-12) to relate diffusion distance to the variance of a normal distribution.

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