

California Environmental Protection Agency

Air Resources Board

Monitoring and Laboratory Division Air Quality Surveillance Branch

Quality Assurance Project Plan for Greenhouse Gas Monitoring Network

Version 2.1

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California Environmental Protection Agency
Air Resources Board

Monitoring and Laboratory Division
Air Quality Surveillance Branch

Quality Assurance Section
for
Operating Gas Monitoring System

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Operating Gas Monitoring System
Quality Assurance Section
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Acknowledgement

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TABLE OF CONTENTS		
Section		Page
	Acknowledgement	2
	Table of Contents	3
	Distribution List	4
	Project Organization	4
1	Background	5
2	Objectives	5
3	Description of GHG Monitoring Network	6
3.1	GHG Analyzers and Meteorological Sensors	6
3.2	Sample Tubing	7
3.3	Auxiliary Pumps	7
3.4	Dryers	8
3.5	Sample/Calibration Selection Manifolds	9
3.6	Calibration Standard Gases and Procedures	9
3.7	Sampling and Post-processing	11
4	Estimated Uncertainty	11
4.1	Uncertainty of Calibration Standards	12
4.2	Uncertainty Derived from Target Cylinder Measurements	12
5	Data Handling/Data Management	13
6	Quality Assurance/Quality Control	13
7	GHG Monitoring Training	14
8	Documentation and Records	14
9	Instrument Inspection, Maintenance, and Calibration	14
10	References	21
11	Appendix 1 – Proposed Changes of GHG Measurements at the Sutter Buttes Site	25

FIGURES		
		Page
1	Map of GHG Monitoring Network	16
2	Photos of GHG Monitoring Network Stations	17
3	Schematic Diagram of the San Bernardino Tower CO ₂ , CH ₄ , CO, and N ₂ O Analysis System	18
4	Example of Low Concentration Calibration Gas Measurements at San Bernardino Tower	19
5	Example of High Concentration Calibration Gas Measurements at San Bernardino Tower	20
6	Example of Target Measurements and Evaluation of Instrument Accuracy at San Bernardino Tower	21

Distribution List

To ensure that the intent of CARB quality assurance policies are appropriately distributed so that they are inherent in all applicable ambient air quality data collection processes, the Greenhouse Gas Monitoring Network Quality Assurance Project Plan (QAPP) is distributed to the following:

- Persons listed in Approvals section.
- Monitoring and Laboratory Division (MLD) supervisory and line staff involved in any aspect of this Greenhouse Gas Monitoring Network Program.

Distribution is performed via MLD on-line documentation resources for centralized access. Training of staff members new to the Greenhouse Gas Monitoring Network Program will include QAPP content and location of centralized documents.

Project Organization

Roles and Responsibilities

Mr. Kenneth Stroud is the chief of the Community Air Monitoring Branch (CAMB). In this role, Mr. Stroud will have the responsibility for ensuring that the overall technical and operational goals of this project are met.

Mr. Fernando Amador is the manager of the Community Air Monitoring South Section (CAMS) of the Community Air Monitoring Branch. Mr. Amador will have the responsibility for ensuring that staff are achieving the stated goals and objectives of the project in a timely manner.

MLD staff will be responsible for:

- Preparing and implementing the project QAPP;
- Ensuring that the methods and procedures used in making GHG measurements are adequate to meet the program objectives and that the resulting data are of satisfactory quality;
- Implementing satisfactory quality assurance programs, through systematic instrument calibrations and target measurement evaluations;
- Installing GHG analyzers and sample drying equipment, along with data logging and processing;
- Operating, training, and assisting field personnel in proper operating procedures and maintenance of this system;
- Providing all necessary consumable items, standard gases, and replacement parts to field personnel as needed;
- Performing data review and flagging in MLD's Data Management System (DMS).

1. Background

The California Global Warming Solutions Act of 2006 (AB 32) requires the California Air Resources Board (CARB) to report and verify the statewide greenhouse gas (GHG) emissions inventory. To support this program, the CARB has initiated a series of studies to evaluate, and where needed, improve the statewide GHG emissions inventory. With the growing recognition of the importance of global climate change and to provide GHG emissions data to monitor AB 32 related reductions and program effectiveness in California, the CARB has been working to establish a GHG monitoring network throughout California to evaluate and track the trends in GHG emissions.

The GHG monitoring network currently has seven stations operated by CARB. In order to maximize the extent of the project and to better understand the statewide GHG emissions inventory, CARB also collaborates with multiple research institutions to expand the coverage of the GHG monitoring network in California. Collaborating agencies include the Jet Propulsion Laboratory (JPL, which leads the Megacities Carbon Project), Lawrence Berkeley National Laboratory (LBNL), California Institute of Technology (Caltech), University of California at San Diego, the National Oceanic and Atmospheric Administration (NOAA), the Lawrence Livermore National Laboratory (LLNL), and the Advanced Global Atmospheric Gases Experiment (AGAGE). Collectively, these make up a dense network of GHG measurements in California (Figures 1 and 2).

2. Objectives

The main objective of this Quality Assurance Project Plan (QAPP) is to establish a GHG monitoring network in California that can provide the data quality that meets the World Meteorological Organization (WMO) standards (WMO, 2012). The stringent WMO data quality is required to provide high accuracy data for evaluating the CARB GHG emissions inventory. The CARB also collaborates with research institutions to expand the coverage of the network stations in California and contributes data to study GHG emissions and long term trends. Thus, it is required to have all of the GHG data sets to be the same accuracy and precision.

The WMO measurement accuracies (WMO, 2012) are nitrous oxide (N₂O) within 0.1 parts per billion (ppb), methane (CH₄) within 2 ppb, and carbon dioxide (CO₂) within 0.1 parts per million (ppm). Even though, carbon monoxide (CO) is not a greenhouse gas, it is a widely accepted tracer of anthropogenic combustion emissions and has been applied to correlate with GHG emissions. The WMO measurement accuracy for CO is 3 ppb.

It has been demonstrated that the aforementioned data accuracies are achievable (Fischer, 2014, Andrews et al., 2014), only when air samples are properly treated and instruments are calibrated frequently against certified standard gases. This QAPP is primarily based on three recent publications (Andrews et al., 2014; Welp et al., 2013; Rella, et al., 2013), and consultation

with collaborating researchers (Newman, 2014; Fischer, 2014; Weiss, 2014) to ensure the overall GHG monitoring network project design and implementation are scientifically comprehensive.

3. Description of GHG Monitoring Network

The selection of the GHG monitoring network stations is based on the knowledge of known GHG emission sources and locations, regional wind trajectory studies, available monitoring facilities that are suitable for GHG measurements, and the existing GHG sites operated by collaborators. Once a site is selected, a preliminary site survey including mobile measurements of surrounding GHG sources is conducted to determine if the site is appropriate for representing regional GHG measurements.

3.1 GHG Analyzers and Meteorological Sensors

The measurements for this GHG monitoring network project are ambient air CH₄, CO₂, N₂O, CO, and meteorological parameters (wind speed, wind direction, and ambient temperature). Figure 3 is a schematic diagram of the analysis system at the San Bernardino tower. All other CARB GHG stations will be implemented with the analysis system similar to Figure 3.

The CH₄ and CO₂ monitors used in this project are cavity ringdown analyzers and are capable of both high accuracy and fast measurements of CH₄ (range = 0 – 20 ppm), CO₂ (range = 0 – 1,000 ppm), and water vapor (range = 0 – 70,000 ppm).

The N₂O and CO instruments deployed in this project are cavity enhanced performance N₂O/CO Analyzers. These monitors are capable of both high accuracy and fast measurements of N₂O (range = 0 – 10 ppm), CO (range = 0 – 10 ppm), and water vapor (range = 0 – 70,000 ppm).

Meteorological information is gathered from instruments operating at the monitoring locations. Standard meteorological instrumentation for CARB sites are sonic anemometers to produce wind speeds, wind direction, and ambient temperature.

3.2 Sample Tubing

At each site, the gas analyzers are housed at the base of the tower in a building or portable laboratory built in a trailer or modified sea container. Air is drawn down the tower through sampling lines (Synflex 1300, 1.27 cm/0.5 in. OD tubing, wall thickness=1.57 mm, or comparable tubing). Teflon tubing is less desirable, since it is semi-permeable (NOAA, 2014). Tubing is affixed to the tower using long UV-resistant plastic cable ties or stainless steel hose clamps at approximately 1m intervals. Tubes are run along tower legs and protected whenever possible to minimize wind-related vibration and stress. Each line (including the spare) has a high-surface-area PTFE 0.2 µm filter capsule (Whatman 6711-7502, or comparable filters) on the inlet.

3.3 Auxiliary Pumps

For towers taller than 50 meters, each in situ sampling line has a dedicated pump and is continuously flushed at a typical flow rate of 5 to 9 standard liters per minute (slm; equivalent to the flow rate at $T = 0\text{ }^{\circ}\text{C}$, $P = 1013\text{ hPa}$), which corresponds to a residence time of 4 to 7 minutes in a 500-meter Synflex tube. The pressure drop in a 500-meter sample tube is calculated to be approximately 44 hPa with a Reynolds number of 889 for a flow rate of 5 slm and depends strongly on tubing diameter. The actual pressure drop is likely larger, owing to other components such as the inlet filter and fittings along the line. The tubes are checked for leaks at the time of installation by capping the inlet and pulling a vacuum on the tube, and the test is repeated whenever the inlet filters are replaced, ideally once per year or when climbers are on the tower for repairs. The final pressure achieved during the pump-down is typically $<200\text{ hPa}$. A shut-off valve is used to isolate the evacuated tube from the test pump and a pressure meter is used to monitor the extent to which the capped line will hold the vacuum.

Auxiliary pumps are used upstream of the analyzers so that air is pushed rather than pulled through the analyzers. Some advantages of this design are that (1) the condenser works more effectively at higher pressure, (2) the ambient air is delivered to the analyzers at a pressure similar to the calibration gases, and (3) there is reduced likelihood that leaks will affect the measurements.

Disadvantages are that water is more likely to condense in the sampling lines, and that the sample air is exposed to pumps and associated components, which are not included in the calibration path.

Air from the sampling lines enters the pump enclosure through a set of $7\text{ }\mu\text{m}$ filters (Swagelok S-4F-7, or comparable filters). The filters are intended to protect the pumps and downstream components from particulates in the event that the sample tubing is breached. Each of the sampling lines has a dedicated pump (KNF MPU1763-N828-6.05, or comparable pumps) that compresses the air. Pump outlet pressures are set to 69 kPa (10 psi) above ambient using a back-pressure regulator (ITT GH30XTHMXXXB, or comparable pressure regulators) and monitored using electronic pressure transducers (Cole Parmer 68075-44, 0–25 psig, or comparable transducers). Excess flow is vented through the back-pressure regulator and measured with an electronic mass airflow sensor (Honeywell AWM5102VN, or comparable mass airflow sensors).

Annual maintenance aims to refurbish each pump assembly approximately once per year. Pump diaphragms are replaced, and pumps are tested for compression and vacuum. The “bypass” flow is the portion of the flow that is vented through the backpressure regulator (i.e., equivalent to the total flow minus that portion which is periodically delivered to the analyzers), and provides an indicator of pump performance and/or the need to replace the filter capsule at the tubing inlet. Any leakage of air across a torn sample pump diaphragm will contaminate the sample airstream, and should be avoided. Pumps in the field can be tested for leaks by simply capping the inlet and checking whether the flow drops to zero within an hour.

3.4 Dryers

In the case of spectroscopic measurements, the presence of water vapor can cause spectral interference and can change the pressure broadening of the absorption lines. Water vapor also “dilutes” the mole fraction, since all of the CO₂, CH₄, CO, and N₂O measurements are reported as dry air mole fractions. Liquid water can damage system components, and even low levels of water vapor can interfere with measurements. A humidity difference of 100 ppm of water corresponds to a so-called “dilution offset” of 0.04 ppm CO₂ if not corrected. Water vapor differences among samples and standards can also cause spectral artifacts related to line interferences or pressure broadening of the signal and increase the settling time when switching between air streams. Water vapor artifacts can be reduced or eliminated by drying the sample and humidifying the calibration gases to minimize differences in water content (WMO, 2012, Sect. 12.1). The system described below minimizes humidity differences between the sample airstream and standards by passing sample and standard gas through Nafion membrane dryers. The sample air is dried, while standard gases are humidified.

Air exiting each sample line pump is passed through a chiller to remove the bulk of the water vapor. The chiller is configured with separate glass traps (one for each sample intake line for towers with multiple sampling levels). Each channel has a dedicated peristaltic pump to remove liquid effluent from the trap. The temperature of the cooling element is maintained at a set point of 1.6 °C.

Nafion membrane dryers (Perma Pure MD-110-144P-4 or comparable parts) are used in self-purge configuration to further reduce the sample dew point. The effectiveness of Nafion membrane dryers depends on the relative flow rates and partial pressures through the sample and purge tubing. The exhaust pump reduces the pressure on the purge side of the Nafion dryers, resulting in a faster volume flow rate and improved drying. A nonhazardous desiccant (Drierite; WA Hammond, USA – part number 27070 includes a canister with Swagelok fittings, or comparable desiccants) is used to remove residual water from the analyzer exhaust before it enters the purge housing. The lifetime of the desiccant is several years given the extremely low water content of the analyzer exhaust. Nafion is more effective at cooler temperatures, and rapid temperature changes can produce large changes in the water content of the sample airstream. Therefore, the Nafion dryer is housed in an insulated enclosure equipped with a thermoelectric cooler (Watlow SD6C-HCAF-AARG, or comparable coolers). The box temperature is maintained at approximately 20 °C. The system achieves a sample dew point of approximately –36 °C (at 1013 hPa) or roughly 180 ppm H₂O. Calibration gases are introduced upstream of the Nafion membrane dryers. The Nafion membrane acts as a reservoir for water and is normally equilibrated with the chilled sample air. The dry calibration gases are humidified as they pass through the Nafion dryers and emerge with a dew point that is indistinguishable from that for dried atmospheric sample air. Differences between atmospheric samples and calibration standards are <10 ppm H₂O.

Nafion is slightly permeable to CO₂, and thus CO₂ can be lost from the sample airstream when there is a large partial pressure gradient across the membrane (Ma and Skou, 2007). The pressure inside the membrane is 6 to 8 times higher than on the purge side. Loss across the membrane is problematic only if different between samples and calibration standards, which might occur if CO₂ permeability is strongly dependent on the moisture content of air entering the dryer. Andrews et al. (2014) measured CO₂ loss across the Nafion in the laboratory and found that CO₂ loss across the Nafion membrane is nearly identical for calibration gases and sample gas in the system. Thus, there is no bias resulting from using a Nafion membrane.

3.5 Sample/Calibration Selection Manifolds

Atmospheric samples from the inlet lines are selected through a solenoid valve manifold (Parker Hannifin 009-0933-900, or comparable manifolds). Three-way valves are plumbed in series to minimize dead volumes. The solenoid valves are stainless steel and are rated to 689.5 kPa (100 psi) inlet pressure. Calibration gases are selected using a similar manifold. Solenoid valves were chosen instead of a multi-position valve to increase reliability. Andrews et al. (2014) tested one system with a multi-position valve (10-position ECMT; VICI Valco, USA) with the expectation that the multi-position valve would have less dead volume than the solenoid valve manifolds, but the response time after transitions between calibration gases was not improved, suggesting that other components dominate flushing and equilibration in this system.

3.6 Calibration Standard Gases and Procedures

NOAA's Earth System Research Laboratory (ESRL) has been recognized globally as the "gold standard" for trace gas calibration standards, including GHG. NOAA ESRL is responsible for maintaining the WMO mole fraction calibration scales for CO₂, CH₄, CO, and N₂O (Andrews et al., 2014). CARB uses four primary gas standards from NOAA ESRL for the GHG monitoring network. Upon expiration of the two-to-six-year validity period (CO – two years, CO₂ – three years, N₂O – four years, and CH₄ – six years), the NOAA primary gas standards are shipped back to NOAA for re-certification. These four primary gas standards span typical ambient air concentrations and provide both evaluation of the instrument's linearity and calibration of the secondary transfer standards. The four primary gas NOAA standards are stored in MLD's Sacramento facility and the GHG monitoring network only uses secondary transfer standards to provide calibration gases at each site. Since the NOAA primary gas standards are many times more expensive than those from commercial gas suppliers, secondary transfer standard gases are purchased from contracted gas suppliers to minimize the operational costs.

At each GHG monitoring site, the "**Periodic Two-point Calibration and Target Check**" procedure is applied for the analysis system. This procedure provides a periodic calibration line every four hours for each analyzer and uses it to evaluate how accurate each analyzer is when measuring from a known concentration target check gas cylinder. At each station, there are three secondary transfer

standard gas cylinders, each contains CO₂, CH₄, CO, and N₂O. Two of the secondary transfer standard gas cylinders, with gas concentrations that bracket typical ambient air concentrations at mid-day, are used to establish periodic calibration lines. The third secondary transfer standard gas cylinder provides known concentrations of gases to calculate the instruments' accuracy and precision. One of the two analyzers is programmed to control a series of solenoid valves to introduce air either from calibration gases or target check cylinders to both CO₂/CH₄ and CO/N₂O analyzers simultaneously.

Before installation of these known concentration cylinders, all of these secondary transfer standards are calibrated against the primary NOAA standards using at a CARB GHG station. Once the secondary transfer standards are calibrated, they are stored at a MLD facility for future installation at stations. Each gas cylinder typically lasts for eight months. Secondary transfer standards are purchased from commercial gas suppliers, but their certified concentrations are not accurate enough to calibrate GHG analyzers. It is necessary to re-calibrate them against the NOAA primary standards using the procedures described below.

Calibration of secondary transfer standards:

a) At a CARB GHG station, connect all four NOAA standard gas cylinders and a set of four secondary gas cylinders to the eight-port valve box (Figure 3).
b) Set valve sequence to run ten minutes from each cylinder.
c) Check that each cylinder's measurements appear to settle for the first cycle of valve sequence.
d) Let the sequence cycle through the NOAA standards and secondary standards four times.
e) Verify the results are sufficiently precise. The precision thresholds for CO ₂ , CH ₄ , CO and N ₂ O are standard error of measurements of 0.05 ppm, 0.5 ppb, 0.5 ppb, and 0.04 ppb, respectively, and the slope of last two minutes of measurement are 0.05 ppm/minute, 0.5 ppb/minute, 0.5 ppb/minute, and 0.04 ppb/minute, respectively.
f) Once the above are confirmed, the four-point calibration curve/line based on the NOAA standards responses are applied to calculate each of the secondary standard concentrations.
g) Document the secondary standard concentrations and cylinder numbers.

3.7 Sampling and Post-processing

a) The valve sequencer is programmed to measure from each of the high and low secondary transfer standards for ten minutes every four hours with both CO ₂ /CH ₄ and CO/N ₂ O analyzers simultaneously. A third secondary transfer standard "target" cylinder (with concentrations halfway between high and low secondary transfer standards) is measured for ten minutes between these (two hours after the high and low secondary transfer standards). The remaining time is spent measuring the ambient air (when applicable, switching between tower levels).
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| b) Post measurement data processing. In order to allow the tubing and analyzers to stabilize when switching among ambient air, standard gases, or sampling heights, the data processing codes are programmed to discard the first five minutes of data for the system to flush, and report the data corresponding to the final five minutes of each ten-minute sampling interval. |
| c) The slope and offset of calibration line calculated using the four-hour cycle with the high and low secondary transfer standards are applied to calculate the measurements from the tower and target cylinders. |
| d) The calculated target measurements are examined to ensure low noise and small offset from the true value (i.e., N ₂ O within 0.1 ppb, CH ₄ within 2 ppb, CO ₂ within 0.1 ppm, and CO within 3 ppb). The data will be flagged if any of the target measurements exceed the above criteria. |

4. Estimated Uncertainty

The method developed by Andrews et al. (2014) provides plausible time varying uncertainty estimates for individual CO₂, CH₄, CO, and N₂O measurements. The uncertainty algorithms quantitatively track the major sources of error affecting the measurements. For applications like inverse modeling to estimate GHG surface fluxes, the most important considerations are long-term reproducibility and compatibility of measurements. That is, we need to understand the extent to which we can confidently interpret differences among measurements made at the same site and within and across networks from hour to hour, month to month, and year to year.

4.1 Uncertainty of Calibration Standards

According to Andrews et al. (2014), field standards are calibrated in the laboratory relative to WMO standards before and after deployment. For CO₂, pre- and post-deployment calibrations are available for 177 tanks since 2004. The mean difference was 0.02 ± 0.05 ppm (post minus pre) and 14 cylinders had absolute differences >0.1 ppm, 7 had differences >0.15 ppm, and none had differences >0.2 ppm. For the 59 CO standards with pre and post-deployment calibration data, the mean difference was 3.2 ± 2.6 ppb. The distribution is strongly skewed toward positive values, with six cylinders drifting up by more than 5 ppb and two drifting more than 10 ppb over their lifetime.

4.2 Uncertainty Derived from Target Cylinder Measurements

The target cylinder measurements provide an independent check on estimated uncertainty values. It is defined to be the 68th percentile of the absolute difference between target measured and assigned values. This is based on the idea that the difference between the measured and assigned target values should fall within the one standard deviation measurement uncertainty 68% of the time. The assigned value is constant over the lifetime of the cylinder, and therefore is a bias rather than a random error. Errors in the measurements from the analyzers, errors in the water corrections, and potential problems delivering air to the analyzers are all sources of uncertainty in these comparisons.

Figures 4, 5, and 6 are example daily results of **“Periodic Two-point Calibration and Target Check”** at the San Bernardino site. Figures 4 and 5 are the low and high calibration measurements of the secondary transfer standards, respectively. Figure 6 is the “Target Check” results based on the low and high calibration lines of each gas. Using Figure 6 as an example, the cylinder number (CC81138) is shown on top of each measurement panel. Following the cylinder number is the daily averaged target concentration of the gas based on the periodic calibration measurements, standard deviation and standard error of the measurements in that day, and the difference between the averaged target measurement (red line) and the assigned “true” target value (blue line). In this case, the discrepancies are 0.05 ppm, 0.2 ppb, 0.18 ppb, and 0.01 ppb for CO₂, CH₄, CO, and N₂O, respectively. All the above reported errors are well below the required WMO accuracy requirements. Again, the WMO measurement accuracy requirements are within 0.1 ppm, 2 ppb, 3 ppb, and 0.1 ppb for CO₂, CH₄, CO, and N₂O, respectively. MLD staff will examine and resolve the issues when target checks exceed the WMO limits. Typically, potential issues include instrument malfunction, low calibration gas pressure, leaks, or station room temperature fluctuation.

5. Data Handling/Data Management

All the measurement data are collected on a local data logger (i.e., CARBlogger) and transmitted to MLD server for processing. Once the data are screened and verified for the required accuracies, they are marked as “Reviewed” on the MLD’s DMS database for later uses.

As described above, a valve sequencer controls the valve switching among ambient air and calibration gases. The onsite data logger records the concentrations and flags whether each data point is ambient air or calibration gas. A CARBlogger with computer codes to calculate the instrument’s calibration line and the accuracy of the target measurements following the “Periodic Two-point Calibration and Target Check” procedure. The same calibration line is used to calculate the ambient air concentrations for the following four hours. All these preliminary data are stored on MLD’s DMS to be screened. Once the preliminary data are reviewed and validated, they will be marked as final and “locked” for future use.

6. Quality Assurance/Quality Control

MLD conducts Quality Assurance/Quality Control (QA/QC) procedures similar to the MLD Standard Operation Procedures for Data Review and Validation (SOP 610) for criteria pollutants. First level review is conducted by MLD site operators. In this review, all the preliminary data of each month on DMS are reviewed and flagged for abnormal data points (e.g., instrument malfunction, filter changes, target accuracies). Upon the completion of the first level review, the field check sheets, monthly site activity log, and the review data are further reviewed by an assigned MLD second level review staff to confirm data quality. MLD site operators fill out field check sheets to document field activities. In accordance

with standard air monitoring practices, MLD performs instrument calibrations every six months and after major instrument maintenance. During these calibrations, instruments will be challenged with NOAA primary standards to verify their accuracies.

7. GHG Monitoring Training

In order to achieve a minimum level of competence and acceptable level of data quality, appropriate training will be made available to MLD employees supporting the GHG Monitoring Network Program, commensurate with their duties. Such training consists of in-person, teleconferences, and on-the-job training by MLD staff. Instrument manufacturers may offer limited instrument maintenance training. One-on-one training will be available for new MLD staff for fundamental GHG measurement theory, instrument design, site installation and operation, field logbook documentation, data quality needs, and data review on DMS. A Standard Operation Procedure (SOP) will be developed for maintaining and operating GHG instrument and detailed instructions for troubleshooting and calibrating specific analyzers or support equipment.

8. Documentation and Records

Field notebooks – notebooks are issued for each sampling site for the operator to record activities. The notebooks contain the appropriate notes for routine operations, as well as inspection and maintenance information. These notes are submitted monthly along with GHG data review package.

Monthly Quality Control Maintenance Check Sheet – each GHG analyzer has a check sheet at the station. Site operator records operation parameters and notes each time when the site operator visits the station. These check sheets are submitted monthly along with the GHG data review package.

All raw data required for the calculation of a calibrated GHG concentration and QA/QC data are collected electronically via CARBlogger and sent to DMS daily.

9. Instrument Inspection, Maintenance, and Calibration

In addition to daily checks of instrument status on DMS, site operators will visit the station and inspect instrument monthly and record notes on the notebook and Monthly Quality Control Maintenance Check Sheet. As described in Section 3.6, the analyzers are calibrated every 4 hours using the secondary transfer standards. Independent calibration checks are performed every six months using the NOAA primary standards by MLD staff (other than the site operators). The NOAA primary standards will be introduced directly from the sample inlet. The first five minutes of data during the stabilization time will be discarded, and then record the readings for the next five minutes. CARBlogger will record and calculate the concentrations and stored the data on DMS. Calibration reports are prepared for the six-month calibration checks using these data and compared with NOAA's concentration certificates. MLD staff will examine and resolve the issues when the NOAA calibration checks are exceeded the WMO limits.

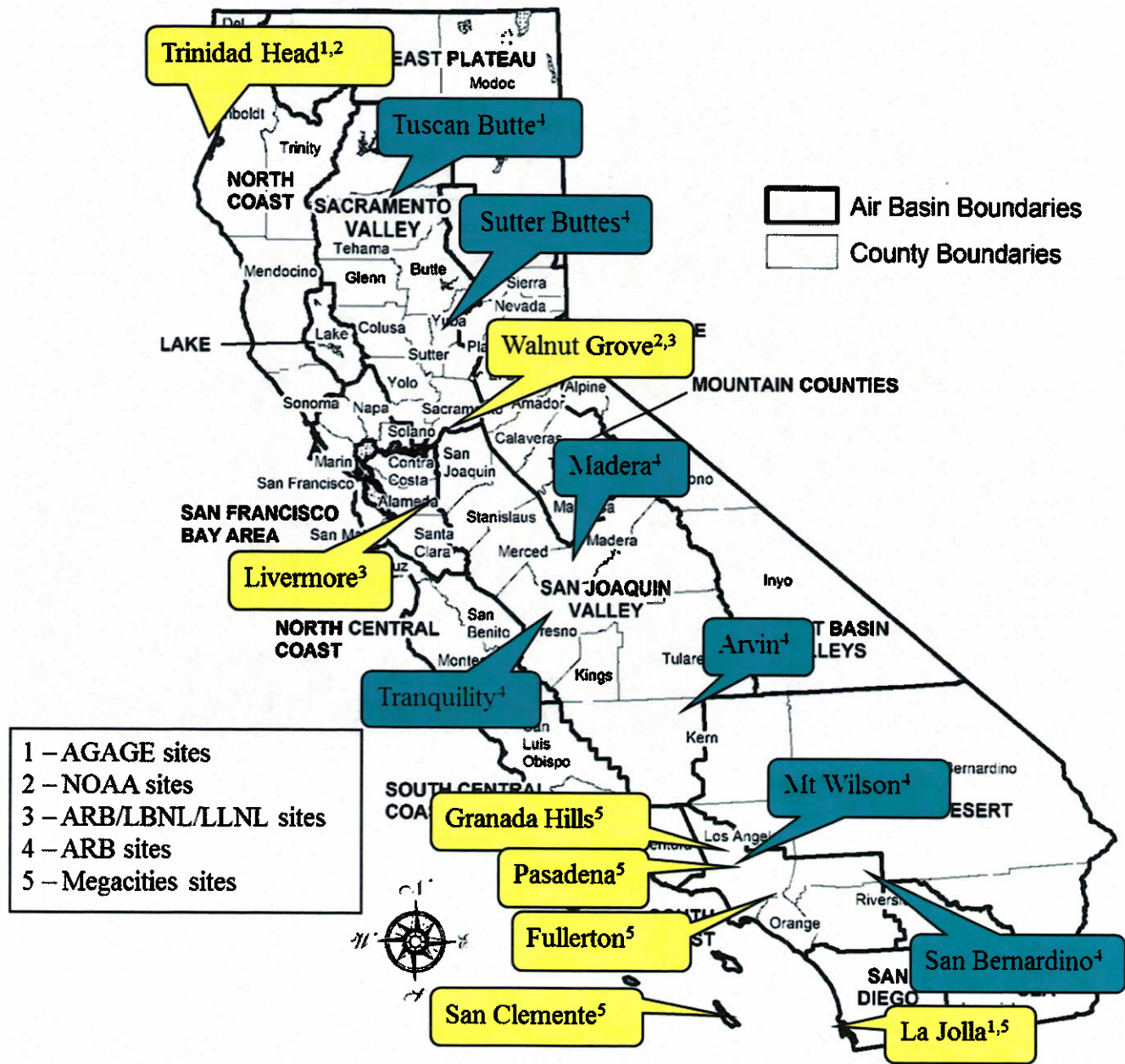


Figure 1. Map of GHG Monitoring Network
 Cyan labels indicate CARB sites, while yellow labels indicate sites operated by other organizations (universities, national laboratories, federal agencies, and consortia of organizations).



Figure 2. Photos of GHG Monitoring Network Stations (upper right – Tranquility; upper left – Sutter Buttes; lower right – San Bernardino; and lower left – instrument rack at San Bernardino)

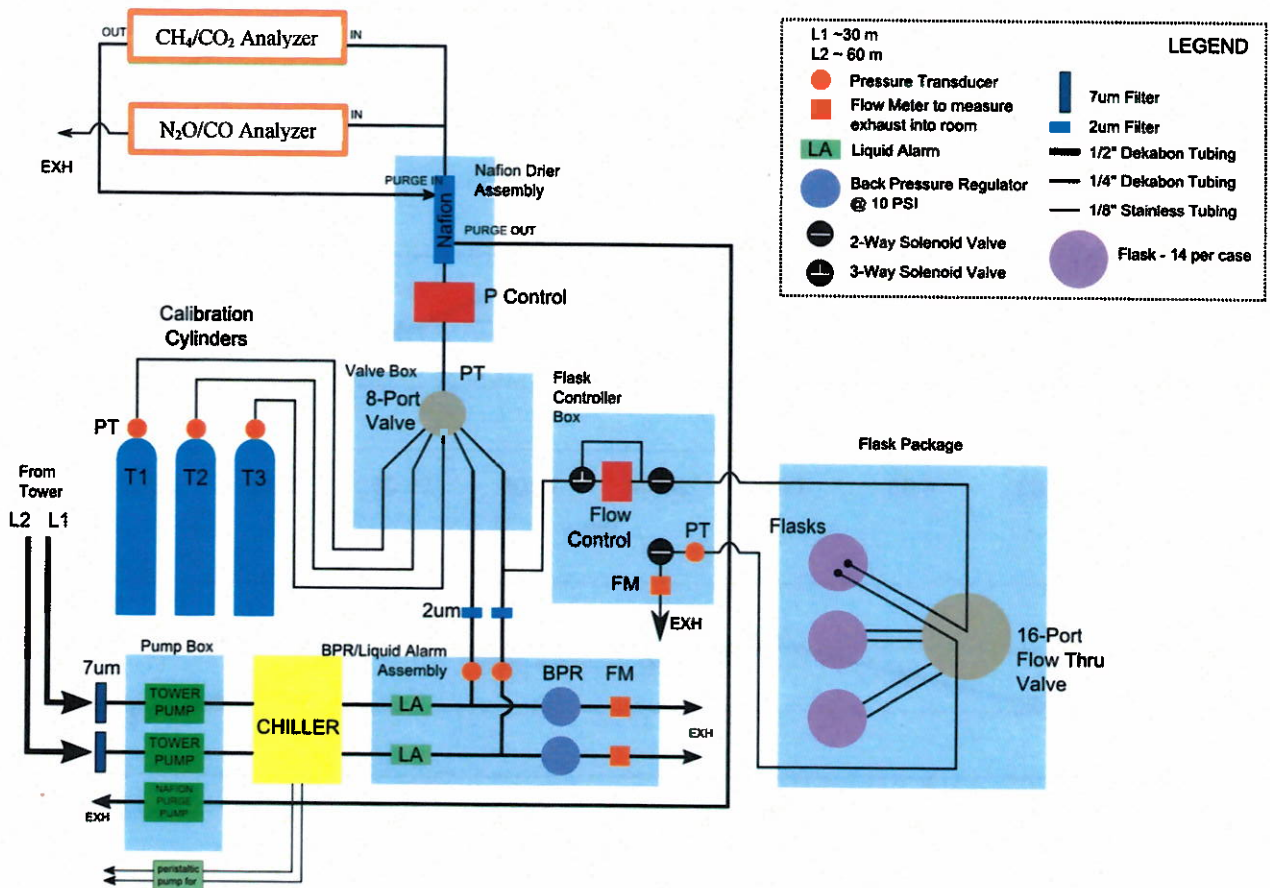


Figure 3. Schematic Diagram of the San Bernardino Tower CO₂, CH₄, CO, and N₂O Analysis System

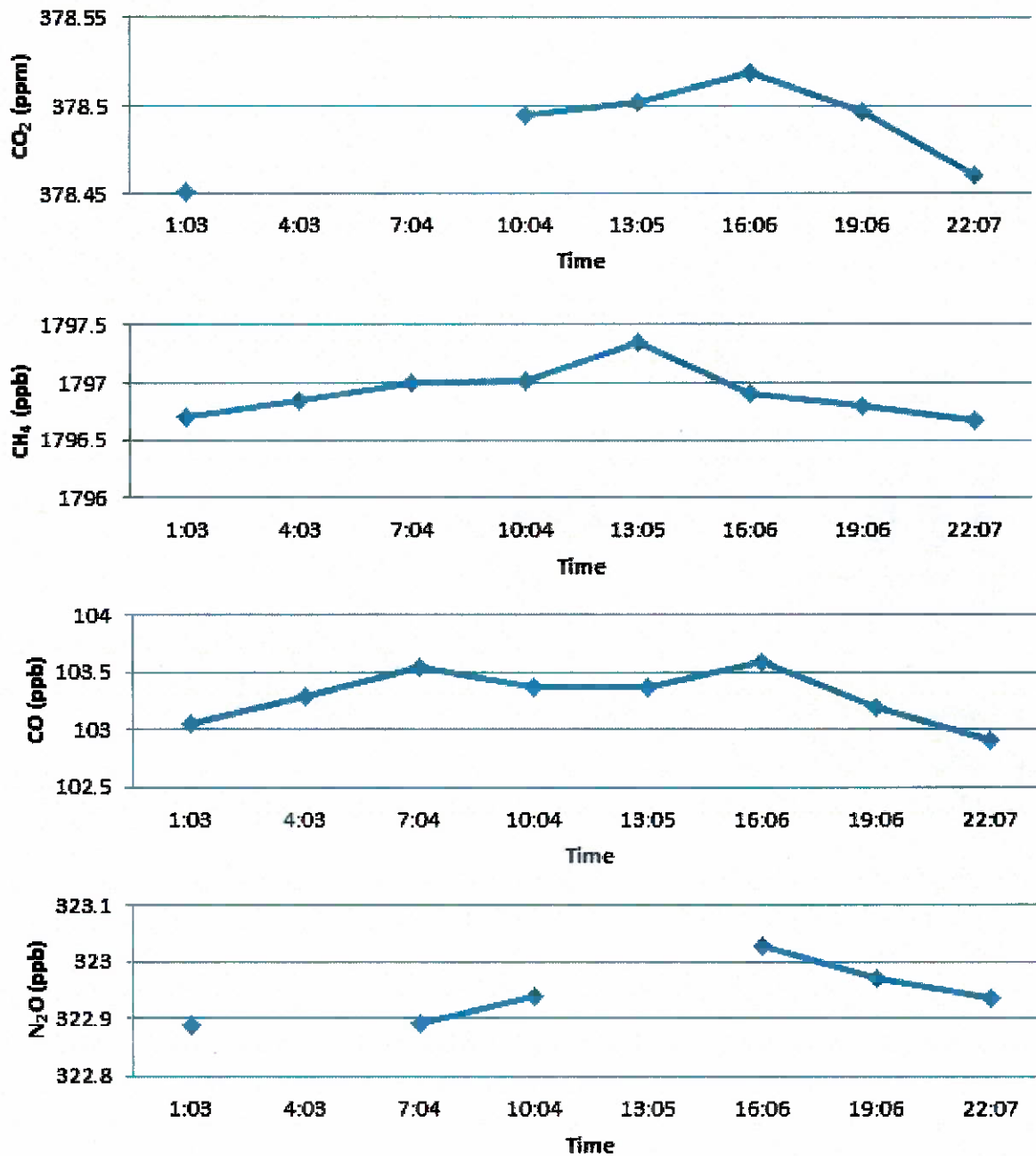


Figure 4. Example of Low Concentration Calibration Gas Measurements at San Bernardino Tower on January 11, 2015. Using CO₂ as an example, the daily average was 378.49 ppm, standard deviation – 0.02 ppm, and standard error – 0.01 ppm of the low calibration gas measurements in that day. Missing values are due to the measurements exceed precision thresholds (see Section 3.6 for details)

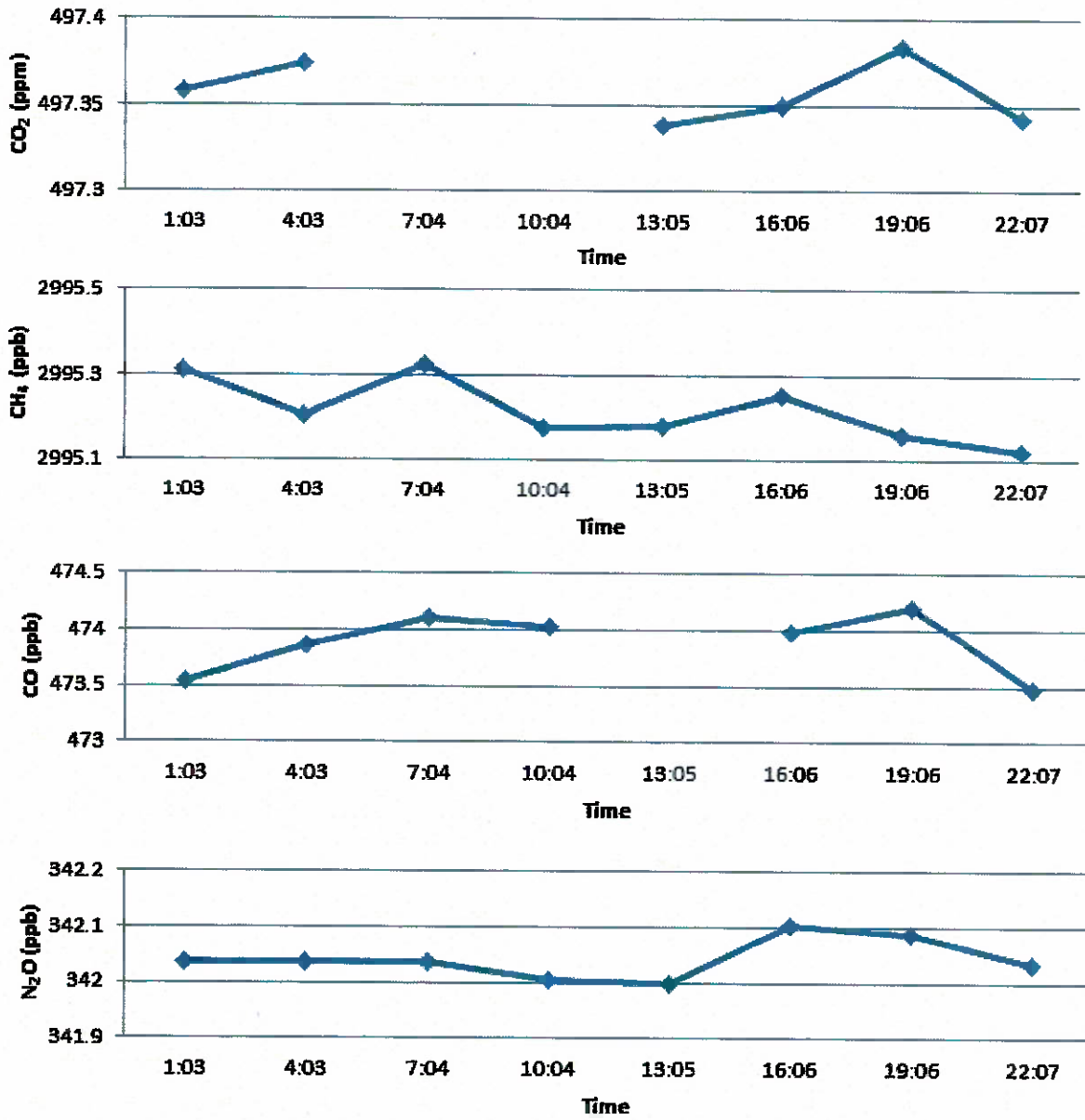


Figure 5. Example of High Concentration Calibration Gas Measurements at San Bernardino Tower on January 11, 2015. Using CO₂ as an example, the daily average was 497.36 ppm, standard deviation – 0.02 ppm, and standard error – 0.01 ppm of the high calibration gas measurements in that day. Missing values are due to the measurements exceed precision thresholds (see Section 3.6 for details)

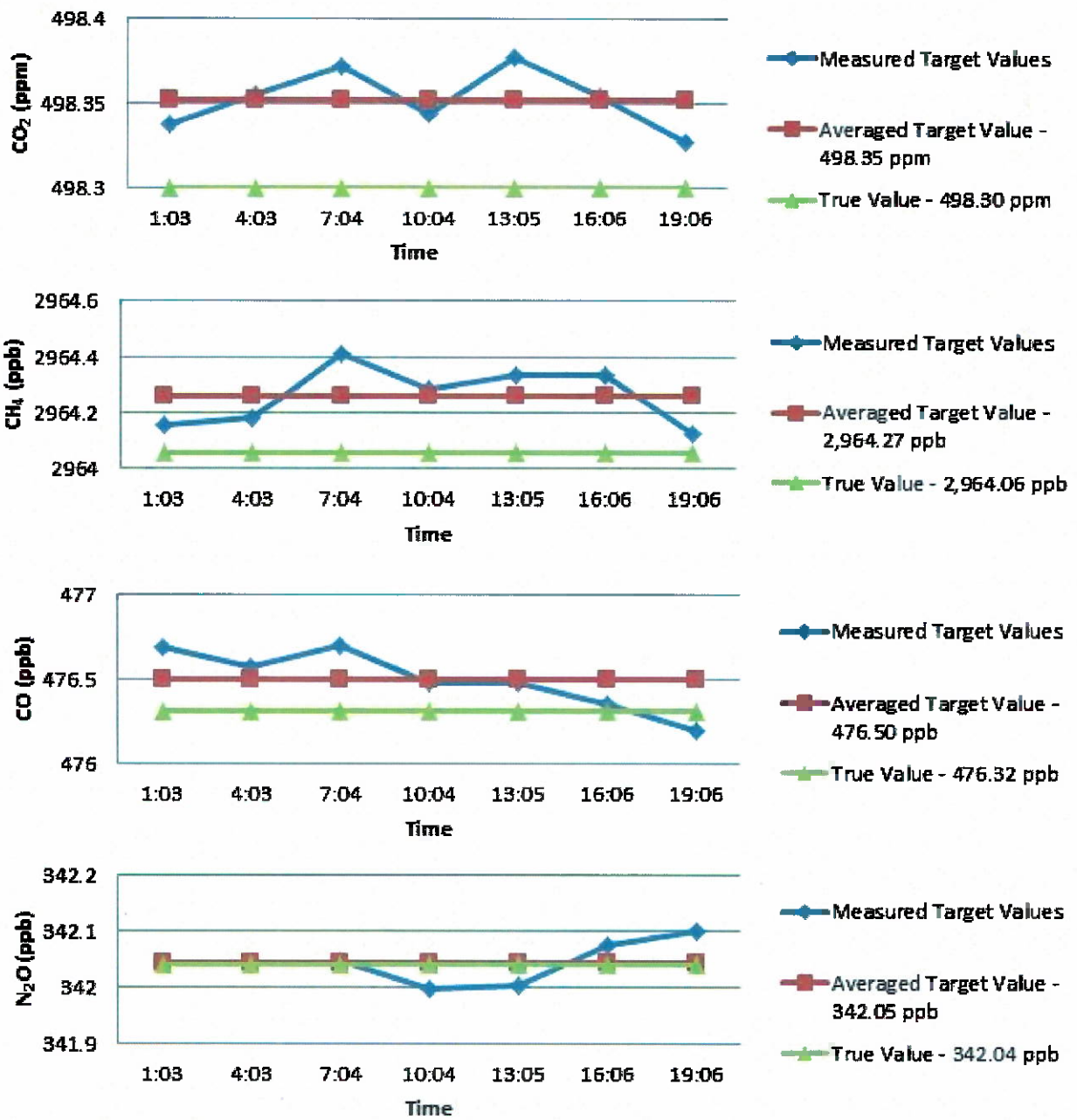


Figure 6. Example of Target Measurements and Evaluation of Instrument Accuracy at San Bernardino Tower on January 11, 2015 (as shown in this figure, the measured CH₄ target is 2964.27 ppb. Since the “true” CH₄ value is 2964.06 ppb, the discrepancy is calculated to be 0.21 ppb which is well below the WMO requirement of 2 ppb for CH₄.)

10. References:

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Appendix 1. Proposed Changes of GHG Measurements at the Sutter Buttes Site

This document describes the proposed changes of greenhouse gas (GHG) sampling, drying, and instrument calibration setups. For GHG emissions inventory analysis (i.e., via inverse modeling) and long term emission trend monitoring purposes, the proposed changes are necessary to standardize GHG measurements which follow NOAA's GHG measurement tower network procedures (Andrews et al., 2014).

Current Status:

1. Figure A1 shows the current gas line configuration at the Sutter Buttes station. Ambient air from the rooftop intake is drawn to a glass manifold, which provides air for CH₄/CO₂ and N₂O/CO, and ozone analyzers. This sample inlet and manifold configuration introduces cross contamination between GHG and ozone. For example, when MLD staff conduct routine ozone calibrations, zero air and ozone calibration gas enter manifold, which is shared with the CH₄/CO₂ and N₂O/CO instruments. During ozone calibrations, ambient air is largely diluted with zero air or ozone calibration gas.
2. Two particle filters, one for the CH₄/CO₂ analyzer and the other for the N₂O/CO analyzer, are shown in Figure A1. For each analyzer, after the particle filters, air is directed to a switching valve and then to the inlet of analyzer.
3. Figure A2 shows the current valve sequencer GUI, indicating 10 minutes of precision check followed by 1,370 minutes air measurements (23 hours cycle).

Proposed changes:

1. Install a dedicated air intake, particle filter, and switching valve system for both CH₄/CO₂ and N₂O/CO analyzers (Figure A3). Ambient air from the rooftop is drawn through a Synflex tubing inlet. Ambient air is first filtered with a 5 micron particle filter, through switching valves, then enters a Nafion dryer. A zero air generator provides dry counter flow purge air to the Nafion to remove moisture from ambient sample air (Figures A3).
2. Three solenoid valves are controlled by the valve sequencer to switch among ambient air, low calibration gas, high calibration gas, and target calibration gas. (The three-solenoid-valve system can be replaced by a Valco 8-port valve, if available.)
3. The valve sequencer GUI will be modified to four steps – three 10-minute calibration gas measurements followed by 210 minutes of air measurements (4 hours cycle).

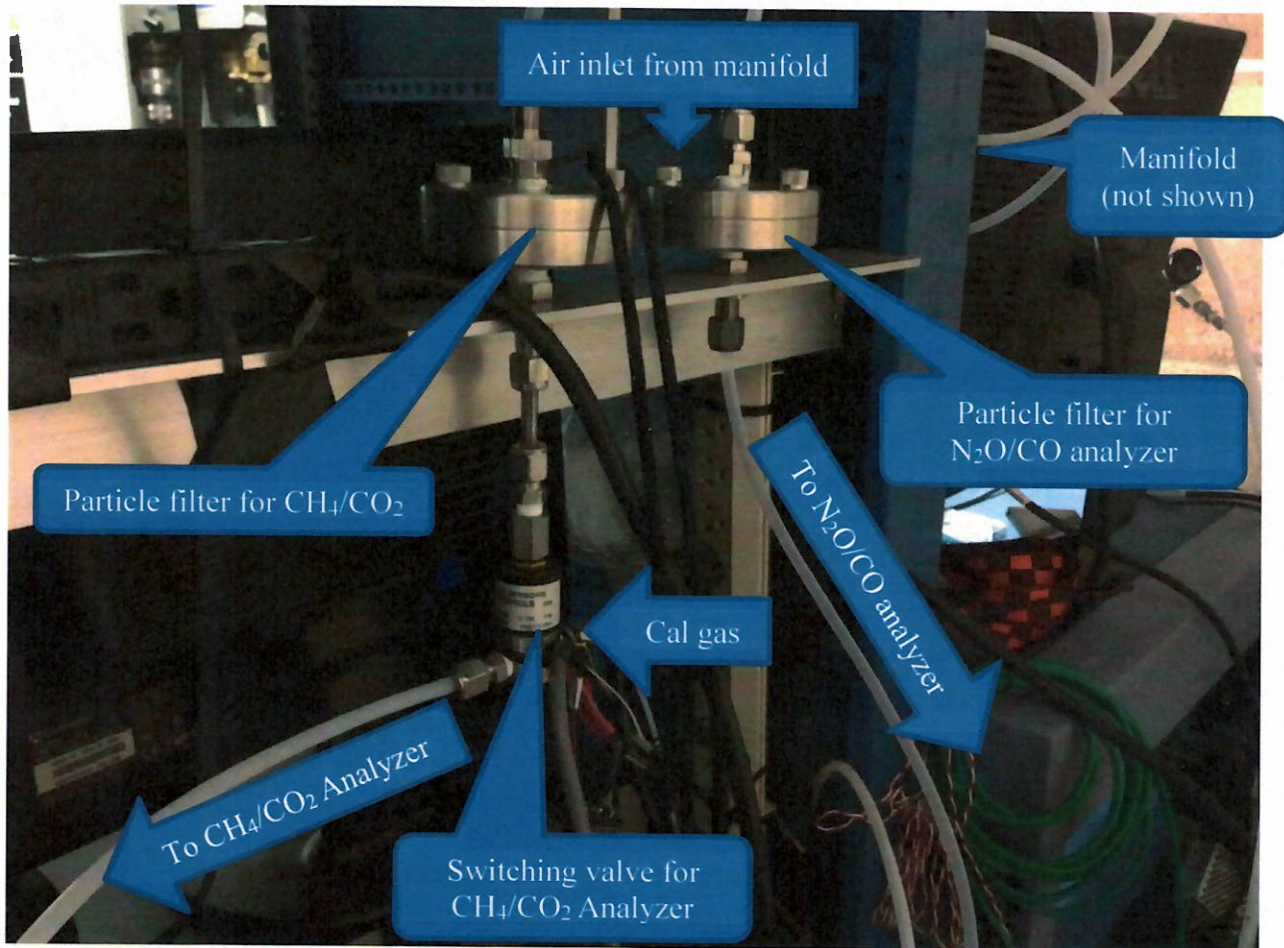


Figure A1. Current Gas Line Configuration at the Sutter Buttes Station. Ambient air from the rooftop intake is drawn to a glass manifold (not shown) which provides air for CH₄/CO₂, N₂O/CO, and ozone analyzers.

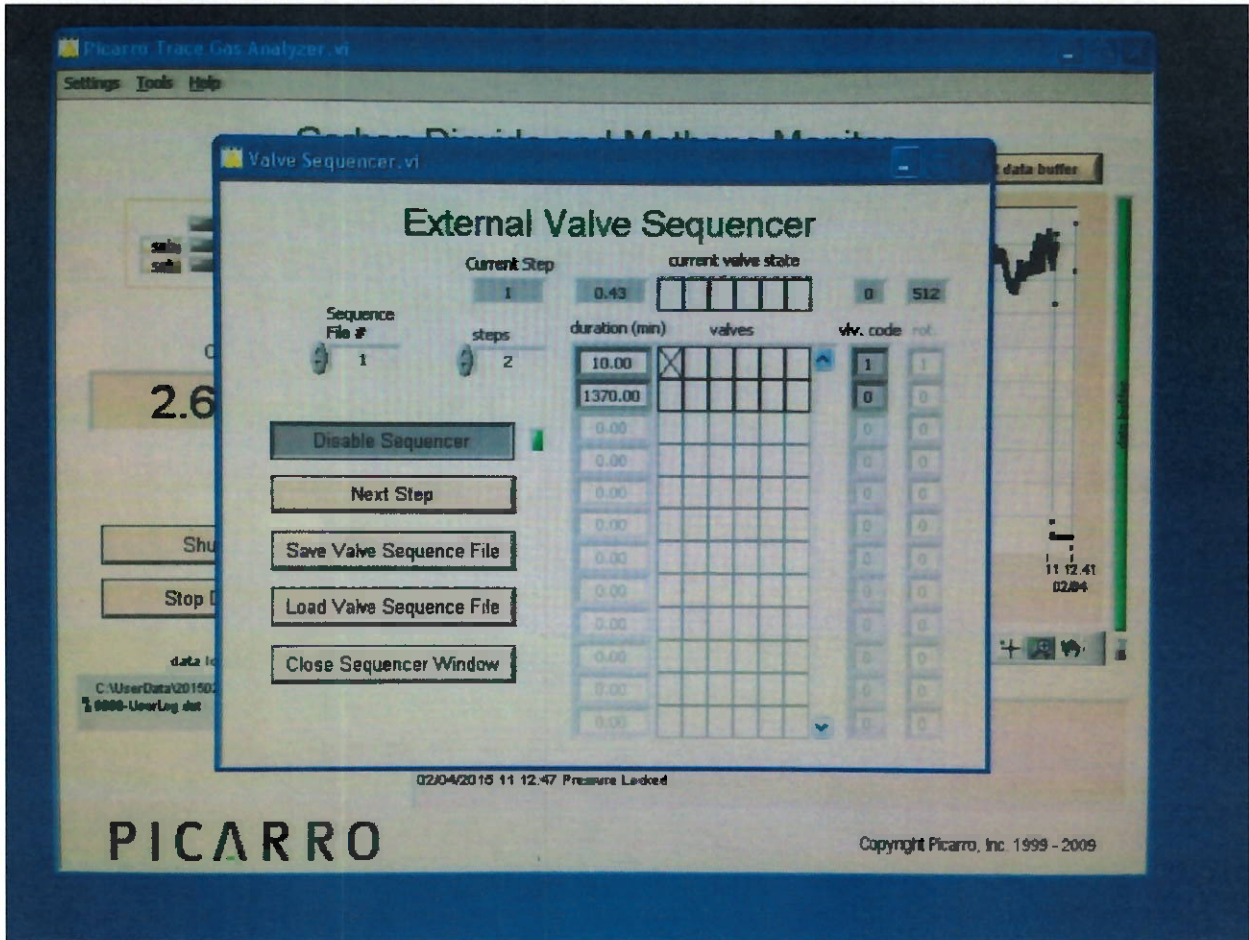


Figure A2. Current Valve Sequencer GUI – indicating 10 minutes of precision check followed by 1,370 minutes air measurements. For the proposed calibration, the sequencer will be modified to four steps – three 10-minute calibration gas measurements followed by 210 minutes of air measurements.

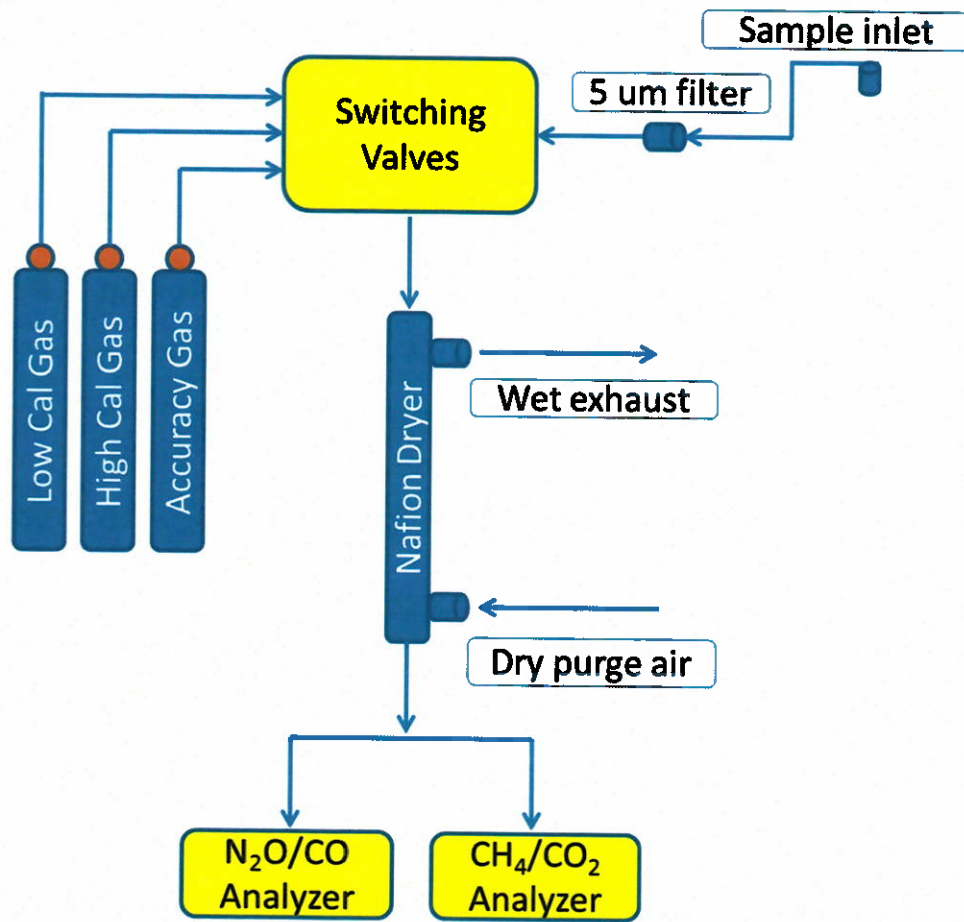


Figure A3. Proposed Sampling, Air Drying, and Calibration Gases Configuration

