Metadata for Atmospheric Measurements at the Commerce City Fixed (CCF) Monitoring Station

8 November 2023 Revision

Site location

During the study period the station was located at two different sites ~0.2 miles apart on the same street.

Location 1: Data start until 8/12/2022
39.8128 °N, 104.9476 °W, 1564 m asl (5131 ft asl)
(3421 E 64th Ave, Commerce City, CO 80022)

Location 2: 8/15/2022 until data end
39.8126 °N, 104.9439 °W, 1569 m asl (5147 ft asl)
(3700 E 64th Ave, Commerce City, CO 80022)

The station facility is a climate-controlled, insulated trailer approximately 16 ft long x 8 ft wide x 8 ft tall. Affixed to the trailer is a 10 m aluminum tower which supports the meteorological equipment and air sampling inlet lines.

Wind Speed / Wind Direction

Wind conditions are recorded with a Campbell Scientific MetSENS500, and RM Young Wind Monitor AQ, 05305-PT, mounted on a meteorological tower at 9.2 m height. Data reported prior to 01/11/2022 (m/d/y) were collected with a RM Young Wind Monitor, after 01/11/2022 (inclusive) reported data are from the MetSENS500. Every 6 months, wind speed and wind direction calibration checks are performed by an operator on the RM Young Wind Monitor, using a vane angle stand (RM Young, 18112) and an anemometer drive (RM Young, 200-15,000 RPM, 18802) standard. For the wind direction, South (180 degrees), West (270 degrees), East (90 degrees) and North (0 degrees) positions are checked, rotating the sensor clockwise and then counterclockwise, for a total of 8 points. For the wind speed, 4 speeds are used: 600 rpm (3.07 m/s), 1700 rpm (8.70 m/s), 3300 rpm (16.90 m/s) and 5400 rpm (27.65 m/s) in both directions (clockwise and counterclockwise) along with a zero check for a total of 9 points. Audits were performed by the Colorado Department of Public Health and Environment (CDPHE) on the RM Young Wind Monitor: near the start of measurements on 7 February 2022 and 8 June 2022. For these audits, the wind speed sensor had 0.0% error for both clockwise and counterclockwise directions across all audited wind speeds. The wind direction sensor and vane alignment had <3 degrees composite error for all wind directions. The stated resolution for the MetSENS500 wind speed is 0.01 m/s and for wind direction is 1 degree with ±3 degree accuracy. The lower detection limit (LDL) for the MetSENS500 wind speed is 0.01 m/s. Undetected wind is reported as half of the LDL, or 0.005 m/s, and in these instances the wind direction is reported as NaN.

Temperature, Relative Humidity, Barometric Pressure

Temperature, relative humidity, and barometric pressure are measured with a Campbell Scientific MetSENS500 mounted on a meteorological tower at 9.1 m height above the surface using the factory

calibration. Two audits were performed by the Colorado Department of Public Health and Environment (CDPHE) of the accuracy of the temperature and relative humidity readings on 7 February 2022 and 24 April 2023. The instrument passed in all audit criteria with temperature reading accuracy error of 0.3 and 0.1 °C, at each audit respectively (pass is ±2 °C), relative humidity having 0.2% and 2.5% error, respectively (pass is ±5%), and pressure error -3.1 mmHg at the 2nd audit (not done at the 1st audit, pass is ±10 mmHg). The manufacturer stated resolution of the temperature measurement is 0.1 degree Celsius with ±3 degree C accuracy. The stated relative humidity resolution is 0.1% with ±2% accuracy. The stated resolution of the pressure measurement is 0.1 hPa with ±0.5 hPa accuracy.

Solar radiation

Incoming solar radiation is monitored with an Apogee SP-110-SS pyranometer on the meteorological tower at 9.1 m height above the surface. The sensor dome was cleaned every two months for the initial study period until July 2022 after which it was cleaned every month.

Ozone (O_3)

Ozone is recorded with a Thermo Scientific model 49C UV absorption monitor. Ambient air is sampled from an inlet mounted at 8.5 m height above the surface. The sampling line consists of 10 m length, ¼ inch o.d., 5/32 inch i.d. PFA tubing, equipped with an inlet PFA filter holder that houses a 5 micron Teflon membrane filter. The membrane inlet filters were replaced every two months for the initial study period until July 2022 after which the filters are replaced every month. The time resolution of the ozone monitoring is one minute. The monitoring and calibration protocol follow the federal regulatory monitoring requirements according to the specifications of '40 Code of Federal Regulations (CFR) Part 58'. The calibration scale is referenced against the EPA Region 8 primary ozone reference standard. Daily zero and span checks are performed automatically using a Thermo Scientific 49C calibrator unit. These checks are performed at night by introducing the calibration gases through the calibration valve of the instrument. First, zero air is introduced for 6 minutes, followed by 80 ppb of ozone for 6 more minutes. Two hours later, a mid-range check at 50 ppb is performed for 6 minutes. Quarterly, a full range linearity check is performed using the same calibrator unit. Six different levels of ozone are introduced: 0 ppb, 25 ppb, 50 ppb, 100 ppb, 200 pbb, 400 ppb. Yearly, a calibration check is performed using a level 2 standard (also a Thermo Scientific 49C calibrator unit) following the same protocol as the quarterly checks. The level 2 standard was last referenced against the EPA Region 8 primary ozone reference standard on May 4th 2022. Two audits of the 49C were performed by the Colorado Department of Public Health and Environment (CDPHE) on 8 June 2022 and 24 April 2023. The instrument passed all audit criteria with a calibration agreement slope 1.005 and an offset of -0.054 ppb at the June 2022 audit, and slope 0.998 and offset -3.6e-5 at the April 2023 audit, meeting EPA measurement quality requirements. The lower detection limit (LDL) for ozone is 1 ppb as reported by the instrument manufacturer. Measurements below this value are replaced with ½ of the LDL, 0.5 ppb.

Hydrogen Sulfide (H_2S)

H_2S is analyzed by gas-phase ultraviolet fluorescence with a Teledyne T101 analyzer. Ambient air is pulled at 650 scc/min from an inlet mounted at 8.5 m height above the surface. The sampling line

consists of 10 m length, ¼ inch o.d., 5/32 inch i.d. PFA tubing equipped with an inlet PFA filter holder that houses a 5 micron Teflon membrane filter. The membrane inlet filters were replaced every two months for the initial study period until July 2022 after which the filters are replaced every month.

Calibrations are performed by dynamic dilution of a 5.06 parts per million (ppm) H_2S primary EPA-grade standard (EPA protocol grade gas, Praxair, production date 02/07/2022, EY0002356), using a Thermo Fisher Scientific 146i Multi-gas Calibrator. Weekly zero and span checks are performed by an operator. The output of the calibrator is introduced through the span valve of the instrument. Zero air is generated from a Parker zero-air generator (HPZA-7000) followed by passing through Sofnofil and Charcoal scrubbers. Zero air is introduced first for 10 min, followed by 200 ppb H_2S for 15 min. Quarterly, full calibrations of the H_2S analyzer are performed using the output of the calibrator to introduce span gas to the span port of the instrument and zero air through the zero air port of the analyzer (occurring 04/05/2022, 08/23/2022, 11/02/2022, 2/09/2023, 07/24/2023). For these calibrations, a zero adjustment is made first, followed by H_2S span adjustments using 200 ppb H_2S. Every 6 months, a 6-level linearity check is performed (0 ppb, 25 ppb, 50 ppb, 75 ppb, 100 ppb, 200 ppb). The lower detection limit reported by the manufacturer is 0.4 ppb. Measurements below this value are reported as ½ of the LDL, 0.2 ppb.

Sulfur Dioxide (SO_2)

SO_2 is analyzed by gas-phase ultraviolet fluorescence with a Teledyne T101 analyzer. Ambient air is pulled at 650 scc/min from an inlet mounted at 8.5 m height above the surface. The sampling line consists of 10 m length, ¼ inch o.d., 5/32 inch i.d. PFA tubing equipped with an inlet PFA filter holder that houses a 5 micron Teflon membrane filter. The membrane inlet filters were replaced every two months for the initial study period until July 2022 after which the filters are replaced every month. The monitoring and calibration protocol follow the federal regulatory monitoring requirements according to the specifications of '40 Code of Federal Regulations (CFR) Part 58'. Calibrations are performed by dynamic dilution of a 4.94 parts per million (ppm) SO_2 primary EPA-grade standard (EPA protocol grade gas, Praxair, production date 02/09/2022), using a Thermo Scientific 146i Multi-gas Calibrator. Weekly zero and span checks are performed by an operator. The output of the calibrator is introduced through the span valve of the instrument. Zero air generated is from a Parker zero-air generator (HPZA-7000) followed by passing the output through Sofnofil and Charcoal scrubbers. Zero air is introduced first for 10 min, followed by 200 ppb SO_2 for 15 min. Quarterly, full calibrations of the SO_2 analyzer are performed using the output of the calibrator to introduce span gas to the span port of the instrument and zero air through the zero air port of the analyzer (occurring 04/05/2022, 08/23/2022, 11/02/2022, 2/09/2023, 07/24/2023). For these calibrations, a zero adjustment is made first, followed by span adjustments using 200 ppb SO_2. Every 6 months, a 6-level linearity check is performed (0 ppb, 25 ppb, 50 ppb, 75 ppb, 100 ppb, 200 ppb). Two audits of the T101 SO_2 measurement were performed by CDPHE: 8 June 2022 and 24 April 2023. The instrument passed all audit criteria across the five measurement levels at both audits, with a calibration agreement slope 0.89 and an offset of -0.180 ppb at the June 2022 audit and slope 0.92 and offset -0.114 at the April 2023 audit, meeting EPA measurement quality requirements of $\pm$15%. The lower detection limit reported by the manufacturer is 0.4 ppb. Measurements below this value are reported as ½ of the LDL, 0.2 ppb.

H_2S / SO_2 Corrections:

T101 Measurement Mode correction

The T101 analyzer cycles between an H_2S and SO_2 measurement every ten minutes. Unfortunately, the instrument does not clearly identify which species, H_2S or SO_2, is being measured at a given time. Boulder AIR has worked with Teledyne API for a solution; however, no such solution has been identified at this point. A clear indicator of the measurement mode (H_2S or SO_2) is indicated by the change in sample pressure. Additional pneumatics elements (SO_2 scrubber, moly-converter, additional tubing and values) are required for the H_2S measurement compared to the SO_2 measurement. The result is a comparatively lower sample pressure during H_2S measurement periods.

The following methodology is applied to identify the measurement operating mode, whether H_2S or SO_2, of the T101 analyzer. Measurement mode flags are generated using an algorithm, detailed below and defined in Table 1, to indicate the measurement mode at a given point in time.

A reference pressure, P_{ref}, is used to normalize the sample pressure, P_{sample}, against fluctuations in barometric pressure, $P_{barometric}$. A constant, P_{offset}, is used to ensure the value of P_{ref} remains positive. Pressure values are reported in units of in-Hg.

$$P_{ref} = P_{sample} - P_{barometric} + P_{offset}$$

$$P_{offset} = 30 \text{ in-Hg}$$

On a running basis, a step change in P_{ref} indicates the beginning of a change in the measurement mode, either H_2S or SO_2. A step change, P_{delta}, is defined as the absolute value of the change in pressure between measurements spaced by 2 minutes. Therefore, a change in the absolute value of P_{delta} greater than or equal to a minimum threshold, $P_{cutoff,}$ triggers a measurement mode change.

$$P_{delta} = P_{ref,\, i-3} - P_{ref,\, i-5}$$

$$P_{cutoff} = \pm 1.5 \text{ in-Hg}$$

if $|P_{delta}| \geq P_{cutoff}$, then a mode change is detected.

If P_{delta} is less than the negative cutoff threshold, $(-)P_{cutoff}$, then the instrument is determined to have switched into H_2S mode. If P_{delta} is greater than the positive cutoff threshold, $(+)P_{cutoff}$, then the instrument is determined to have switched into SO_2 mode. Three minutes of transition time is granted for the measurement to reach equilibrium after a measurement mode change. This transition period also guards against situations where the mode changes at a slightly different pace or the averaging period does not line up well across the minute timestamp. The algorithm also assigns a flag when neither H_2S or SO_2 should be reported, using a flag = 0. These instances include the transition period during a mode change or interferences such as irregular or missing pressure measurements. A transition period is defined as the preceding four minutes of data once a measurement mode change is detected. Irregular pressure readings such as a sample pressure or barometric pressure of less than 15 in-Hg, or missing sample pressure or barometric pressure are flagged as non- H_2S or SO_2 measurements. In these cases of irregular pressure readings, the preceding 10 minutes and subsequent 20 minutes of data are flagged accordingly.

Table 1: T101 measurement mode algorithm

Algorithm	**Measurement Mode Description**
$P_{delta} \leq (-)P_{cutoff}$ ie. $P_{ref, i-3} - P_{ref, i-5} \leq -1.5$ in-Hg	H_2S
$P_{delta} \geq (+)P_{cutoff}$ ie. $P_{ref, i-3} - P_{ref, i-5} \geq 1.5$ in-Hg	SO_2
for $\lvert P_{delta} \rvert \geq P_{cutoff}$, $T101\_Mode_{i-4, i-3, i-2, i-1} = 0$ ie. $\lvert P_{ref, i-3} - P_{ref, i-5} \rvert \geq 1.5$ in-Hg, $T101\_Mode_{i-4, i-3, i-2, i-1} = 0$	Transition period
$P_{sample} < 15$ in-Hg $P_{barometric} < 15$ in-Hg Missing P_{sample} Missing $P_{barometric}$ ie. $T101\_Mode_{i-10, \ldots i+20} = 0$	Irregular pressure measurement

H_2S /SO_2 slope and offset corrections

Slope and offset corrections detailed in the Table 2 were applied to the data record.

Table 2: T101 slope and offset corrections

Start	**Stop**	***H_2S Correction***	***SO_2 Correction***
2021-12-27 12:00:00 UTC	2022-02-04 21:45:00 UTC	0.89 slope correction, -0.5 ppb offset	0.94 slope correction, -0.4 ppb offset
2022-02-04 21:46:00 UTC	2022-04-05 20:48:00 UTC	0.89 slope correction, no offset	0.94 slope correction, no offset

Carbon Monoxide (CO)

Carbon monoxide is monitored with a Picarro G2401 cavity ring down spectrometer. Ambient air is sampled at 400 scc/min from an inlet at 8.5 m height. The sampling line consists of 10 m length, ¼ inch o.d., 5/32 inch i.d. PFA tubing equipped with an inlet PFA filter holder that houses a 5 micron Teflon membrane filter. The membrane inlet filters were replaced every two months for the initial study period until July 2022 after which the filters are replaced every month. The monitoring and calibration protocol follow the federal regulatory monitoring requirements according to the specifications of '40 Code of Federal Regulations (CFR) Part 58'. The manufacturer's calibration settings are applied. Calibration checks are conducted every 49 hours by introducing a breathing air grade ambient air gas mixture from a compressed tank (fill date 08/01/2022). Every 6 months, a calibration check and 5-level linearity check (0 ppb, 100 ppb, 200 ppb, 400 ppb, 1000 ppb) is performed by dynamic dilution of a 50.8 parts per million (ppm) CO primary EPA-grade standard (EPA protocol grade gas, Praxair, production date 06/09/2022) with zero air using a Thermo Scientific 146i Multi-gas Calibrator. Zero air is supplied from a compressed UHP grade zero-air cylinder (General Air).

Carbon Dioxide (CO_2)

Carbon dioxide is monitored with a Picarro G2401 cavity ring down spectrometer. Ambient air is sampled at 400 scc/min from an inlet at 8.5 m height. The sampling line consists of 10 m length, ¼ inch o.d., 5/32 inch i.d. PFA tubing equipped with an inlet PFA filter holder that houses a 5 micron Teflon membrane filter. The membrane inlet filters were replaced every two months for the initial study period until July 2022 after which the filters are replaced every month. The manufacturer's calibration settings are applied. Calibration checks are conducted every 49 hours by introducing a breathing air grade ambient air gas mixture from a compressed tank (626.69 ppm CO_2). The CO_2 mole fraction of this test atmosphere has been cross-referenced against the NOAA Global Atmospheric Monitoring Laboratory (GML) CO_2 scale and is estimated to have an accuracy error of <3 ppm. After ~3 months of use the test atmosphere is again cross-referenced to the NOAA GML scale to account for potential drift. Every 6 months, a calibration check and 5-level linearity check are performed by dynamic dilution of a 4.90% CO_2 primary EPA-grade standard (EPA protocol grade gas, Praxair, production date 06/09/2022) with zero air using a Thermo Scientific 146i Multi-gas Calibrator. Zero air is supplied from a compressed UHP grade zero-air cylinder (General Air).

Methane (CH_4)

Methane is monitored with a Picarro G2401 cavity ring down spectrometer. Ambient air is sampled at 400 scc/min from an inlet at 8.5 m height. The sampling line consists of 10 m length, ¼ inch o.d., 5/32 inch i.d. PFA tubing equipped with an inlet PFA filter holder that houses a 5 micron Teflon membrane filter. The membrane inlet filters were replaced every two months for the initial study period until July 2022 after which the filters are replaced every month. The manufacturer's calibration settings are applied. Calibration checks are done every 49 hours by introducing a breathing air grade compressed gas from a tank (2480.7 ppb CH_4). The methane mole fraction of this test atmosphere has been cross-referenced to the NOAA GML methane scale before use and is estimated to have an accuracy error of <2 ppb. After ~3 months of use the test atmosphere is again cross-referenced to the NOAA GML scale to account for potential drift. Every 6 months, a calibration check is performed with an 1852.18 ppb CH_4 primary EPA-grade standard from NOAA (certification date 04/2015). Additionally, a calibration check and 5-level linearity check are performed by dynamic dilution of a 497 ppm CH_4 primary EPA-grade standard (EPA protocol grade gas, Praxair, production date 06/09/2022) with zero air using a Thermo Scientific 146i Multi-gas Calibrator. Zero air is supplied from a compressed UHP grade zero-air cylinder (General Air).

Nitrogen Oxides (NO_x)

NO and NO_2 are monitored with a Teledyne Model API T200UP chemiluminescence analyzer. This analyzer uses a photolytic converter for the NO_2 determination. The sampling line consists of 10 m length, ¼ inch o.d., 5/32 inch i.d. PFA tubing equipped with an inlet PFA filter holder that houses a 5 micron Teflon membrane filter. The sampling inlet is mounted on a meteorological tower at 8.5 m height. The membrane inlet filters were replaced every two months for the initial study period until July 2022 after which the filters are replaced every month. The monitoring and calibration protocol follow the federal regulatory monitoring requirements according to the specifications of '40 Code of Federal Regulations (CFR) Part 58'. Calibrations are performed using dynamic dilution and titration of a 10.03 parts per million (ppm) NO primary EPA-grade standard (EPA protocol grade gas, Praxair,

production date 01/12/2022, EY0002528) with a Thermo Scientific 146i Multi-gas Calibrator equipped with a Gas Phase Titration system (GPT). The output of the calibrator is introduced through the span port of the instrument. Zero air is generated from a Parker zero-air generator (HPZA-7000) followed by Sofnofil and Charcoal scrubbers. Quarterly, full calibrations of the NO_x analyzer are performed using the output of the calibrator to introduce span gas to the span port of the instrument and zero air through the zero air port of the analyzer (occurring 04/04/2022, 06/07/2022, 08/30/2022, 11/02/2022, 02/03/2023, 07/05/2023). For these calibrations, a zero adjustment is made first, followed by NO and NO_x span adjustments using 180 ppb NO. The conversion efficiency adjustment is done next, at 2 different levels using the GPT: 150 ppb NO_2 (for 180 NO_x, 17.5% O_3) and 20 ppb NO_2 (for 40 ppb NO_x, 10% O_3). A linearity check for NO_2 is then performed using 9 levels of NO_2 (0, 20, 40, 80, 120, 160, 180, 320, 500 ppb). Two audits were performed by CDPHE on 8 June 2022 and 24 April 2023. For both audits the instrument passed all audit criteria for flow rates, NO/NOx, and gas-phase titration NO conversion efficiency, and met EPA measurement quality requirements. The detailed reports are available upon request. The lower detection limit reported by the manufacturer for NO, NO_2, and NO_x is 0.05 ppb. Measurements below this value are replaced with ½ of the LDL, 0.025 ppb.

Particulate Matter

A GRIMM EDM180 monitor is used for the particulates monitoring. This analyzer measures particles in the 0.25 – 32 µm (micrometer) size range by a laser scattering technique. Air is sampled from an inlet stack protruding approximately 1 m above the instrument shelter roof at ~1.2 L/min. The instrument has EPA certification, and the protocol follows requirements for regulatory PM monitoring. Two size ranges are reported: PM10 (coarse particles) for all particle mass smaller than 10 µm, and PM2.5 (fine particles) for all particle mass smaller than 2.5 µm. Weekly flow rate checks (volumetric flow meter) and zero tests using a 0.05 micron particle filter are performed by an operator at the sample inlet. Every 6 months, a field test is performed by an operator to check the instrument performance. For these tests, a GRIMM Field Test Kit 185 creates an aerosol by atomizing a diluted polystyrene latex standard suspension (1 micron and 2.5 micron, Durag, Inc) which is introduced directly into the instrument inlet. The 6-month maintenance also includes: leak check, cleaning of sample inlet pipe, cleaning of sample air duct inside the optical chamber, flow rate audit with mass flow meter, ambient pressure verification with independent manometer, and internal filters replaced as needed. The PM10 upper detection limit of the instrument is 6500 µg/m³. The lower detection limit for PM10 and PM2.5 is 0.1 µg/m³ as reported by the manufacturer.

Radiation (alpha)

Radioactivity (alpha decay from radon gas and radon progeny on particulates) is monitored with two instruments at a height of 2 m above ground level. A Bertin Instruments AlphaGUARD DF2000 instrument is used for the measurement of the alpha radiation emitted from radon gas (Radon 222 and Radon 220) via a sample line of ¼ inch i.d. PFA tubing at a sample rate of ~2 L/min. A second instrument, the AlphaPM radon progeny monitor, measures alpha radiation emitted from radon progenies attached to particulate matter. The AlphaPM is in an airtight, temperature-controlled metal enclosure inside the instrument shelter and receives sample air through a 2-inch diameter (2 NPT) 12-inch long aluminum inlet pipe that protrudes through the shelter wall. The inlet pipe is heated to 30

degrees C to maintain above freezing air temperatures reaching the instrument. Air is circulated through the enclosure at approximately 5 to 6 L/min pulled with a small diaphragm pump, and the AlphaPM draws in sample air with its internal pump at a rate of 1.2 L/min. The AlphaPM filter is replaced approximately every 2 weeks. Both instruments have a synchronized 10-minute measurement cycle. Manufacturer calibration settings are used. The manufacturer recommends the instruments to be returned to the factory for a calibration check after five years of operation. The lower detection limit reported by the manufacturer for both instruments for alpha radiation from radon gas and radon progeny on particulates is 2 Bq/m^3 (0.054 pCi/L). Measurements below this value are reported as ½ of the LDL, 1 Bq/m^3 (0.027 pCi/L).

Volatile Organic Compounds

Volatile Organic Compounds (VOCs) are monitored with a preconcentration unit interfaced to a gas chromatograph (GC) using a flame ionization detector (FID) and a mass spectrometer (MS) detector. Sample air is pulled from an inlet at 8.5 m above the surface at a purge rate of 1.5 L/min. The sampling line consists of 10 m length, ¼ inch o.d., 5/32 inch i.d. PFA tubing equipped with an inlet PFA filter holder that houses a 5 micron Teflon membrane filter. The sampling line is inside a conduit that is heated to 40 ^oC. The membrane inlet filters were replaced every two months for the initial study period until July 2022 after which the filters are replaced every month. Hourly, VOCs are extracted over a 10-minute time window at 40 cc/min by pre-concentration with a Markes International UNITY-CIA Advantage-xr thermal desorption instrument. Sample air is dried by flowing through a section of quartz tubing (Markes U-T1KORI) cooled to a temperature of -30 ^oC (Markes International Kori-xr) before collection on a sorbent media focusing trap (Markes U-T3ATX-2S). VOCs are then transferred by rapid heating to a GC system for analysis. The GC (Agilent 8860 GC with Agilent 5977B mass spectrometry detector) is equipped with a primary 60m DB-624 column, after which a column switch facilitates directing lighter VOCs (ethane through iso-butane) to a 30 m alumina PLOT column, while heavier VOCs are directed to a second 30 m DB-624 column. VOCs are quantified by FID and mass spectrometry. With the FID, compound identification and quantification are accomplished using PeakSimple software (SRI Instruments, version 4.89). Within PeakSimple, specifically programmed peak integration is done automatically following each run. The tabulated peak area results are processed by automated scripts using monthly updated calibration carbon response factors (CRF) and effective carbon numbers (ECN) to calculate mixing ratios, which are reported in real time on the program website.

Approximately fifteen VOCs are traced and quantified routinely. A subset of selected VOC tracers (ethane, propane, ethene, propene, i-butane, n-butane, i-pentane, n-pentane, cyclopentane, n-hexane, n-octane, benzene, toluene, ethyl-benzene, *m&p*-, *o*-xylene) are plotted on the web portal. Data represent the 10-minute mean VOC mole fractions over the 10-minute sample collection period, with the sample timestamp at the middle of the sampling interval.

The calibration scale is tied to the World Meteorological Organization (WMO) Global Atmospheric Watch (GAW) VOCs scale, using a certified multicomponent 2-ppb primary calibration standard (Table 3) acquired from the U.K. National Physics Laboratory (calibration date 2/11/2020) – the central calibration laboratory for VOCs recommended by WMO-GAW program. The calibration standard is run weekly by an operator. Calibration carbon response factors (CRF) are updated monthly using the averaged result of the standard samples run the prior month, and are applied to the previous

month's data record retroactively. Realtime data use the CRF values continuing from the prior month. In addition, a 200-ppb NPL standard and a high mole fraction VOC standard dilution curve are run annually to check for the linearity of the instrument response at high levels. The high mole fraction standard (635.4 ppb ethane, 640.6 ppb propane, 532.1 ppb i-butane, 532.1 n-butane, 320.8 ppb i-pentane, 320.8 ppb n-pentane) was diluted to various mixing ratios to create an instrument response curve (ratio of the measured/expected mole fraction vs. measured mole fraction). A zero air (blank) sample is run after each set of 45 ambient samples (approximately every two days). Zero air is generated from a Parker zero-air generator (HPZA-7000) followed by Sofnofil and Charcoal scrubbers.

Table 3: National Physics Laboratory VOC calibration standard composition

Database component name	mole fraction (ppbv)	Uncertainty (ppbv)	Name on certificate
ethane	2.06	0.07	
ethene	2.01	0.07	
propane	2.03	0.07	
propene	2.02	0.05	
i-butane	2.07	0.06	2-methylpropane
acetylene	2.14	0.11	ethyne
n-butane	2.05	0.05	
trans-2-butene	2.05	0.05	trans-but-2-ene
1-butene	2.04	0.05	but-1-ene
cis-2-butene	2.05	0.05	cis-but-2-ene
i-pentane	2.02	0.05	2-methylbutane
n-pentane	2.03	0.05	
1_3-butadiene	2.07	0.05	1,3-butadiene
trans-pent-2-ene	2.04	0.05	
pent-1-ene	2.07	0.05	
2-methylpentane	2.13	0.05	
n-hexane	2.13	0.05	
isoprene	2.12	0.05	
n-heptane	2.13	0.05	
benzene	2.02	0.07	
2_2_4_trimethylpentane	2.00	0.05	2,2,4-trimethylpentane
n-octane	2.01	0.05	
toluene	1.96	0.05	
ethyl-benzene	2.12	0.06	
m&p-xylene	4.12	0.11	m-xylene+p-xylene
o-xylene	2.03	0.06	
1_3_5_trimethylbenzene	1.98	0.05	1,3,5-trimethylbenzene
1_2_4_trimethylbenzene	2.02	0.05	1,2,4-trimethylbenzene
1_2_3_trimethylbenzene	2.08	0.05	1,2,3-trimethylbenzene

Two xylene isomers, meta-xylene and para-xylene, elute very closely together in the chromatogram and often cannot be separated as individual peaks. The results for these two isomers are therefore reported at the sum of both.

All VOC data are reported in nanomoles per mole by volume (nmol mol^{-1}, i.e. 10^{-9}). The more commonly used unit ppb (parts-per-billion by volume) is used as a surrogate.

VOC lower detection limits (LDL) were calculated from the smallest, reliably identifiable FID peak area and the compound CRFs calculated monthly from the weekly standard runs. Since the calculation of LDL varies with the instrument response calibrated monthly, the lowest values seen in the data will also vary monthly. Representative lower detection limits from March 2023 are provided in Table 4. VOC species with no detected or quantifiable peak in the GC chromatograms are recorded as ½ of the lower detection limit (which similarly vary monthly).

Table 4: VOCs lower detection limits.

VOC	LDL Value (ppb)
ethane	0.031
ethene	0.039
propane	0.020
propene	0.021
i-butane	0.016
n-butane	0.016
acetylene	0.113
i-pentane	0.013
n-pentane	0.013
1,3-butadiene	0.018
n-hexane	0.011
isoprene	0.014
n-heptane	0.010
benzene	0.011
2,2,4-trimethylpentane	0.008
n-octane	0.009
toluene	0.010
ethyl-benzene	0.009
m&p-xylene	0.009
o-xylene	0.009
1,3,5-trimethylbenzene	0.008

VOC data corrections:

Zero-air blank subtractions

Blank peak area subtractions are determined using the mean peak area results of zero air samples during a particular time window if a detectable peak is present for a given compound. Most often this is delineated on a monthly basis, or following significant system work (e.g. installation of a new absorbent trap). Most VOCs show blank values below the limit of detection, or well below the response seen in ambient levels, and are therefore deemed negligible**.**

Compound	Start date (UTC)	End date (UTC)	Peak area subtraction	Approximate mixing ratio of subtraction (ppb)
propane	08/18/22 0:00	12/01/22 0:00	-0.24	0.034
propane	12/01/22 0:00	12/15/22 0:00	-0.19	0.028
propane	12/15/22 0:00	02/28/23 0:00	-0.15	0.022
benzene	12/01/21 0:00	5/11/22 18:00	-0.86	0.078
benzene	05/11/22 18:00	08/18/22 0:00	-1.14	0.103
benzene	08/18/22 0:00	09/15/22 0:00	-1.01	0.091
benzene	09/15/22 0:00	12/01/22 0:00	-0.33	0.029
benzene	12/01/22 0:00	01/15/23 0:00	-1.21	0.110
benzene	01/15/23 0:00		-0.36	0.033

High mole fraction correction

A high mole fraction standard was run to test the VOC system for linearity at high levels. A high mole fraction standard (635.4 ppb ethane, 640.6 ppb propane, 532.1 ppb i-butane, 532.1 n-butane, 320.8 ppb i-pentane, 320.8 ppb n-pentane) was diluted to various mixing ratios to create an instrument response curve (ratio of the measured/expected mole fraction vs. measured mole fraction). Based on measured ambient measurements collected over the study period, non-linear response correction was only applicable to propane measurements. A 2nd order polynomial was fit to the curve. Measurements were corrected to an upper bound of 1500 ppb.

If the measured propane value was above 208 ppb, we applied the following correction:

$$x \cdot \frac{1}{ax^2 + bx + c} = x_c$$

Where:

x : Measured mole fraction of propane at CCF in parts per billion (ppb)

x_c: Corrected mole fraction of propane at CCF in parts per billion (ppb)

a : 9.88531231e-06

b : 3.70470000e-03

c : 6.38470028e-01

Dimethyl sulfide (DMS)

DMS was sampled, analyzed, and quantified alongside the VOCs by preconcentration and GC-FID. Peak identification was based on GC retention index and confirmed by mass spectrometry. DMS was quantified by FID, using the same carbon response factor (CRF) and effective carbon number (ECN) as ethane, a technique reported in the literature[1, 2] for the quantification of organosulfur compounds by FID[1, 2]. The lower detection limit of DMS was 0.031 ppb.

[1] Perraud, V., Meinardi, S., Blake, D. R., and Finlayson-Pitts, B. J.: Challenges associated with the sampling and analysis of organosulfur compounds in air using real-time PTR-ToF-MS and offline GC-FID, Atmos. Meas. Tech., 9, 1325–1340, https://doi.org/10.5194/amt-9-1325-2016, 2016.

[2] Simpson, I.J., Colman, J.J., Swanson, A.L. *et al.* Aircraft Measurements of Dimethyl Sulfide (DMS) Using a Whole Air Sampling Technique. *Journal of Atmospheric Chemistry* **39**, 191–213 (2001). https://doi.org/10.1023/A:1010608529779

Hydrogen Cyanide (HCN)

HCN was quantified using the VOC GC/MS system using selected ion monitoring (SIM) mode. HCN mole fractions were determined in reference to trichlorotrifluoroethane (CFC-113). This chlorofluorocarbon (CFC) is a stable gas in the atmosphere that shows very low variability in its ambient mole fraction, and therefore, its monitoring results can be used as a reference standard for tracing the MS detector response. Monthly measurements of CFC-113 at Niwot Ridge, CO[1] vary by less than 1%. For each sample, the peak areas of HCN (mass-to-charge ratio 27.0 m/z) and CFC-113 (101.0 m/z) were quantified. HCN was determined as the ratio of the HCN peak area divided by the CFC-113 peak area, multiplied by a calibration factor. Calibrations were performed monthly by dynamic dilution of a 102.6 ppb certified gas standard (± 5% analytical accuracy) (Apel Riemer Environmental, Inc., production date 04/03/2022). Calibration factors (slope and offset) were determined by a linear curve fit to the multipoint dynamic dilutions of the HCN gas standard. The resulting mole fraction of HCN used in dynamic dilution calibrations ranged between 1.5 ppb to 12.0 ppb.

$$\mathrm{HCN}_{ppb} = a * \frac{\mathrm{HCN}_{PA}}{\mathrm{CFC\text{-}113}_{PA}} + b$$

Two calibration factors were applied to HCN data. The detection limit (DL) of HCN was determined from the smallest, reliably identifiable, MS peak areas of HCN and CFC-113. The calibration factors and detection limits applied to the data are listed in the below table.

Start (UTC)	End (UTC)	Slope (a)	Offset (b)	DL (ppb)
2022-11-01 23:00:00	2023-02-22 21:00:00	4.79	1.09	1.20
2023-02-22 23:00:00	2023-08-10 00:00:00	1.88	0.49	0.55

[1] NOAA Global Monitoring Laboratory, Niwot Ridge, CO site C-1 (40.04 N, 105.54 W, elevation: 3018 m). https://gml.noaa.gov/dv/data/index.php?category=Halocompounds&parameter_name=CFC-113&site=NWR