Metadata for Atmospheric Measurements at the Longmont Union Reservoir (LUR) Monitoring station

Boulder A.I.R.
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Site location

40.1762 N, 105.0477 W, 1514 m asl (4966 ft asl)

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

Wind Speed / Wind Direction

Wind conditions are recorded with an RM Young Wind Monitor AQ, 05305-PT, mounted on the meteorological tower at 9.2 m height. 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. An audit has been performed by the Colorado Department of Public Health and Environment (CDPHE) on the RM Young Wind Monitor on 7 February 2022. 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 <2 degrees composite error for all wind directions. The lower detection limit (LDL) for the RM Young wind speed is 0.4 m/s. Undetected wind is reported as half of the LDL, 0.2 m/s, and in these instances the wind direction is reported as NaN. The ½LDL correction is applied to the original 1-minute data, not to any further averaged data (e.g. 5-minute or hourly).

Temperature, Relative Humidity

Temperature and relative humidity are measured with a Campbell Scientific CS215-L50-PT probe housed inside a RM Young 6-Plate Solar Radiation Shield mounted on the meteorological tower at 9.1 m height above the surface using the factory calibration. An audit was 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. The instrument passed in all audit criteria with temperature reading accuracy having an error of 0.7 degrees C (passing is <2 degrees C), and relative humidity having a 1.3% error (passing is <5%). The manufacturer stated resolution of the CS215-L temperature measurement is 0.01 ^{o}C, with a lower limit of -40 ^{o}C. The stated relative humidity resolution is 0.03%.

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 is cleaned every 2 months.

Ozone (O_3)

Ozone is recorded with a Thermo Fisher Scientific model 49C UV absorption monitor. Ambient air is sampled from an inlet mounted at 8.6 m height above ground. 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. Inlet filters are replaced every two months. 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 U.S. EPA '40 Code of Federal Regulations (CFR) Part 58'.

The calibration scale is referenced against an EPA Region 8 primary ozone reference standard using a Thermo Fisher Scientific 49C calibrator unit level 2 standard. The level 2 standard was last referenced against an EPA Region 8 primary ozone reference standard on 4 May 2022 and 21 Feb 2024. Daily zero and span checks are performed automatically using a Thermo Fisher Scientific 49C calibrator unit located at LUR. 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. Also quarterly an inlet check is performed by feeding the calibrator output through the inlet filter on the tower and the entire inlet line to the instrument, and then running a standard calibration check. Yearly, a calibration check is performed using a level 2 standard (a Thermo Fisher Scientific 49C calibrator unit) following the same protocol as for the quarterly checks. From calibration check performance, the following correction has been applied to the data:

Start	End	Slope	Intercept
06/11/2022 22:47 UTC	10/13/2022 19:40 UTC	1.026	-0.4

An audit of the 49C was performed by the Colorado Department of Public Health and Environment (CDPHE) on 8 October 2021. The instrument passed all audit criteria with a calibration agreement slope 0.972 and an offset of 0.25 ppb, 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. The ½LDL correction is applied to the original 1-minute data, not to any further averaged data (e.g. 5-minute or hourly). Uncertainty is calculated as the greater of 1.6 ppb or 3.9% for 1-minute data and was assessed within the range of 0 ppb to 400 ppb.

Carbon Dioxide (CO_2)

Carbon dioxide is monitored with a Picarro G2301 cavity ring down spectrometer. Ambient air is sampled at 400 scc/min from an inlet at 8.6 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. Membrane filters are replaced every two months. Sample air is dried immediately before the instrument sample port using Nafion tubing with counterpurge flow dried with Drierite to between 0.08% and 0.09% H_2O, a dewpoint of around -27 ^oC. The Nafion dryer was added 05/2024.

The manufacturer's calibration settings are applied. Calibration checks are conducted every 49 hours by introducing in sequence two NOAA certified calibration gases that are referenced against the NOAA Global Monitoring Laboratory CO_2 scale (600.51 ppm CO_2, 390.33 ppm CO_2). The standards were last reanalyzed by NOAA on 7 May 2024 (original certificate 25 June 2019). 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) that is diluted with zero air using a Thermo Fisher Scientific 146i Multi-gas Calibrator. Zero air is supplied from a compressed UHP grade zero-air cylinder (General Air). Uncertainty is calculated as the greater of 0.07% or 0.34ppm for 1-minute data and was assessed within the range of 390.33 ppm to 600.51 ppm. For values outside this range, the uncertainty may be higher.

Instrument Drift Corrections

A monthly percent error correction to account for instrument drift (the analyzer's deviation from the standard) was applied to all historical CO_2 data in October 2024. This correction is calculated and applied biannually thereafter to maintain accuracy and minimize deviations.

Methane (CH_4)

Methane is monitored with a Picarro G2301 cavity ring down spectrometer. Ambient air is sampled at 400 scc/min from an inlet at 8.6 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. Membrane filters are replaced every two months. Sample air is dried immediately before the instrument sample port using Nafion tubing with counterpurge flow dried with Drierite to between 0.08% and 0.09% H_2O, a dewpoint of around -27 ^oC.

The manufacturer's calibration settings are applied. Calibration checks are conducted every 49 hours by introducing in sequence two NOAA certified calibration gases that are referenced against the NOAA Global Monitoring Laboratory CH_4 scale (3072.8 ppb CH_4, 1827.3 ppb CH_4). The standards were last reanalyzed by NOAA on 7 May 2024 (original certificate 25 June 2019). Every 6 months, a calibration check is performed with an 1852.18 ppb CH_4 primary 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 Fisher Scientific 146i Multi-gas Calibrator. Zero air is supplied from a compressed UHP grade zero-air cylinder (General Air). Uncertainty is calculated as the greater of 4.96 ppb or 0.20% for 1-minute data and was assessed within the range of 1827.3 ppb to 3072.8 ppb. For values outside this range, the uncertainty may be higher.

Instrument Drift Corrections

A monthly percent error correction to account for instrument drift (the analyzer's deviation from the standard) was applied to all historical methane data in October 2024. This correction is calculated and applied biannually thereafter to maintain accuracy and minimize deviations.

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 a PFA filter holder that houses a 5 micron Teflon membrane filter. Membrane filters are replaced every two months. The sampling inlet is mounted on the meteorological tower at 8.6 m height. The monitoring and calibration protocol follow the U.S. 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 10.15 parts per million (ppm) NO primary EPA-grade standard (EPA protocol grade gas, Praxair, production date 09/25/2019) with a Thermo Fisher 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 by running compressed air through 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. For these calibrations, a zero adjustment is made first, followed by NO and NO_x span adjustments using 180 ppb NO. Then, a 6-level linearity check is performed (0 ppb NO, 20 ppb NO, 40 ppb NO, 80 ppb NO, 120 ppb NO, 180 ppb NO). The conversion efficiency adjustment is done next, at 2 different levels using the GPT: 150 ppb NO_2 (for 180 NOx) and 20 ppb NO_2 (for 40 ppb NOx). A linearity check for NO_2 is then performed using 6 levels of NO_2 (20 ppb, 40 ppb, 80 ppb, 120 ppb, 160 ppb, 320 ppb). Weekly, calibration checks are performed for zero, a single span value of 160 ppb NO, and a single NO_2 mid-point value using the same calibrator connected to the span port of the analyzer, with the zero air sourced via the calibrator into the span port of the analyzer. An audit was performed by CDPHE on 8 October 2021. 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 report is 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. The ½LDL correction is applied to the original 1-minute data, not to any further averaged data (e.g. 5-minute or hourly). Uncertainty for all NOx measurements is calculated as the greater of 0.5 ppb or 5.5% for 1-minute data and was assessed within the range of 0 ppb to 500 ppb.

Particulate Matter

A GRIMM EDM180 monitor is used for measuring particulate matter (PM). 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 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, an aerosol test mixture is generated with a GRIMM Field Test Kit 185 by atomizing a diluted polystyrene latex standard suspension (1 micron and 2.5 micron, NIST traceable, Durag, Inc). The test mixture 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 lower detection limit for PM10 and PM2.5 is 0.1 µg/m³ as reported by the manufacturer. Measurements below this value are replaced with ½ of the LDL, 0.05 µg/m³. The ½LDL correction is applied to the original 1-minute data, not to any further averaged data (e.g. 5-minute or hourly). Uncertainty is calculated as 17% for PM10 and 15.5% for 1-minute data.

Volatile Organic Compounds

Volatile Organic Compounds (VOCs) are monitored with a custom-made preconcentration system interfaced to an Agilent 6890 gas chromatograph (GC) using a flame ionization detector (FID) detector. Sample air is pulled from an inlet at 8.6 m above the surface on the meteorological tower at a purge rate of 1.5 L/min. The sampling line consists of 12 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 which is replaced every two months. The sampling line is inside a conduit heated to 40^{o}C. Hourly, VOCs are extracted over a 10-minute time window at 40 cc/min. To preconcentrate VOCs, sample air is directed through a Peltier-cooled water freezeout trap that is held at -45^{o}C. The dried air then flows through an ozone scrubber that contains sodium-thiosulfate-impregnated glass wool, replaced annually. VOCs are then extracted from the downstream air flow on a micro-adsorbent trap (Carboxen 1000 and Carboxen 1016) held at -40^{o}C. VOCs are transferred by rapid heating of the micro-adsorbent trap to 290^{o}C and purged onto an alumina PLOT GC column (Al_2O_3/KCl PLOT, 50 m, 0.53 mm i.d., 15 um film thickness). After temperature-programmed separation, compound identification and quantification are accomplished with the FID using PeakSimple software (SRI Instruments, version 4.53). 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 twenty VOCs are traced and quantified routinely. A subset of selected VOC tracers are plotted on the web portal (https://www.bouldair.com/longmont.htm).

Beginning in April 2024 the list of quantified VOCs was expanded from 19 to 33 compounds:

ethane
ethene
propane
cyclopropane
propene
i-butane
n-butane
acetylene
trans-2-butene
1-butene
i-butene
cis-2-butene
cyclopentane

i-pentane
n-pentane
1,3-butadiene
trans-2-pentene
1-pentene
cyclohexane
2-methylpentane
3-methylpentane
n-hexane
isoprene
C7H16_alkane_isomers*
n-heptane
benzene
2,2,4-trimethylpentane
C8H18_alkane_isomers*
n-octane
toluene
ethyl-benzene
m&p-xylene
o-xylene

*C7H16_alkane_isomers includes:
2,2-dimethylpentane
2,4-dimethylpentane
methylcyclohexane
2,2,3-trimethylbutane
3,3-dimethylpentane
ethylcyclopentane
2,3-dimethylpentane
3-ethylpentane
3-methylhexane
2-methylhexane

*C8H18_alkane_isomers includes:
4-methylheptane
n-propylcyclopentane
2-methylheptane
3-methylheptane

Data represent the 10-minute mean VOC mole fractions over the 10-minute sample collection period, with the recorded time stamp at the middle of that sampling period.

The calibration scale is tied to the World Meteorological Organization (WMO) Global Atmospheric Watch (GAW) VOCs scale, using a certified multicomponent 10-ppb primary standard (Table 1)

acquired from the U.K. National Physics Laboratory (NPL, cylinder number D723236, calibration date 2 March 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 NPL 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. Compounds not in the NPL standard use the average CRF value of the respective carbon number alkanes or alkenes (e.g. i-butene's CRF is the average CRF of trans-2-butene, 1-butene, and cis-2-butene).

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) is 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 and a lab-calibrated multi-component working standard are run every 65 runs (~every three days). Zero-air is generated with a custom-built catalytic system using platinum on alumina pellets heated to 380C.

Table 1: National Physics Laboratory VOC calibration standard composition.

Database component name	mole fraction (ppbv)	Uncertainty (ppbv)	Name on certificate
ethane	9.88	0.20	
ethene	9.70	0.20	
propane	9.76	0.20	
propene	9.70	0.20	
i-butane	9.94	0.25	2-methylpropane
acetylene	10.20	0.50	ethyne
n-butane	9.86	0.20	
trans-2-butene	9.89	0.20	trans-but-2-ene
1-butene	9.84	0.20	but-1-ene
cis-2-butene	9.86	0.20	cis-but-2-ene
i-pentane	9.73	0.20	2-methylbutane
n-pentane	9.77	0.20	
1_3-butadiene	9.97	0.20	1,3-butadiene
trans-pent-2-ene	9.82	0.20	
pent-1-ene	9.98	0.20	
2-methylpentane	10.25	0.21	
n-hexane	10.25	0.21	
isoprene	10.21	0.21	
n-heptane	10.27	0.21	
benzene	9.71	0.20	
2_2_4_trimethylpentane	9.64	0.20	2,2,4-trimethylpentane
n-octane	9.67	0.20	
toluene	9.44	0.24	

ethyl-benzene	10.21	0.26	
m&p-xylene	19.90	0.50	m-xylene+p-xylene
o-xylene	9.77	0.25	
1_3_5_trimethylbenzene	9.55	0.24	1,3,5-trimethylbenzene
1_2_4_trimethylbenzene	9.71	0.25	1,2,4-trimethylbenzene
1_2_3_trimethylbenzene	10.03	0.31	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 isomers are therefore reported at the sum of both.

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 2. 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 2: VOCs lower detection limits.

VOC	**LDL Value (ppb)**
ethane	0.025
ethene	0.024
propane	0.017
propene	0.017
i-butane	0.013
n-butane	0.013
acetylene	0.035
i-pentane	0.010
n-pentane	0.010
1,3-butadiene	0.013
n-hexane	0.009
isoprene	0.010
n-heptane	0.008
benzene	0.009
2,2,4-trimethylpentane	0.007
n-octane	0.007
toluene	0.007

ethyl-benzene	0.007
m&p-xylene	0.007
o-xylene	0.008
1,3,5-trimethylbenzene	0.009

VOC data corrections:

Zero-air blank subtractions

Blanks are assessed from the periodic collection of the VOC-scrubbed zero air. Blank peak area subtractions are determined using the mean peak area of zero air runs during a particular time window that 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**.** Blank peak area value subtraction for benzene and toluene occur as follows. These peak area subtractions have been applied and are accounted for in the data set.

Compound	Start date (UTC)	End date (UTC)	Peak area subtraction	Approximate mixing ratio of subtraction (ppb)
benzene	08/12/2022 0:00	09/01/2022 0:00	-0.2	0.012
toluene	08/12/2022 0:00	09/01/2022 0:00	-0.7	0.035
toluene	09/01/2022 0:00	10/01/2022 0:00	-0.5	0.025
toluene	10/01/2022 0:00		-0.45	0.022

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, a non-linear response correction was applicable to high ethane and propane measurements. A 2nd order polynomial was fit to the curve for both species.

Ethane:
Measurements were corrected to an upper bound of 780 ppb.
If the measured ethane value was above 459.8 ppb, we applied the following correction:

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

x : Measured mole fraction of ethane at LUR in parts per billion (ppb)

x_c : Corrected mole fraction of ethane at LUR in parts per billion (ppb)

a : -1.84950786e-06

b : 1.18248558e-03

c : 8.47291287e-01

Propane:
Measurements were corrected to an upper bound of 765 ppb.
If the measured propane value was above 192.99 ppb, we applied the following correction:

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

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

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

a : -2.24862830e-06

b : 4.37527020e-04

c : 9.99310912e-01