# Metadata for Atmospheric Measurements at the Boulder Reservoir (BRZ) Monitoring station

Boulder A.I.R.
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**Site location**

40.0700 N, 105.2202 W, 1586 m asl (5204 ft asl)

The station facility is a climate-controlled, insulated instrument shelter maintained by the Colorado Department of Public Health and Environment (CDPHE), approximately 10 ft long x 8 ft wide x 9 ft tall. Attached to the building is a 15 ft aluminum post 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 a cross arm of the aluminum post at 5.2 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 29 October 2021. 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 <3.2 degrees composite error for all wind directions (<5 degrees is passing). 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, or 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 MetSENS500 mounted on a cross arm of the aluminum post at 5.2 m height above the surface using the factory calibration. The manufacturer stated resolution of the temperature measurement is 0.1 degree Celsius with ±0.3 degree C accuracy. The stated relative humidity resolution is 0.1% with ±2% accuracy.

**Methane ($CH_4$)**

Methane is monitored by gas chromatography with flame ionization detection. Ambient air is pulled continuously from an inlet mounted at 4.7 m height above the ground at a purge rate of 1.6 L/min. The sampling line is made of ¼ inch PFA-lined stainless steel, approximately 8 m length in total. The

line has a 5 micron Teflon membrane inlet filter that is changed every two months. A fraction of this sampling flow is directed to the methane analyzer. This instrument is a SRI Model 310 gas chromatograph. Air is flowed continuously through a 3 ml sampling loop. Every 10 min, the purge is halted, and after 5 seconds the air sample is injected onto a 1/8 inch o.d. - 2 m length packed column (Porapack Q, 80-100 mesh). Separation is by isothermal gas chromatography at 40$^{o}$C, and signals are recorded with a flame ionization detector (FID). The integrated peak area is used for quantification. Blanks are negligible, and there is no blank value consideration for quantification. The instrument response is considered linear.

Calibrations are conducted by injection of a secondary real air standard. A secondary calibration standard was run between each ambient sample until December 2018. Since January 2019, the secondary standard is run every other ambient sample. Secondary standards are quantified against primary standards that were obtained from the NOAA Global Monitoring Laboratory in Boulder, Colorado. The secondary calibration standards are compared to the primary standards approximately 5-6 times through the life of the cylinder. Samples are quantified using the sample response (peak area), divided by the response of the nearest standard run (always within 30 minutes), then multiplied by the known value of the working standard. Where a standard was unavailable, a moving average of earlier standard runs was substituted. A list of calibration standards used is provided in Table 1.

Table 1

List of $CH_4$ calibration standards

Primary standards:

| Cylinder # | ID | CH4 (ppbv) | Last Calibration at NOAA |
|---|---|---|---|
| DDF016 | BA#4 | 1898.73 | 1/20/2012 |
| FF30481 | AL#1 | 1852.18 | 4/1/2017 |
| CA01980 | DK#1 | 1838.5 | 12/13/2018 |
| CB11846 | DK#2 | 1925.5 | 12/13/2018 |
| CC7157 | DK#3 | 2050.6 | 12/13/2018 |
| CA06236 | NOAA STD3 | 3072.8 | 2019 |
| CA03334 | NOAA STD4 | 1827.3 | 2019 |

Secondary standards:

| Cylinder # | ID | CH4 (ppbv) | Period used on site |
|---|---|---|---|
| IMT28809 | BA#7 | 1873.7 | 03/2017-01/2018 |
| APZ865 | BA#6 | 1853.2 | 01/2018-01/16/2019 |
| IMT78033 | BA#8 | 1867.1 | 01/16/2019-04/27/2020 |
| | BA#5 | 1869.1 | 04/27/2020-02/19/2021 |
| CC738525 | OF#1 | 2627.8 | 02-19/2021-09/09/2021 |
| CC738523 | OF#2 | 2408.0 | 09/09/2021-04/28/2022 |
| CC738516 | OF#3 | 2369.2 | 04/28/2022-08/13/2022 |
| CC738518 | OF#4 | 2313.9 | 08/13/2022-present |

Secondary standard (compressed gas, breathing air (BA) quantifications:

BA#7 quantification:

| Date | Calc. ppb | uncert. | +/- ppb | Ref. Standard |
|---|---|---|---|---|
| 3/1/2017 | 1872.3 | 0.52% | 9.8 | BA#4 |
| 4/19/2017 | 1878.4 | 0.35% | 6.6 | BA#4 |
| 8/3/2017 | 1873.4 | 0.26% | 4.9 | AL#1 |
| 8/11/2017 | 1871.3 | 0.12% | 2.2 | AL#1 |
| 11/7/2017 | 1875.9 | 0.11% | 2.0 | AL#1 |
| 1/31/2018 | 1871.1 | 0.22% | 4.0 | AL#1 |
| AVG | 1873.7 | | | |
| STDEV | 2.6 | | | |
| RSD | 0.14% | | | |

BA#6 quantification:

| Date | Calc. ppb | uncert. | +/- ppb | Ref. Standard |
|---|---|---|---|---|
| 1/31/2018 | 1855.3 | 0.23% | 4.2 | AL#1 |
| 2/15/2018 | 1854.4 | 0.33% | 6.2 | AL#1 |
| 3/20/2018 | 1854.2 | 0.19% | 3.5 | AL#1 |
| 9/5/2018 | 1853.7 | 0.41% | 7.7 | AL#1 |
| 11/7/2018 | 1848.5 | 0.11% | 2.0 | AL#1 |
| AVG | 1853.2 | | | |
| STDEV | 2.4 | | | |
| RSD | 0.13% | | | |

BA#6 quantification on Picarro:
01/17/2019: 1853.4 ppbv
Ref standards (NOAA): DK#1, DK#2, DK#3

BA#8 quantification:

| Date | Calc. ppb | uncert. | +/- ppb | Ref. STD |
|---|---|---|---|---|
| 1/16/2019 | 1867.2 | 0.32% | 6.0 | AL#1 |
| 04/09/2019 | 1869.9 | 0.20% | 3.7 | AL#1 |
| 12/03/2019 | 1869.3 | 0.09% | 1.6 | AL#1 |
| 04/27/2020 | 1873.6 | 0.28% | 5.3 | AL#1 |
| AVG | 1870.0 | | | |
| STDEV | 2.4 | | | |
| RSD | 0.13% | | | |

BA#8 quantification on Picarro:
01/15/2019: 1867.9 ppbv
Ref standards (NOAA): DK#1, DK#2, DK#3

BA#5 quantification:

| Date | Calc. ppb | uncert. | +/- ppb | Ref. STD |
|---|---|---|---|---|
| 04/27/2020 | 1868.5 | 0.16% | 3.0 | AL#1 |
| 12/21/2020 | 1869.7 | 0.22% | 4.1 | AL#1 |
| AVG | 1869.1 | | | |
| STDEV | 0.6 | | | |
| RSD | 0.03% | | | |

OF#1 quantification:

| Date | Calc. ppb | uncert. | +/- ppb | Ref. STD |
|---|---|---|---|---|
| 02/19/2021 | 2625.0 | 0.36% | 9.6 | BA#5 |
| 04/23/2021 | 2630.6 | 0.38% | 10.0 | AL#1 |
| AVG | 2627.8 | | | |
| STDEV | 2.8 | | | |
| RSD | 0.11% | | | |

OF#1 quantification on BSE Picarro:
02/17/2021: 2627 ppbv

OF#2 quantification:

| Date | Calc. ppb | uncert. | +/- ppb | Ref. STD |
|---|---|---|---|---|
| 09/9/2021 | 2408.0 | 0.27% | 6.5 | AL#1 |

OF#2 quantification on BSE Picarro:
09/07/2021: 2410 ppbv

OF#3 quantification:

OF#3 quantification on LUR Picarro:
04/27/2022: 2369.2 ppbv

Ref standards: NOAA STD3, NOAA STD4

OF#4 quantification:

OF#4 quantification on LUR Picarro:
07/18/2022: 2313.9 ppbv

Ref standards: NOAA STD3, NOAA STD4

**Nitrogen Oxides ($NO_x$)**

NO and $NO_2$ are monitored with a Thermo Environmental Corp. 42TL analyzer with a molybdenum oxide (MoO) catalyst. From the beginning of the program to 12/3/2019 a Model 42C-TL was used. On that date it was then replaced by a brand new Thermo Environmental Corp. 42iQTL monitor.

Ambient air is pulled continuously from an inlet mounted at 4.7 m height above the ground at a rate of 1 L/min. The sampling line is made of ¼ inch OD, 5/32 inch ID PFA tubing, approximately 6 m length in total. The line has a 5 micron Teflon membrane inlet filter that is changed every two months. The Thermo Environmental Corp. 42TL instrument has two operational modes. First NO is measured via NO + $O_3$ chemiluminescence. In the second mode, $NO_2$ is measured by redirecting air through the MoO converter, which causes $NO_2$ – and other oxidized nitrogen compounds – to convert to NO. The measured NO signal in this mode constitutes the sum of NO and $NO_2$ (and potentially other oxidized nitrogen compounds). The $NO_2$ mixing ratio is then determined by subtracting from the signal the NO result measured in the first measurement mode.

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 5.07 parts per million (ppm) NO primary EPA-grade standard (EPA protocol grade gas, Scott Marrin, calibration date 06/2016) 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 and a single span value of 160 ppb NO 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 29 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 (LDL) reported by the manufacturer for NO, $NO_2$, and $NO_x$ is 0.05 ppb. Any readings below that threshold are replaced in the data record by ½ this LDL value, i.e. with 0.025 ppbv, both for NO and for $NO_x$. The ½LDL correction is applied to the original 1-minute data, not to any further averaged data (e.g. 5-minute or hourly).

**Volatile Organic Compounds**

Volatile Organic Compounds (VOCs) are monitored with a custom-made preconcentration system interfaced to an SRI Model 310 gas chromatograph (GC) using a flame ionization detector (FID) detector. Sample air is pulled continuously from an inlet at 4.7 m above the surface at a purge rate of 1.6 L/min. The sampling line consists of 8 m length, ¼ inch o.d. PFA-lined stainless steel tubing, equipped with an inlet PFA filter holder that houses a 5 micron Teflon membrane filter which is replaced every two months. A fraction of this sampling flow is directed to the VOCs analyzer. 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. Hydrogen carrier gas is provided by an SRI Model H2-100 hydrogen generator. The dried air then flows through an ozone scrubber, replaced annually (a ¼ inch x 10 cm stainless steel tubing filled with sodium thiosulfate impregnated glass wool). 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 4.54). 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. Data represent 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.

Approximately 20-30 VOCs are traced and quantified routinely.

Beginning in April 2024 the list of quantified VOCs was expanded from 18 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

The calibration scale is tied to the World Meteorological Organization (WMO) Global Atmospheric Watch (GAW) VOCs scale, using a certified multicomponent 4-ppb primary standard (Table 2) acquired from the U.K. National Physics Laboratory (NPL, calibration date 12/15/2015) – 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 multi-component working standard (~100 ppb levels, NOAA GMD, calibration date 10/12/2012, Table 3) are run every 90 runs (~every three to four days). Zero air is generated from a Parker zero-air generator followed by Sofnofil and Charcoal scrubbers.

Table 2: National Physics Laboratory VOC calibration standard composition.

| Database component name | mole fraction (ppbv) | Uncertainty (ppbv) | Name on certificate |
|---|---|---|---|
| ethane | 4.04 | 0.08 | |
| ethene | 3.89 | 0.08 | |
| propane | 4.07 | 0.08 | |
| propene | 4.00 | 0.08 | |
| i-butane | 4.18 | 0.11 | 2-methylpropane |
| acetylene | 4.11 | 0.21 | ethyne |
| n-butane | 3.96 | 0.08 | |
| trans-2-butene | 3.95 | 0.08 | trans-but-2-ene |
| 1-butene | 3.96 | 0.08 | but-1-ene |
| cis-2-butene | 4.01 | 0.08 | cis-but-2-ene |
| i-pentane | 4.03 | 0.08 | 2-methylbutane |
| n-pentane | 4.03 | 0.08 | |
| 1_3-butadiene | 3.95 | 0.08 | 1,3-butadiene |
| trans-pent-2-ene | 3.95 | 0.08 | |
| pent-1-ene | 3.96 | 0.08 | |
| 2-methylpentane | 4.04 | 0.08 | |
| n-hexane | 3.97 | 0.08 | |
| isoprene | 4.01 | 0.09 | |
| n-heptane | 4.00 | 0.08 | |
| benzene | 3.99 | 0.08 | |
| 2_2_4_trimethylpentane | 3.97 | 0.08 | 2,2,4-trimethylpentane |
| n-octane | 4.01 | 0.08 | octane |
| toluene | 3.98 | 0.10 | |
| ethyl-benzene | 3.98 | 0.10 | |
| m&p-xylene | 8.00 | 0.20 | m-xylene+p-xylene |
| o-xylene | 3.98 | 0.10 | |
| 1_3_5_trimethylbenzene | 3.99 | 0.10 | 1,3,5-trimethylbenzene |
| 1_2_4_trimethylbenzene | 4.01 | 0.11 | 1,2,4-trimethylbenzene |
| 1_2_3_trimethylbenzene | 4.02 | 0.11 | 1,2,3-trimethylbenzene |

Table 3: NOAA GMD working standard composition

| Component name | mole fraction (ppbv) | Uncertainty (ppbv) |
|---|---|---|

| | | |
|---|---|---|
| ethane | 143.56 | 0.1 |
| propane | 153.16 | 0.1 |
| i-butane | 26.67 | 0.02 |
| n-butane | 57.28 | 0.04 |
| i-pentane | 23.28 | 0.02 |
| n-pentane | 26.6 | 0.02 |
| hexane | 10.3 | 0.01 |
| benzene | 15.62 | 0.01 |
| toluene | 8.67 | 0.01 |

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 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 | 0.019 |
| ethene | 0.019 |
| propane | 0.012 |
| propene | 0.012 |
| i-butane | 0.009 |
| n-butane | 0.009 |
| acetylene | 0.025 |
| i-pentane | 0.007 |
| n-pentane | 0.007 |
| 1,3-butadiene | 0.010 |
| n-hexane | 0.006 |
| isoprene | 0.007 |
| n-heptane | 0.006 |
| benzene | 0.006 |

| | |
|---|---|
| 2,2,4-trimethylpentane | 0.006 |
| n-octane | 0.006 |
| Toluene | 0.005 |
| ethyl-benzene | 0.006 |
| m&p-xylene | 0.006 |
| o-xylene | 0.006 |
| 1,3,5-trimethylbenzene | 0.007 |

VOC data corrections:

*Zero-air blank subtractions*

Blanks are assessed from the periodic collection of the VOC-scrubbed zero air runs. 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 occurs 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 | 04/05/2017 0:00 | 06/01/2017 0:00 | -0.48 | 0.028 |
| | 01/01/2020 0:00 | 12/15/2022 0:00 | -0.17 | 0.009 |
| | 12/15/2022 0:00 | 01/15/2023 0:00 | -0.28 | 0.011 |
| | 01/15/2023 0:00 | | -0.35 | 0.013 |
| toluene | 04/05/2017 0:00 | 06/01/2017 0:00 | -1.0 – -0.35* | 0.065 – 0.022* |
| toluene | 01/01/2020 0:00 | 01/01/2021 0:00 | -0.10 | 0.004 |
| toluene | 12/15/2022 0:00 | | -0.14 | 0.005 |

*Toluene blank values had an obvious trend during the first two months of monitoring, starting with higher values (~ 1.0) that then gradually dropped with time (~0.35 towards the end). A quadratic curve was fit to the data from 4/5/2017 - 6/1/2017. The blank peak area correction was determined from a best matched (by time) value from the fitting curve. This blank correction was steadily declining during this period and corresponded to approximate mixing ratio corrections ranging from 0.065 – 0.022 ppb.