Supplementary Material for:

An Unusual Winter Ozone Event in Colorado

Andrew O. Langford[1], Raul J. Alvarez II[1], Kenneth C. Aikin[1,2], Sunil Baidar[1,2], W. Alan Brewer[1], Steven S. Brown[1], Matthew M. Coggon[1,2], Patrick D. Cullis[2,3], Jessica B. Gilman[1], Georgios I. Gkatzelis[1,2*], Detlev Helmig[4], Bryan J. Johnson[3], K. Emma Knowland[5,6], Rajesh Kumar[7], Aaron D. Lamplugh[1,2**], Audra McClure-Begley[2,3], Brandi J. McCarty[1,2], Ann M. Middlebrook[1], Gabriele Pfister[8], Jeff Peischl[1,2,3], Irina Petropavlovskikh[2,3], Pamela S. Rickly[1,2**], Andrew W. Rollins[1], Scott P. Sandberg[1], Christoph J. Senff[1,2], Carsten Warneke[1]

[1]NOAA Chemical Sciences Laboratory, Boulder, CO 80305, USA.

[2]Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO, 80309, USA.

[3]NOAA Global Monitoring Laboratory, Boulder, CO 80305, USA.

[4]Boulder Air LLC, Boulder, Colorado, 80301, USA.

[5]Morgan State University, GESTAR-II, Baltimore, MD, 21251, USA.

[6]NASA Goddard Space Flight Center, Global Modeling and Assimilation Office, Greenbelt, MD, USA.

[7]NSF NCAR Research Applications Laboratory, Boulder, CO, USA, 80307, USA.

[8]NSF NCAR Atmospheric Chemistry Observations and Modeling Laboratory, Boulder, CO, USA, 80307, USA.

*Now at Institute of Energy and Climate Research, IEK-8: Troposphere, Forschungszentrum Jülich GmbH, Jülich, Germany.

** Now at Air Pollution Control Division, Colorado Department of Public Health and Environment, Denver, CO, 80246, USA.

Correspondence to: Andrew O. Langford (andrew.o.langford@noaa.gov)

1 Surface Ozone Measurements

Our analysis is based in part on measurements (Table S1) made by the Air Pollution Control Division (APCD of the Colorado Department of Public Health and Environment (CDPHE)), which maintains a network of O_3 monitors to meet the requirements of the U.S. Clean Air Act and the U.S. Environmental Protection Agency (EPA). These regulatory monitors are subject to stringent standards with the monitor siting determined primarily by population distributions. These data are reported to the EPA Air Quality System (AQS) and are available to the public (https://www.epa.gov/aqs). The U.S. National Park Service (NPS) also maintains O_3 monitors at most of the National Parks (https://www.nps.gov/subjects/air/current-data.htm) including the Long's Peak monitor at Rocky Mountain National Park. These regulatory monitors also report to the EPA AQS.

The NOAA Global Monitoring Laboratory (GML) also makes routine non-regulatory measurements at a number of locations worldwide. These non-regulatory measurements are not reported to the AQS, but are available online (https://gml.noaa.gov/ozwv/). The NOAA Chemical Sciences Laboratory (CSL) also makes non-routine O_3 measurements to support various field campaigns as well as semi-regular measurements in Boulder to support the TOPAZ lidar operations (https://csl.noaa.gov/groups/csl3/measurements/2018boulder/2020.php).

Finally, Boulder A.I.R. maintains a small network of O_3 monitors under contract with local governments in the Denver-Boulder area. These measurements are available at: https://www.bouldair.com/.

Table S1: Regulatory and non-regulatory ozone monitors used in the study.

Name	Abbrev.	AQS	Lat.	Lon.	Elev. (m)	Agency
Ft Collins-West	FTCW	80690011	40.593	-105.141	1571	CDPHE
Ft Collins	FTC	80691004	40.577	-105.079	1525	CDPHE
Greeley	GRET	81230009	40.386	-104.737	1484	CDPHE
Rocky Mt NP (Long's Peak)	RMNP	80690007	40.278	-105.546	2748	NPS
Union Reservoir	LUR	N/A	40.176	-105.048	1514	A.I.R.
Longmont Airport	LMA	N/A	40.164	-105.163	1540	A.I.R.
Table Mountain	BOS	N/A	40.125	-105.237	1691	NOAA
Boulder Res.	BOUR	80130014	40.070	-105.220	1585	CDPHE
Niwot Ridge	NWR	N/A	40.036	-105.544	3026	NOAA
DSRC	DSRC	N/A	39.991	-105.264	1672	NOAA
Rocky Flats-North	RFN	80590006	39.913	-105.189	1803	CDPHE
Welby	WBY	80013001	39.838	-104.950	1556	CDPHE
Blackhawk	BHWK	80470003	39.793	-105.491	2635	CDPHE
La Casa	CASA	80310026	39.779	-105.005	1602	CDPHE
Camp	CAMP	80310002	39.751	-104.988	1593	CDPHE
National Renewable	NREL	80590011	39.743	-105.179	1833	CDPHE
Welch	WCH	80590005	39.639	-105.139	1744	CDPHE
Aurora East	AURE	80050006	39.639	-104.569	1795	CDPHE
Highland Reservoir	HLD	80050002	39.568	-104.957	1746	CDPHE
Chatfield State Park	CHAT	80350004	39.534	-105.070	1676	CDPHE

2 NOAA DSRC Measurements

The NOAA chemical Sciences Laboratory conducted a large suite of i*n-situ* measurements at the NOAA David Skaggs Research Center (DSRC) in Boulder, CO between 30 March and 31 August of 2020 to study changes in emissions within the Colorado Front Range urban area as a result of the COVID-19 lockdown. Ambient air was sampled either from the roof of the building or window ports. Additional details about these measurements can be found in Rickly et al. (2022).

NO and NO_2 and total NO_x were measured using a Thermo Scientific Model 42i NO-NO_2-NO_x Analyzer with a molybdenum converter and CO, N_2O, and H_2O were measured using a modified Los Gatos Research infrared laser off-axis integrated-cavity-output spectrometer (OA-ICOS). CO_2 and CH_4 were measured with a Picarro 1301-m cavity ringdown spectrometer. The VOC measurements were conducted by gas chromatography mass spectrometry (GC-MS) (Lerner et al., 2017) and proton transfer reaction time-of-flight mass spectrometry (PTR-ToF-MS) (Yuan et al., 2016). The GC-MS technique uses an integrated whole air sampler (iWAS) based on Stirling coolers to cryogenically trap and preconcentrate analytes for an interval of 20-minutes to attain a detection limit <1 ppt and 1σ uncertainty <10% with isomer separation for a wide suite of C2 to C10 organic compounds (Lerner et al., 2017). The PTR-ToF-MS measures a wide range of polar and unsaturated primary and secondary VOC species with a proton affinity greater than water using a chemical ionization mass spectrometer exploiting H_3O^+ reagent ions. The PTR-ToF-MS operates at 1 Hz with a detection limit of 10–100 parts-per-trillion by volume (pptv) depending on the species.

The number, volume, and surface area of the fine particulate mass was measured using an Ultra-High Sensitivity Aerosol Spectrometer (UHSAS) from Droplet Measurement Techniques (DMT) (Kupc et al., 2018). This optical counter is sensitive to particles with diameters between 0.08 and 0.7 µm.

Finally, surface O_3 was measured with a commercial UV absorption monitor (2B Technologies model 205) that continuously sampled air 5 m a.g.l. at the TOPAZ truck. The truck was also equipped with an automated weather station (Airmar 150WX) to measure meteorological parameters (Langford et al., 2022).

3 Boulder A.I.R. Measurements

Boulder A.I.R. maintains several air quality monitoring stations in the Boulder-Denver area. These include the Longmont Municipal Airport (LMA) and Longmont Union Reservoir (LUR) locations used in this study. The primary LUR station maintains a large suite of measurements including NO, NO_2, O_3, CH_4, CO_2, and about 20 VOCs, as well as meteorological parameters. The LMA station, since relocated, measured O_3. Boulder A.I.R. also measured a suite of VOCs and at the CDPHE station at the Boulder Reservoir (BOUR) (Pollack et al., 2021). A continuous live feed of the measurements from the currently active stations is publicly available online at https://www.bouldair.com/.

The LUR measurements ambient air sampled from a height of 8.6 m above the surface. Ozone was measured with a Thermo Fisher Scientific model 49C UV absorption monitor and CO_2 and CH_4 were measured using a Picarro G2301 cavity ring down spectrometer that was periodically calibrated using a Thermo Fisher Scientific 146i Multi-gas Calibrator. NO and NO_2 were monitored with a Teledyne Model API T200UP chemiluminescence analyzer that uses a photolytic converter for the NO_2 determination. Approximately twenty VOCs were routinely quantified.

The LUR station also operates a GRIMM EDM180 monitor to measure particulate matter (PM) using a laser scattering technique. This analyzer measures particles in the 0.25 – 32 µm (micrometer) size range with two size ranges 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.

Solar radiation was monitored with an Apogee SP-110-SS pyranometer mounted on the meteorological tower at 9.1 m height above the surface and wind conditions were recorded with an RM Young Wind Monitor AQ, 05305-PT, mounted on the meteorological tower at 9.2 m. 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.

Additional details are available at https://www.bouldair.com/longmont.htm.

References

Kupc, A., Williamson, C., Wagner, N. L., Richardson, M., and Brock, C. A.: Modification, calibration, and performance of the Ultra-High Sensitivity Aerosol Spectrometer for particle size distribution and volatility measurements during the Atmospheric Tomography Mission (ATom) airborne campaign, Atmos. Meas. Tech., 11, 369-383, 10.5194/amt-11-369-2018, 2018.

Langford, A. O., Senff, C. J., Alvarez Ii, R. J., Aikin, K. C., Baidar, S., Bonin, T. A., Brewer, W. A., Brioude, J., Brown, S. S., Burley, J. D., Caputi, D. J., Conley, S. A., Cullis, P. D., Decker, Z. C. J., Evan, S., Kirgis, G., Lin, M., Pagowski, M., Peischl, J., Petropavlovskikh, I., Pierce, R. B., Ryerson, T. B., Sandberg, S. P., Sterling, C. W., Weickmann, A. M., and Zhang, L.: The Fires, Asian, and Stratospheric Transport–Las Vegas Ozone Study (FAST-LVOS), Atmos. Chem. Phys., 22, 1707-1737, 10.5194/acp-22-1707-2022, 2022.

Lerner, B. M., Gilman, J. B., Aikin, K. C., Atlas, E. L., Goldan, P. D., Graus, M., Hendershot, R., Isaacman-VanWertz, G. A., Koss, A., Kuster, W. C., Lueb, R. A., McLaughlin, R. J., Peischl, J., Sueper, D., Ryerson, T. B., Tokarek, T. W., Warneke, C., Yuan, B., and de Gouw, J. A.: An improved, automated whole air sampler and gas chromatography mass spectrometry analysis system for volatile organic compounds in the atmosphere, Atmos Meas Tech, 10, 291-313, 10.5194/amt-10-291-2017, 2017.

Pollack, I. B., Helmig, D., O'Dell, K., and Fischer, E. V.: Seasonality and Source Apportionment of Nonmethane Volatile Organic Compounds at Boulder Reservoir, Colorado, Between 2017 and 2019, J. Geophys. Res.-Atmos., 126, ARTN e2020JD034234 10.1029/2020JD034234, 2021.

Yuan, B., Koss, A., Warneke, C., Gilman, J. B., Lerner, B. M., Stark, H., and de Gouw, J. A.: A high-resolution time-of-flight chemical ionization mass spectrometer utilizing hydronium ions (H3O+ ToF-CIMS) for measurements of volatile organic compounds in the atmosphere, Atmos Meas Tech, 9, 2735-2752, 10.5194/amt-9-2735-2016, 2016.