



Air quality impacts from the development of unconventional oil and gas well pads: Air toxics and other volatile organic compounds

I-Ting Ku^a, Yong Zhou^a, Arsineh Hecobian^a, Katherine Benedict^{a,1}, Brent Buck^b, Emily Lachenmayer^a, Bryan Terry^{b,2}, Morgan Frazier^b, Jie Zhang^{a,3}, Da Pan^a, Lena Low^a, Amy Sullivan^a, Jeffrey L. Collett Jr.^{a,*}

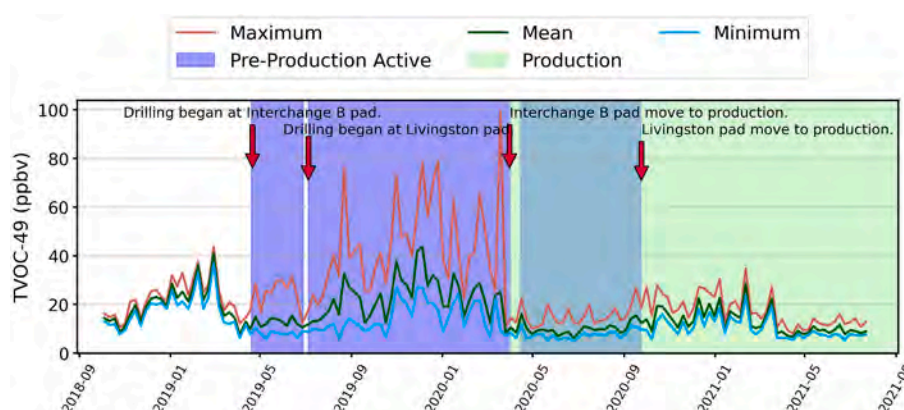
^a Department of Atmospheric Science, Colorado State University, Fort Collins, CO, 80523, USA

^b Ajax Analytics, Inc., Fort Collins, CO, USA

HIGHLIGHTS

- Increased VOC concentrations observed during oil and gas (O&G) well development.
- Emissions studied during well drilling, completions, and production.
- Up to several hundred ppbv of benzene measured in transient O&G plumes.
- Opportunities identified for reducing emissions from unconventional O&G development.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:

Unconventional oil and gas development
Denver-Julesburg Basin
Emissions
Drilling
Benzene
Photoionization detector (PID)

ABSTRACT

Unconventional oil and natural gas development (UOGD) has expanded rapidly across the United States in recent decades and raised concerns about associated air quality impacts. While significant effort has been made to quantify methane emissions, relatively few observations have been made of Volatile Organic Compounds (VOCs), especially during drilling and completion of new wells. Extensive air monitoring during development of several large, multi-well pads in Broomfield, Colorado, in the Denver-Julesburg Basin, provides a novel opportunity to examine changes in local air toxics and other VOC concentrations during well drilling and completions and production. These operations offer an especially useful case to study as several management practices were implemented to reduce emissions (e.g., electrified, grid-powered drill rigs and closed loop fluid handling systems to reduce truck traffic and limit fluid handling on the pad). With simultaneous measurements of methane and 50 VOCs from October 2018 to December 2022 at as many as 19 sites near well pads, in adjacent neighborhoods,

* Corresponding author.

E-mail address: collett@colostate.edu (J.L. Collett).

¹ now at Los Alamos National Laboratory, Los Alamos, NM, USA.

² now at Pennsylvania Department of Environmental Protection, Harrisburg, PA, USA.

³ now at Atmospheric Sciences Research Center, University at Albany, State University of New York, Albany, NY, USA.

<https://doi.org/10.1016/j.atmosenv.2023.120187>

Received 3 August 2023; Received in revised form 26 October 2023; Accepted 31 October 2023

Available online 1 November 2023

1352-2310/© 2023 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

and at a more distant reference location, we identify impacts from each phase of well development and production. Use of weekly, time-integrated canisters, a Proton Transfer Reaction Mass Spectrometer (PTR-MS), continuous photoionization detectors (PID) to trigger canister collection upon detection of VOC-rich plumes, and an instrumented vehicle, provided a powerful suite of measurements to characterize both transient plumes and longer-term changes in air quality. Prior to the start of well development, VOC gradients were small across Broomfield. Once drilling commenced, concentrations of oil and gas (O&G) related VOCs, including alkanes and aromatics, increased around active well pads. Concentration increases were clearly apparent during certain operations, including drilling, coil tubing/millout operations, and production tubing installation. Emissions of C₈–C₁₀ n-alkanes during drilling operations highlighted the importance of VOC emissions from synthetic drilling mud chosen to reduce odor impacts. More than 90 samples were collected of transient plumes. Using composition measurements, meteorological data, and information about well pad activities, these plumes were connected with specific UOGD operations including drilling, flowback, and production equipment maintenance. The chemical signatures of these plumes differed by operation type (e.g., C₈–C₁₀ n-alkanes constituted a larger fraction of measured VOCs in drilling-related plumes). Concentrations of individual, oil and gas-related VOCs in these plumes were often several orders of magnitude higher than in background air, with maximum ethane and benzene concentrations of 79,600 and 819 ppbv, respectively. Because these plumes typically impact a monitoring site for just several minutes, they are easily missed by slower-responding instruments. Study measurements highlight future emission mitigation opportunities during UOGD operations, including better control of emissions from shakers that separate drill cuttings from drilling mud, production separator maintenance operations, and periodic emptying of sand cans during flowback operations.

1. Introduction

Volatile organic compounds (VOCs) are emitted by a wide range of natural and anthropogenic sources, including vegetation, wildfires, traffic, volatile chemical products, and oil and gas extraction (Atkinson and Arey, 2003; Gkatzelis et al., 2021; Permar et al., 2021; Russo et al., 2010; Simpson et al., 2010; Yokelson et al., 2003). VOCs play an important role in atmospheric chemistry by influencing atmospheric oxidative capacity, including the abundance of ozone (O₃), hydroxyl radical (OH), and hydroperoxides (Helmig et al., 2014; Hobbs et al., 2003; Yokelson et al., 2009). VOC contributions to ozone production are of particular interest given the challenge many communities face in reducing unhealthy ozone levels (Benedict et al., 2019; Lindaas et al., 2019; Peng et al., 2021). Some VOCs are important precursors to secondary organic aerosol (SOA) production (Akagi et al., 2012; Evanski-Cole et al., 2017) and some are air toxics that act as carcinogens and/or otherwise impact human health (McKenzie et al., 2018; McMullin et al., 2018; O'Dell et al., 2020).

The oil and natural gas (O&G) industry is an important emitter of NO_x (NO_x = NO + NO₂) methane (CH₄), and a wide range of VOCs (Cheadle et al., 2017). Improved extraction techniques, including horizontal drilling and hydraulic fracturing, have enabled rapid expansion of unconventional oil and gas development (UOGD) in the United States (U.S.). These advances in technology helped the U.S. become the world's largest producer of both oil and natural gas (U.S. Energy Information Administration (U.S. EIA), <https://www.eia.gov/todayinenergy/detail.php?id=48756>, accessed on 20 February 2023). U.S. UOGD occurs in both rural and populated regions and growing development has raised concerns about impacts on the environment and human health. Numerous studies have examined methane emissions from the O&G industry; fewer studies (e.g., Buzcu and Fraser (2006); Buzcu-Guven and Fraser (2008); Gilman et al. (2009); Hecobian et al. (2019); Leuchner and Rappenglück (2010); Prenni et al. (2016); Roest and Schade (2020); Rutter et al. (2015); Ryerson et al. (2003)) have examined emissions and air quality impacts of O&G VOCs. Many VOC-focused studies have looked at combined emissions from a large number of sources in an O&G production basin. Long-term study of O&G emissions from development of individual O&G well pads remains uncommon. Bari et al. (2016) conducted a long-term study of the impact of emissions from Alberta oil sands development on the surrounding community, examining concentrations of VOCs and their trends in time and comparing them to chronic and acute health risk screening criteria. Jaroslowski et al. (2022) reported air pollutant concentration changes during the development of shale gas wells in Poland. Both studies highlight the value of continuous

ambient monitoring to inform the public and other stakeholders about air quality impacts of UOGD. Such information is critical to evaluate potential health risks from UOGD in populated regions and to identify strategies to reduce O&G air pollutant emissions and associated impacts through process improvement in the technologically complex and evolving operational practices associated with new well development.

The State of Colorado, home to the Piceance and Denver-Julesburg (DJ) Basins and approximately 50,000 active O&G wells (Colorado Oil & Gas Conservation Commission (COGCC), <https://cogcc.state.co.us/data2.html#/downloads>, accessed on 16 May 2023), ranked seventh among U.S. states for overall 2021 energy production (U.S. EIA, <https://www.eia.gov/state/print.php?sid=CO>, accessed on 20 February 2023). Home to the majority of Colorado's wells, the Denver-Julesburg Basin (DJB) sits NE of the Denver metropolitan area and within the Denver Metro/North Front Range ozone non-attainment area. Considerable UOGD within the basin occurs near residential areas. Several studies have been conducted in the DJB to characterize VOC emissions and source contributions (Abeleira et al., 2017; Gilman et al., 2013; Pétron et al., 2012; Pétron et al., 2014; Pollack et al., 2021; Swarthout et al., 2013; Thompson et al., 2014). These studies report strong O&G influence on regional air quality, including O₃ (Abeleira et al., 2017; Benedict et al., 2019; Gilman et al., 2013; Lindaas et al., 2019; McDuffie et al., 2016; Sullivan et al., 2016; Swarthout et al., 2013). McKenzie et al. (2018) assessed health risks from air pollutants emitted by O&G facilities suggesting higher acute and chronic health risks for residents living close to these facilities. Even in 2012, prior to recent UOGD and population growth, 19% of the population in the DJ Basin lived within 1.6 km of an active O&G well site (McKenzie et al., 2016).

UOGD typically involves several steps, including well drilling (often including long horizontal legs to better access layered hydrocarbon deposits), hydraulic fracturing (the creation of fractures in the hydrocarbon formation to aid in O&G recovery), and flowback (the return of injected fracturing fluids and produced water from the formation to the surface) (U.S. EPA, <https://www.epa.gov/uog/process-unconventional-natural-gas-production>, accessed on 17 May 2023; Field et al., 2014; Hecobian et al., 2019; Orak et al., 2021). Each of these steps is a complex process and intermediate activities (e.g., coiled tubing operations/millout and installation of production tubing) are also scheduled. For large pads with many wells, these processes extend over several months to a year before wells are in production. Current understanding of O&G well pad emissions comes, in part, from shorter-term snapshots of process level emissions (e.g., Hecobian et al. (2019)). An analysis utilizing measured emissions distributions (Hecobian et al., 2019), regional meteorological conditions, and dispersion modeling

simulations assessed human health risks from exposure to VOCs emitted from O&G operations (Holder et al., 2019) and informed statewide implementation of a 2000 foot (610 m) setback distance to better protect residential populations. Long-term air toxics observations around O&G operations, however, are needed to assess the accuracy of modeled concentration fields and exposures. Further, UOGD emissions have changed as operators implement new, emission-reducing practices.

Plans for the development of six new large, multi-well O&G pads in areas close to neighborhoods and schools in the City and County of Broomfield, Colorado (CCOB, population 76,000) raised local concerns that spurred development of an operator agreement incorporating several management practices to help protect the environment, public health, and safety of residents. These included use of grid-powered electric drill rigs, installation of pipelines and use of closed loop fluid handling systems to reduce truck traffic and reduce air emissions during transport of water and O&G products, and eliminating use of permanent, on-site storage tanks. An extensive monitoring program was also designed and periodically updated to determine air quality impacts during different UOGD operational phases. Major phases of interest included well drilling, hydraulic fracturing (fracking), flowback, production, and shorter-term processes including coiled tubing operations/millout, installation of production tubing, and production site maintenance activities. Air monitoring, begun prior to development and continued through pad production, included extensive spatial monitoring across the community to document air quality changes near well pads and in nearby residential neighborhoods. Weekly integrated measurements were included to examine spatial gradients and air pollutant exposure on longer (chronic) timescales. Fast measurements (seconds to minutes) were incorporated to better reveal plumes associated with transient emissions and short (acute) exposure events. Findings from this program are presented here to provide important and novel insight into the air quality impacts of modern UOGD operations with extensive best management practices (BMPs) and to help identify operations where opportunities remain for future emission reductions.

2. Methods

2.1. Site description and UOGD operations schedule

Broomfield is located 22 km NW of Denver in the SW corner of the DJ Basin (Fig. 1a). Air monitoring was initiated in October 2018 and

continued through 2022. Measurements discussed include sites equipped with canisters for weekly VOC sampling and real-time photoionization detectors equipped to trigger canisters for characterizing transient VOC plumes. Monitoring sites included ten locations near O&G well pads, eight in nearby neighborhoods, and one at a more distant regional background site (Broomfield Commons ~5–7 km SSE of the new well pads). A proton transfer reaction mass spectrometer (PTR-MS) was operated at a neighborhood location for continuous measurement of benzene, toluene, ethylbenzene, and xylenes (BTEX). As many as 19 sites were operational at a time and a core set of near-pad, neighborhood, and background sites operated throughout the study period. Detailed site information and sampling schedules are shown in Fig. 1b, Fig. S1, and Tables S1 and S2. A hybrid sport utility vehicle was equipped for fast mobile measurement of methane and ethyne (acetylene, C_2H_2) and in-plume collection of canister grab samples for VOC speciation.

Each of the six developed well pads included 8 to 17 wells that underwent drilling, hydraulic fracturing, and flowback before being placed into production. A detailed operations schedule for development of the first two new O&G well pads is shown in Table S3. The Interchange B pad and the Livingston pad were first to be developed, during 2019 and 2020. With the advent of the COVID pandemic and reorganization and merger of the O&G operator, the remaining pads (Interchange A, NWPWKY A & B, and United) were not developed until 2021–2022.

2.2. Sample collection

2.2.1. PID continuous air monitoring systems

Beginning in 2020, real-time monitoring systems (APIS, Inc., OR, USA) were deployed to measure a suite of VOCs and meteorological parameters across the Broomfield air monitoring network. Each Apis unit is equipped with wind, humidity, pressure and temperature sensors. VOCs are detected using a 10.6 eV high sensitivity Photoionization Detector (PID) sensor (MiniPIDs-HS, ION Science Inc., TX, USA). The PID is calibrated using isobutylene; response varies by species and is interpreted here as a semi-quantitative measurement of the integrated mix of total VOC (TVOC) photoionized at 10.6 eV. Response factors for individual VOCs are available from the manufacturer (TA-02, <http://www.ionscience.com/usa>). The Apis PID sensor features a measurement range from 0.5 ppbv to 3 ppmv (isobutylene equivalent). The sensor has a 15 s sampling rate and reported 1 min integrated data for TVOC and meteorological parameters. Acetone bump tests were

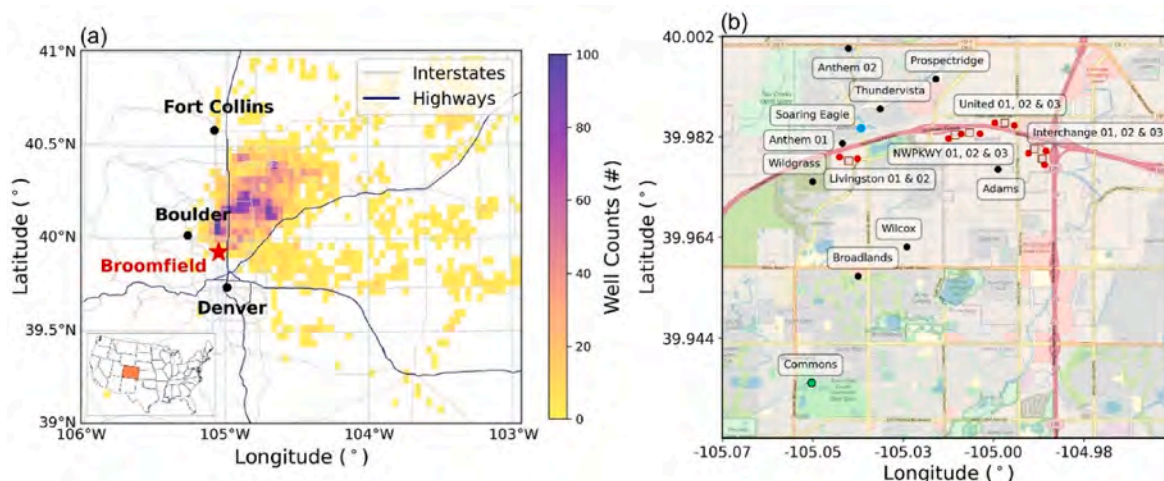


Fig. 1. (a) Map of the study region. The red star marks the location of Broomfield, approximately 22 km NNW of Denver; well counts are overlaid on the map (COGCC, <https://cogcc.state.co.us/data2.html#/downloads>, accessed on 10 May, 2023) (b) Map of the Broomfield air quality monitoring program sites. Brown squares indicate the six well pad locations. Red dots indicate air monitoring sites set up around O&G pads; black dots represent neighborhood monitoring sites; the green dot represents the background site (Commons); the blue dot shows the PTR-MS location at Soaring Eagle Park (base map courtesy of OpenStreetMap, <https://www.openstreetmap.org/>).

conducted in the field to ensure PID functionality. While the PID response is a semiquantitative indicator of the TVOC mixing ratio, it generally works well to detect rapid changes associated with arrival of VOC-rich plumes. During typical background conditions in Broomfield, the PID baseline signal ranged from 80 to 150 mV with ± 10 mV drift. Apis PID systems were coupled with automatic canister triggering devices to collect air samples (~ 15 s fill time) in evacuated 1.4-L Silonite®-coated canisters (Entech Instruments, CA, USA). The trigger threshold was initially set at ~ 300 mV across the network and later increased to 500 mV (neighborhood impact sites, Table S1) and 800 mV–1500 mV (near-pad O&G sites, Table S1) in order to better capture peak VOC plume concentration levels. While environmental interference or sensor aging sometimes led to collection of false positive samples (i.e., triggered canister VOC concentrations were not significantly elevated above background), the system overall worked well to detect and characterize plumes with elevated VOC concentrations and VOC compositions indicative of oil and gas emissions. In total 91 PID-triggered canister samples with significantly elevated VOC concentrations (at least 3 standard deviations above the weekly mean total VOC concentration at the Commons reference site) were collected between February 2020 and December 2022.

2.2.2. Weekly whole air canister samples

Weekly air samples were collected using evacuated 6.0-L Silonite®-coated stainless steel canisters coupled with CS1200E flow regulation systems (both from Entech Instruments). The flow control system enabled each canister to slowly fill over a 7-day sample period. Canisters were cleaned using an Entech 3100 Canister cleaning system before field deployment by evacuating the canister to 10^{-2} torr and purging with ultra-high purity nitrogen for 8 cycles at 80 °C. Laboratory blank samples were collected by filling cleaned canisters with ultra-high purity nitrogen.

The weekly canister sampling schedule across the monitoring network is shown in Fig. S1. Briefly, weekly air sample canisters were collected at four sites (Anthem 01, Commons, Interchange 01, and Livingston 02) from October 2018–January 2019. Afterward, once well development was underway, six to eighteen weekly air sample canisters were deployed across the monitoring network according to the varying pre-production activities at the well pads. 1324 weekly integrated samples, collected from 4 October 2018 to 29 July 2021, are included in this study, encompassing the full well development cycle and early stages of production for the first two well pads, Interchange B and Livingston.

2.2.3. Proton-transfer-reaction mass spectrometer

A quadrupole proton transfer reaction mass spectrometer (PTR-MS; Ionicon Analytik, Innsbruck, Austria) was operated beginning April 2020 at the Soaring Eagle Park neighborhood site to continuously monitor (measurement cycle ~ 90 s) BTEX (benzene, toluene, ethylbenzene, and xylene) and select other compound concentrations. The PTR-MS was installed in a climate-controlled shelter operated by Boulder AIR LLC. The sample inlet was ~ 10 m above the ground; a diaphragm pump drew air at ~ 9.5 mL min $^{-1}$ through a PFA Teflon tube with a sample sub-stream of ~ 2 mL min $^{-1}$ drawn into the PTR-MS. The instrument drift tube pressure and temperature were 2.2 mbar and 45 °C, respectively; a potential of 570 V was applied over the 9.3 cm of the drift tube resulting in an E/N of 122 Td (Townsend). Ultrapure water was used to produce the H $_3$ O $^+$ reagent ion source, and its flow rate was 6 mL min $^{-1}$ with a discharge current of 4 mA. We applied a specific rate constant for each species of interest with H $_3$ O $^+$ ions as listed in Table S5. Calibrations of the PTR-MS system were done monthly using two calibration standards containing blends of select VOCs in nitrogen diluted with zero air to ambient levels. Compound accuracies for the calibration standards were $< \pm 5\%$ for all species and measurement precisions ranged from 5 to 9%.

2.2.4. Mobile sampling

An instrumented hybrid SUV “plume tracker” (Hecobian et al., 2019) was deployed periodically to survey methane and VOC concentrations across Broomfield and to identify and locate sources of high concentration plumes. The plume tracker was equipped with a Picarro G2203 analyzer (Picarro, Santa Clara, CA), measuring methane and ethyne by cavity ring-down spectroscopy (CRDS) with 2 Hz measurement interval. An AMETEK® Mocon® Baseline 9100 gas chromatograph with PID detector measured BTEX compound concentrations in a 6-min measurement cycle. The inlet for the Picarro was located in front of the vehicle ~ 3 m above ground level and was connected with 4.5 m Teflon® tubing; air was sampled at 0.2 L min $^{-1}$. The inlet for the GC was on the right side of the vehicle, connected with a 1-m Teflon tube sampling at 0.25 L min $^{-1}$. Picarro and AMETEK® Mocon® manufacturer calibrations were verified using certified calibration gases (methane from SCOTT-MARRIN Inc., CA, USA; BTEX from Airgas, PA, USA). The precisions (2 s, 1 RSD) of methane and ethyne were 3 ppbv and < 600 pptv, respectively. Precisions (1 RSD) ranged from 1.6 to 3.7% for BTEX compounds.

An A21 Global Position System (GPS, Hemisphere GNSS Inc., AZ, USA) and Climatronics' Sonimometer™ (P/N 102779-A1-C1-D0; Climatronics Co., NY, USA) were mounted in front of the SUV at a height of ~ 3 m and featured a 2 Hz measurement rate. Measured data were displayed inside the vehicle to aid plume identification. Manually triggered (~ 15 s) whole air samples (evacuated 1.4-L Silonite® canisters) were collected outside the vehicle, in background air and in-plume, and analyzed as outlined above.

2.3. Chemical analysis of air samples

Methane and VOCs were measured in each canister sample by gas chromatography (GC) at the Colorado State University Atmospheric Science Department. Methane was analyzed using a Shimadzu GC-8A equipped with a digital temperature programmer and flame ionization detector (FID). The analytical column consisted of two 6' x 1/8" O.D. stainless steel columns packed with Porapak Q. Samples were injected at room temperature, and the column oven temperature was held at 40 °C. Ultra-high purity nitrogen (Airgas Inc., NI UHP300) was used as a carrier gas and zero air (Airgas Inc., AI UZ300) plus ultra-high purity hydrogen (Airgas Inc., Hy UHP300) was supplied to the FID. A methane standard (SCOTT-MARRIN Inc., CA, USA), $20.41 \pm 1\%$ ppmv in ultrapure nitrogen, was used to calibrate the working standard. At least five working standard injections were analyzed in each analysis batch to assess system drift or malfunction. The methane measurement precision (1 relative standard deviation, RSD) was 4%. The methane method detection limit (MDL) was 0.21 ppmv.

50 VOCs were measured in each canister sample using a custom, multi-channel GC system described in previous studies (Benedict et al., 2019; Sive et al., 2005; Zhou et al., 2005). Briefly, the system includes three GCs and five detectors (three FIDs, one electron capture detector (ECD), and one mass spectrometer (MS)). Analyzed gases included C $_2$ –C $_{10}$ non-methane hydrocarbons (NMHCs, including linear, branched, and cyclic alkanes, alkenes, alkynes, and aromatics) and C $_2$ halocarbons. A complete list of analyzed compounds and their detection limits is included in Table S4. The system was calibrated using a certified mixed hydrocarbon standard (HC Mix56, Airgas, PA, USA). Multiple working standards were analyzed during each analysis batch to check system drift and to derive VOC response factors. The measurement precision (1 RSD) of C $_2$ –C $_{10}$ NMHCs varied from 2% to 18% and from 14% to 20% for C $_2$ halocarbons. The accuracy for the calibration standard is $\pm 5\%$.

2.4. Data analysis

To compare emission profiles during different pre-production activities, 49 non-methane VOCs (excluding ethane) were grouped into nine categories including C $_3$ –C $_7$ n-alkanes, C $_8$ –C $_{10}$ n-alkanes, cyclic

alkanes, branched alkanes, alkenes, BTEX, aromatic hydrocarbons other than BTEX, halogen-containing hydrocarbons, ethyne and isoprene (see Table S6 for compound list). To examine impacts of O&G activities near Broomfield well pads, data are categorized into nine groups based on three sampling location types (background, neighborhood impact, and O&G near-pad sites, Table S1) and three sampling periods (prior to new well pad construction (None), during pre-production activities (well drilling and completions up to the start of production) and after moving to production, Table S2).

We analyze here weekly data collected from the start of the monitoring program through July 2021. During this period wells were drilled, completed, and went into production at the Interchange B and Livingston pads. These two pads are separated by approximately 4 km, facilitating interpretation of local VOC concentration increases during well development operations at either pad. Weekly observations become more difficult to interpret later in the study when multiple well pads were under development in close proximity. We examine data from PID-triggered canister samples collected from deployment in February 2020 through December 2022 to provide a good overview of VOC concentrations in transient plumes detected during UOGD pre-production and production activities. Ascertaining the source(s) influencing a triggered-canister sample is easier than for weekly samples because the 15 s collection period of the triggered-canister sample can be directly compared with wind direction.

3. Results and discussion

3.1. VOC concentrations and their spatial and temporal variations

Fig. 2 compares mixing ratios of six VOC species (ethane, propane, n-hexane, n-octane, benzene and ethyne) collected at three groups of sites (background, neighborhood impact, and near-pad O&G sites) in Broomfield with VOC measurements from previous studies in Colorado. These six species are selected to represent light to heavy alkanes that can

be associated with O&G development, key air toxic benzene (U.S. EPA, <https://www.epa.gov/haps/initial-list-hazardous-air-pollutants-modifications>, accessed on 17 May 2023) that often is found at the highest level relative to established health guideline values (McKenzie et al., 2018), and ethyne, a compound often associated with combustion/traffic emissions (Choi and Ehrman, 2004; Gilman et al., 2013; Pollack et al., 2021; Russo et al., 2010; Thompson et al., 2014). Overall statistics for methane and the full suite of VOCs measured in Broomfield are provided in Table S6. The Broomfield O&G near-pad sites had higher mixing ratios of O&G-related species than observed at Broomfield background and neighborhood impact sites, suggesting impacts from local O&G emissions.

We will examine this hypothesis in greater detail below by investigating spatial patterns in conjunction with detailed timelines of well development at individual well pads.

The mean mixing ratios of the six highlighted VOCs measured in Broomfield are significantly higher than mean values reported for Rocky Mountain National Park (ROMO) (Benedict et al., 2019) and slightly higher than values reported at Boulder Reservoir (Pollack et al., 2021). Although ROMO is impacted by urban and O&G-related emission sources from the Colorado North Front Range (Benedict et al., 2019), dilution during transport to this remote mountain location produces much lower mixing ratios than observed at sites located on the plains. The lower mixing ratios of VOCs at Boulder Reservoir are consistent with its rural location ~20 km NW of Broomfield. Mean Broomfield mixing ratios of ethane, propane, n-hexane and benzene are much lower than those from previous studies at Boulder Atmospheric Observatory (BAO) (Abeleira et al., 2017; Gilman et al., 2013; Swarthout et al., 2013) and other neighborhood locations in Erie (Thompson et al., 2014), located just north of Broomfield. The BAO tower and other Erie sites are close to active O&G operations and the measurements there were made several years prior to our Broomfield observations. Differences in concentrations of these VOCs, which can all be emitted by O&G operations, likely reflect differences in the seasons samples were collected (e.g.,

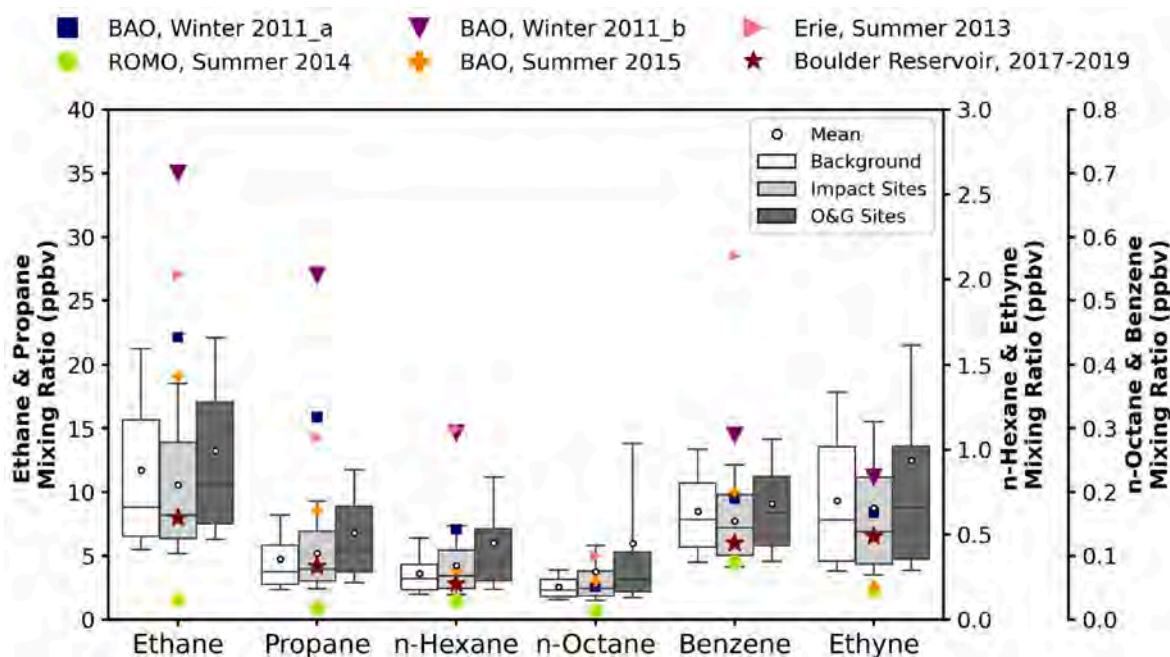


Fig. 2. Statistics of weekly average mixing ratios for six VOCs measured October 2018 to July 2021 across three categories of Broomfield sampling sites (Background, Neighborhood Impact Sites, and near-pad O&G sites). The boxes show the 25th to 75th percentiles of the data, the line represents the 50th percentile, the white dot indicates the mean, and the 10th and 90th percentiles are represented as whiskers. Mean mixing ratios of these VOCs measured in other studies at the Boulder Atmospheric Observatory (BAO) in Erie, Colorado during winter 2011 (dark blue ■ and purple ▼) and summer 2015 (orange +) (Abeleira et al., 2017; Gilman et al., 2013; Swarthout et al., 2013); in Erie, Colorado during spring and summer 2013 (pink ►) (Thompson et al., 2014); at eight rural locations close to Rocky Mountain National Park during summer 2014 (lime ●) (Benedict et al., 2019); and at the Boulder Reservoir in Boulder, Colorado from April 2017 to December 2019 (red ★) (Pollack et al., 2021) are shown for comparison.

winter vs. summer vs. year-round), proximity to regions of major O&G development, and/or emissions reductions due to implementation of new UOGD practices over time in the DJ Basin and during Broomfield UOGD in particular.

Smaller variations are seen across studies in mean mixing ratios of n-octane and ethyne. Ethyne is often considered as a tracer for urban/traffic combustion emissions and observed levels can be much higher than seen here in metropolitan areas such as downtown Denver or in highly industrialized regions (Leuchner and Rappenglück, 2010; Thompson et al., 2014). As outlined below, however, there is strong evidence of a previously unreported O&G source of ethyne in Broomfield. Even though Wilde et al. (2021) and Swarthout et al. (2013) suggested that O&G production is not a key source of heavy alkanes, we found C₈–C₁₀ n-alkanes very strongly enriched locally during Broomfield drilling activities (see discussion below). Roest and Schade (2020) have also observed elevated long-chain hydrocarbons associated with O&G sources in Texas.

Several previous studies show that ethane is a dominant compound among non-methane VOCs both in urban areas and in regions impacted by O&G emissions (Abeleira et al., 2017; Baker et al., 2008; Buzcu and Fraser, 2006; Orak et al., 2021; Pollack et al., 2021; Swarthout et al., 2013). Overall, ethane accounted for 17%–59% of reported non-methane volatile organic compound concentrations in weekly Broomfield samples. To characterize O&G-related hydrocarbon mixing ratio variations without undue influence by the most abundant compounds, O&G-related VOC mixing ratios were calculated by summing all measured alkanes (excluding methane and ethane).

Fig. 3 shows timelines of the minimum, mean, and maximum O&G-related VOC and benzene mixing ratios across all Broomfield sites with O&G development phases highlighted. Drilling began in April 2019 at the Interchange B pad followed by well completion (hydraulic fracturing and flowback) activities, together comprising the pre-production phase. All wells on this pad were in production by March 2020. Livingston pad drilling began in July 2019 and all wells were in production by September 2020. Differences between minimum and maximum O&G-related VOC and benzene mixing ratios measured across Broomfield sites were generally small prior to the start of drilling, increased during well drilling and completion (pre-production) activities, and decreased again as wells went into long term production. Maximum O&G-related VOC values during pre-production activities were measured at near-pad sites 96% of the time, indicating that the increased spread between minimum and maximum O&G-related VOC values was primarily caused by local O&G emissions. The sum of O&G-related VOC compounds ranged from 3.2 ppbv to 93.3 ppbv with an average value of 13.4 ppbv; the maximum value was observed during the week of 19 March 2020 at the Livingston 02 site during Livingston Pad coil tubing/millout operations (the removal of plugs previously used to isolate hydraulic fracturing zones). Weekly average benzene mixing ratios ranged from 0.03 ppbv to 0.80 ppbv with a mean value of 0.16 ppbv. The maximum weekly benzene mixing ratio was seen in the same Livingston 02 sample collected during coil tubing/millout operations; this sample also contained the maximum weekly ethane (61.6 ppbv) and propane (34.1 ppbv) mixing ratios.

The wide range of O&G-related VOC mixing ratios observed during

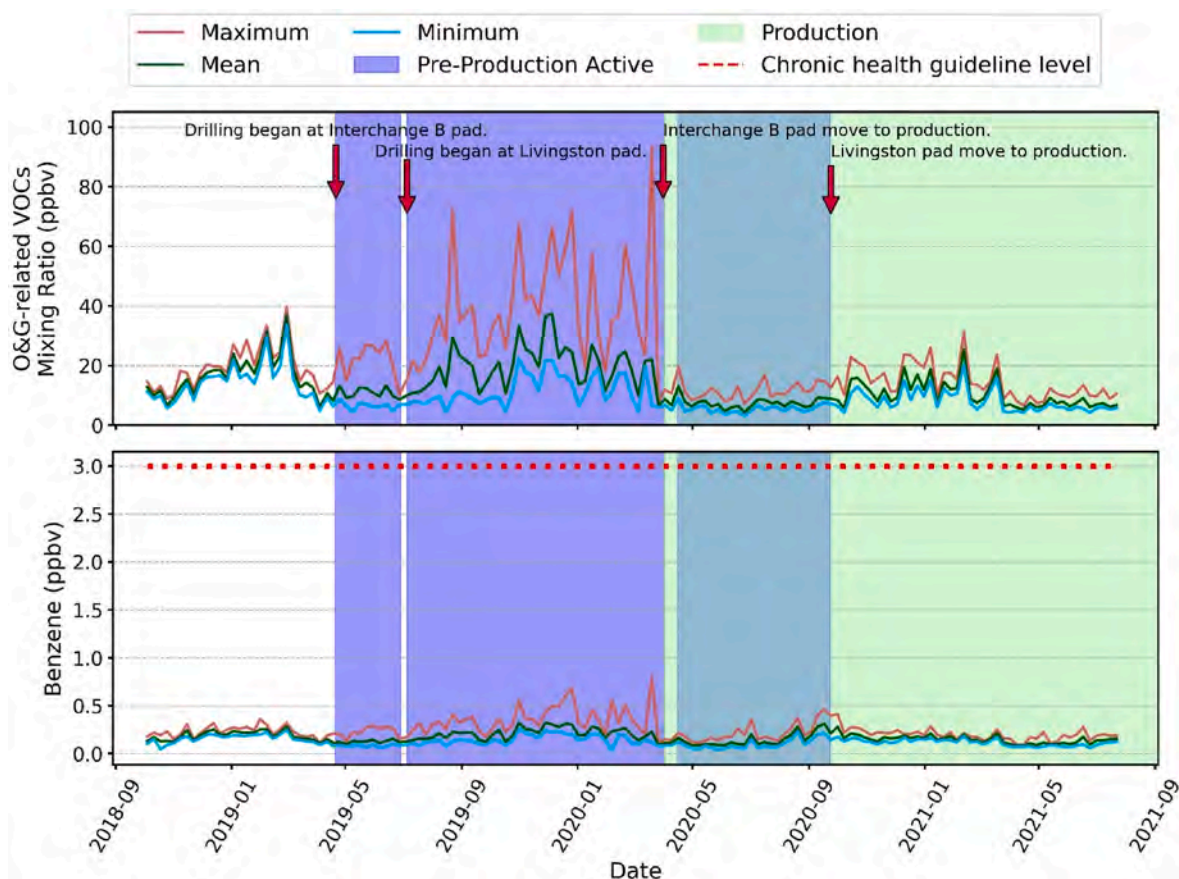


Fig. 3. Time series of the maximum, mean, and minimum mixing ratios of O&G-related volatile organic compounds excluding ethane (top) and of benzene (bottom) observed across the monitoring network in Broomfield from October 2018 to July 2021. Observations started before O&G development and continued during pre-production activities (purple shading) and production (green shading). The blue shading represents the period when the Interchange B pad had moved to production but the Livingston pad was still in pre-production. The red dashed line indicates the 3.0 ppbv chronic health guideline value for benzene exposure (Agency for Toxic Substances and Disease Registry, ATSDR (Wilbur et al., 2007)).

the study reveals significant variability in local air quality and is influenced by several factors. Across the network seasonal changes are driven by changes in emissions, atmospheric stability, and oxidation rates. Spatial concentration differences are influenced by the distance from local emission sources, such as O&G pre-production activities. Monthly variations of weekly O&G-related VOCs across the study's three site categories are shown in Fig. 4a. Consistent with previous studies (Helmig et al., 2014; Pollack et al., 2021; Thompson et al., 2014; Zheng et al., 2018), elevated levels of O&G-related VOCs were observed across all site types during wintertime, when cold temperatures, clear skies, and snow-cover frequently enhance atmospheric stability and enhance accumulation of local pollutant emissions. Fig. 4b compares O&G-related VOC mixing ratios observed, by site type, through various O&G operational phases. Mixing ratios of O&G-related VOCs were significantly (*t*-test, 95% confidence level) higher at near-pad O&G and neighborhood impact sites than at the background site during pre-production operations.

Variations of chemical composition in 10 VOC groups for the three site types during different phases of well development are shown in Fig. S2. C₃–C₇ n-alkanes are the dominant VOC species in the region, accounting for ~76% on average of all measured VOC mixing ratios (TVOC-49, excluding methane and ethane). The Commons background site tended to have slightly lower C₃–C₇ n-alkane and slightly higher alkene, BTEX and ethyne abundance compared to neighborhood impact and near-pad O&G sites even before the start of well pad development. This reflects the location of this site closer to the Denver metro area and further from the large number of O&G wells NE of Broomfield as well as greater traffic density on nearby roads. Previous studies found vehicular emissions were a significant source of alkenes and aromatics in the region (Gilman et al., 2013; Pollack et al., 2021). During pre-production

operations, we observed increased contributions of C₈–C₁₀ n-alkanes, cyclic, and branched alkanes at neighborhood impact and O&G sites. Simpson et al. (2010) reported that > C₅ alkanes and cyclic alkanes are important components of crude oil and several field studies showed that cyclic alkanes were associated with O&G emissions (Gilman et al., 2013; Swarthout et al., 2013). As discussed below, a close association was also seen between Broomfield drilling operations and local concentrations of C₈–C₁₀ n-alkanes.

3.2. Alkane ratios

Different emission sources often feature distinct VOC signatures; therefore, ratios of various VOCs are sometimes used to characterize changing source contributions (Karl et al., 2009; Leuchner and Rappenglück, 2010). For example, the ratio of i-pentane to n-pentane has been established as a robust indicator to distinguish influence from urban/traffic versus O&G emissions (Abeleira et al., 2017; Gilman et al., 2013; Pollack et al., 2021; Swarthout et al., 2013; Thompson et al., 2014; Wilde et al., 2021). Combustion emissions and evaporation of processed petroleum products tend to yield higher abundances of i-pentane (Baker et al., 2008; Leuchner and Rappenglück, 2010; Na et al., 2004; Wilde et al., 2021) while i/n-pentane ratios below 1.0 tend to be indicative of O&G emissions (Ghosh, 2018; Gilman et al., 2013; Halliday et al., 2016; Hecobian et al., 2019; Pollack et al., 2021; Prenni et al., 2016; Swarthout et al., 2013; Thompson et al., 2014; Wilde et al., 2021). The two isomers react at similar rates with OH radicals (Atkinson, 1997), helping to preserve source ratios during atmospheric transport. The i/n-pentane ratio observed in weekly samples in this study was lowest (~0.9) during the pre-production period at the near-pad O&G sites and highest (~1.19) during the production phase at the Commons background site. These values are all lower than mean values measured at Boulder Reservoir (1.26) (Pollack et al., 2021) and in 2018–2020 morning samples in urban downtown Denver (1.25; CDPHE data, https://www.colorado.gov/airquality/tech_doc_repository.aspx, accessed on 27 February 2023), both of which are more distant from regional O&G emissions. The Broomfield values are similar to 2011 measurements at the BAO tower in Erie (0.94–1.11) (Swarthout et al., 2013), located just north of Broomfield and close to O&G operations, except that the pentane ratios at the near-pad sites in Broomfield are lower during pre-production operations. The low i/n-pentane ratios in Broomfield reveal a strong influence from regional O&G activities throughout the study with increased local O&G influence during pre-production activities. Ratios of i/n-butane in the Broomfield study ranged between 0.37 and 0.41, with the lowest values observed during pre-production activities. These are similar to values (0.40–0.42) previously reported in the Denver urban area and the DJB (Halliday et al., 2016) and to the ratio reported for gas matrix samples collected at the Broomfield Livingston and Interchange well pads (<https://cogcc.state.co.us/data.html#/cogis>, accessed on 27 February 2023).

3.3. VOC increases during well pad operations

Although several studies have been conducted around O&G fields and related facilities (Brantley et al., 2014; Esswein et al., 2014; Ghosh, 2018; Helmig et al., 2014; Hildenbrand et al., 2016; Jobson et al., 2004; Macey et al., 2014; Prenni et al., 2016; Warneke et al., 2014; Wilde et al., 2021; Zheng et al., 2018), only a few have included activity-specific monitoring (Colborn et al., 2014; Hecobian et al., 2019; Orak et al., 2021) and often only for limited time periods. Using the Broomfield observations, we are able to examine how VOC concentrations change over time and spatial scales as O&G wells are drilled, completed, and move into production. Because changes in season, prevailing meteorology, and regional emissions all influence VOC concentrations, we consider VOC excess mixing ratios: the mixing ratio at near-pad O&G sites minus the mixing ratio at the Commons background site. Fig. 5 depicts time series of the excess mixing ratios of TVOC-49, ethane,

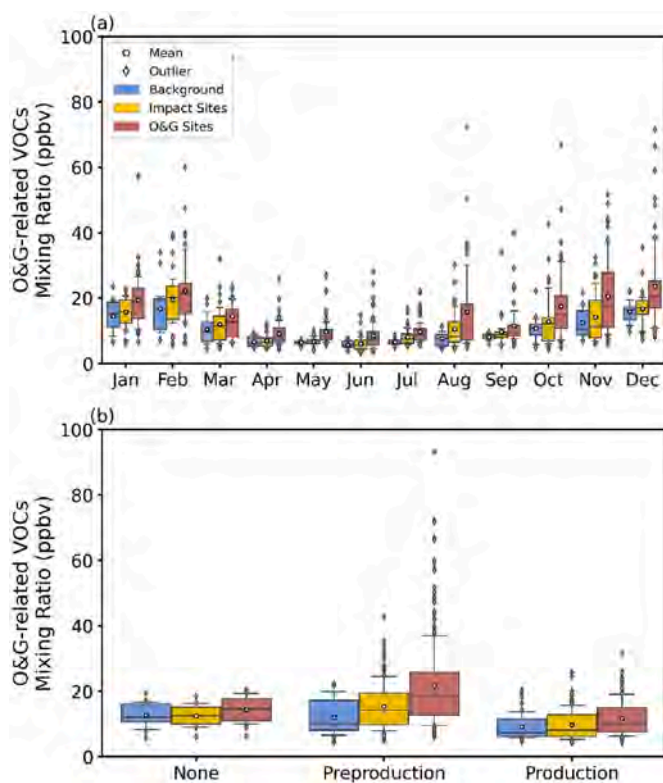


Fig. 4. Box and whisker plots (90th, 75th, 50th, 25th, 10th percentiles) including mean and outlier values of O&G-related VOC mixing ratio for the Broomfield background, neighborhood impact, and near-pad O&G site types. Panel (a) shows observations by month of the year; panel (b) compares mixing ratios before the start of pad construction (none), during drilling and completion (pre-production) activities, and after the well pads went into production.

benzene, C₈–C₁₀ n-alkanes, ethyne, and isoprene at the near-pad O&G sites around the Interchange B and Livingston well pads along with each pad's operations schedule. Similar time series are included in Fig. S3 for alkenes, toluene, BTEX and i/n-pentane ratios. Periods of on-site operations, including drilling, hydraulic fracturing, coiled tubing operations, production tubing installation, and flowback, are illustrated; detailed

operations dates are provided in Table S3. The durations of such operations on a pad can range from days (e.g., coil tubing/millout or production tubing installation) to weeks/months (drilling, hydraulic fracturing, flowback) to years (production).

Excess mixing ratio values for individual VOCs during the period prior to the start of drilling are generally near zero, indicating that

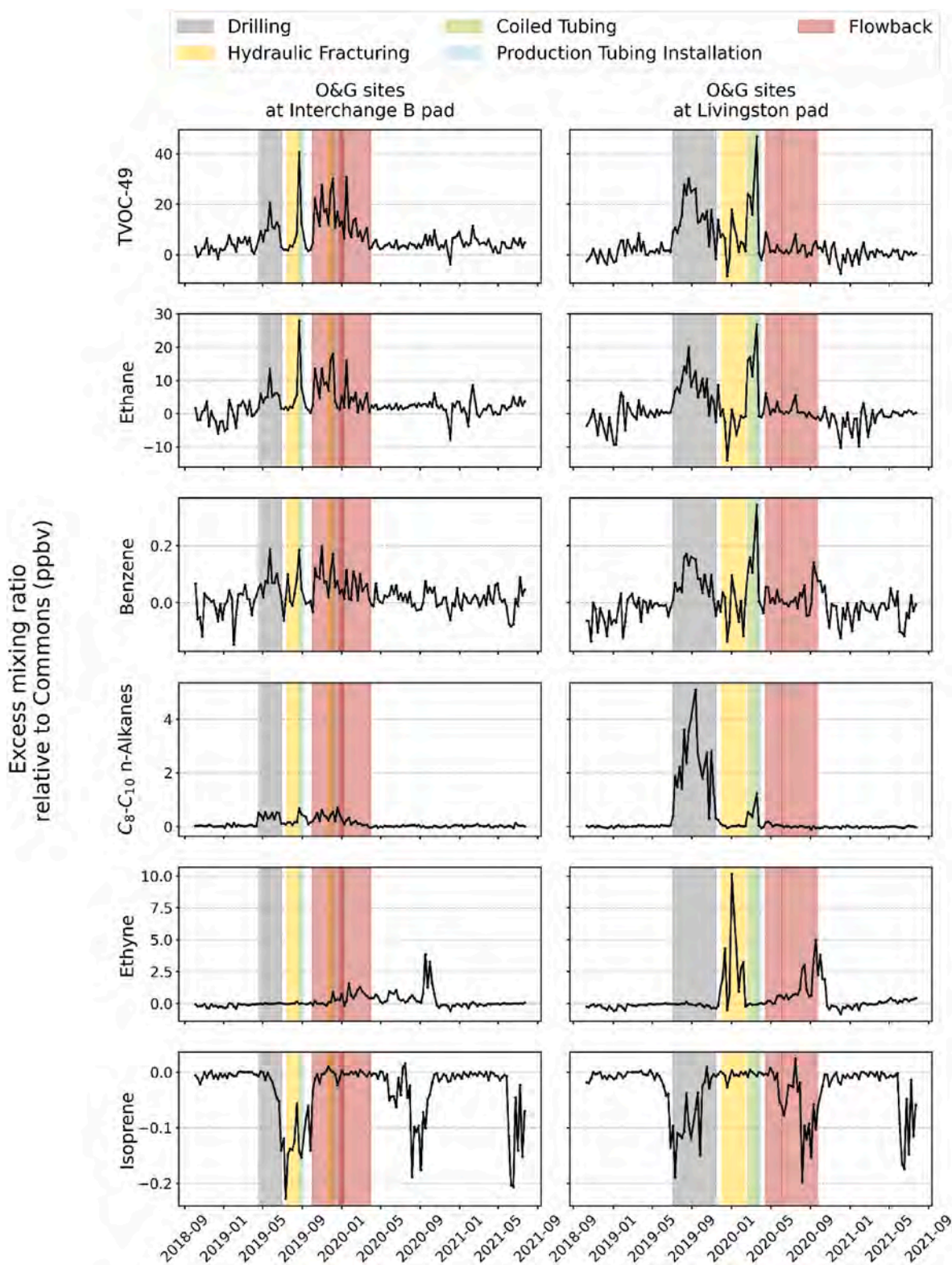


Fig. 5. Time series of various averaged VOC excess mixing ratios (ppbv) at the Interchange B and Livingston near-pad sites relative to the Commons background site. The overlaid colors are different O&G pre-production activities.

gradients in weekly average concentrations of these species across Broomfield were small prior to pad development. Significant local increases in TVOC-49, ethane, benzene, C₈–C₁₀ n-alkane, and ethyne concentrations occur at various points during well pad development. Note that excess mixing ratios of some species rise and fall together during particular operational activities, while peak timing differs between other sets of species. The observed patterns also exhibit some similarities and some differences between the Interchange B and Livingston pads. Timelines of TVOC-49 and ethane excess mixing ratios exhibit similar temporal patterns for each pad. While TVOC-49 does not include ethane concentrations, it does include large contributions from other light alkanes (e.g., C₃–C₇ n-alkanes) that are strongly correlated with ethane in our ambient VOC dataset and in typical O&G emissions. The local increases in TVOC-49 and ethane are readily apparent at the Interchange B pad during drilling, coil tubing/millout, and flowback operations. Emissions of light alkanes occur when material from the subsurface hydrocarbon deposit is released to the atmosphere, especially during drilling through hydrocarbon deposits and during flowback operations when hydraulic fracturing fluids and produced water come to the surface at high temperatures. A lack of significant ethane increases during fracking operations is not surprising since material is being pushed downhole during this period, limiting opportunity for subsurface hydrocarbon venting to the atmosphere. Consistent with our findings here, Hecobian et al. (2019) also found greater emissions of light alkanes during drilling and flowback than during fracking operations in western Colorado. In that study, median ethane emissions during flowback were nearly ten times higher than during drilling. The fact that peak ethane excess mixing ratios during flowback operations at the Broomfield Interchange B pad were only slightly higher than those during drilling suggests that best management practices (e.g., closed loop fluid handling systems) employed to limit on-pad flowback emissions in Broomfield were successful relative to the green completion practices in place in Colorado several years earlier when flowback fluids were typically stored in tanks for some time on the pad. The Broomfield O&G operator made further (undisclosed) changes to control flowback emissions before well completions at the Livingston pad and the lack of any clear increase in the TVOC-49 and ethane excess mixing ratios around the Livingston pad during flowback again suggests a positive outcome of those actions. As noted below, however, short periods of significant VOC emissions during flowback persist and warrant further attention.

Large increases in local concentrations of C₈–C₁₀ n-alkanes were observed during drilling operations at the Livingston pad, with smaller increases apparent during coiled and production tubing operations. A similar pattern was observed during the same set of operations at the Interchange B pad; however, the C₈–C₁₀ n-alkane concentration increases during drilling were less significant than at Livingston. This difference likely reflects a change in the drilling mud used at each pad. Drilling mud helps lubricate the drill bit and aids the return of drill cuttings to the surface. Various hydrocarbon-based drilling mud formulations are used depending on the nature of the reservoir, the location of drilling, and other factors. Gibson D822 petroleum hydrocarbon distillate-based drilling mud, used in drilling operations at the Interchange B pad and during drilling of the first well at the Livingston pad, generated significant odor complaints from nearby residents and prompted a change to the use of a synthetic paraffin Neoflo 4633-based drilling mud beginning with the second well at Livingston. Laboratory headspace analyses of Gibson and Neoflo drilling muds completed in our lab (see Fig. S4) revealed greater abundance of C₈–C₁₀ n-alkanes volatilized from the Neoflo mud, consistent with the increased C₈–C₁₀ n-alkane concentrations seen during drilling operations at Livingston.

Clear enhancements of ethyne were seen near the Livingston pad

during hydraulic fracturing and again during the latter part of flowback and early production. Increased mixing ratios of benzene and of ethene, a common combustion emission, were also observed near the Livingston pad during the second ethyne enhancement period. The ethyne enhancements during fracking are not surprising as this is a period with significant onsite power generation and truck traffic; increases during flowback are unexpected as combustion sources are typically limited on-pad during this phase. Fig. 6a shows timelines of benzene, toluene, and benzene/toluene ratio measured by the PTR-MS at the Soaring Eagle Park site northeast of the Livingston pad. A substantial increase in periods with benzene concentrations above 1 ppb was observed from mid-September to mid-October 2020, the period when high ethyne, benzene, and ethene levels were seen near the Livingston pad. A conditional probability function (CPF) analysis of high (>1 ppbv) benzene concentrations between 12 September and 12 October 2020 shows strong association with transport (at low wind speeds) from the direction of the Livingston pad to the SW (Fig. 6b). Similar transport patterns from July through early September did not generally produce elevated benzene concentrations at Soaring Eagle Park, suggesting the elevated concentration period in September/October represented a new source of emissions rather than a change in transport that brought existing source emissions to the site (Fig. S5). Previous studies have linked elevated ethyne, alkene and benzene abundances to combustion sources such as flaring (Schade and Roest, 2016, 2018) although the benzene:toluene ratios they reported were much lower than the typical values (~5–10) seen here. No flares were operational at the Livingston pad during this period and infrared camera inspections by CCOB inspectors on the Livingston pad also did not reveal evidence of improperly operating emission control devices.

To further inspect these unusual emission plumes and define their origin, the mobile plume tracker was deployed the night of 17 September 2020 to measure spatial patterns in concentrations of methane, ethyne, and BTEX. Fig. 7a shows time series of ethyne, methane, benzene, and toluene mixing ratios from the on-board instruments aligned with species concentrations measured in nine grab canisters collected during the drive. Sharp spikes in ethyne and methane indicate transits through the plume by the moving vehicle, while the two broader periods of high ethyne and methane concentrations represent periods when the vehicle sat stationary inside the plume. This high-ethyne plume features a substantial increase in benzene, but little increase in toluene mixing ratios, consistent with the PTR-MS observations at Soaring Eagle Park. Fig. 7b shows ethyne mixing ratios along the plume tracker path. The observed ethyne concentrations ranged between 0.2 ppbv (a typical background level during the summer-fall season) to 90.9 ppbv with the highest concentrations observed near the SE corner of the Livingston pad. The wind direction during the mobile measurement period was generally from the NW. Low ethyne concentrations upwind (NW) of the pad and the peak concentrations downwind (SE) of the pad indicate the ethyne-rich plume originated on the Livingston pad.

The compositions of the canister samples collected inside the ethyne-rich plumes on the plume-tracker drive were compared with weekly canister samples collected at the Livingston near-pad sites during the June–September period of elevated ethyne. Both showed substantially increased benzene:toluene, benzene:ethyne, and ethyne:methane ratios compared to values typically measured in other periods near Broomfield O&G well pads (see Fig. S6). The strong inter-species correlations in the canister data, the similarities in species ratios between the canister data and the June to September 2020 near-pad Livingston weekly canister data, and the departures of both from typical near-pad signatures in Broomfield all suggest the influence of a consistent source throughout this period. Although benzene:toluene ratios were unusually high again

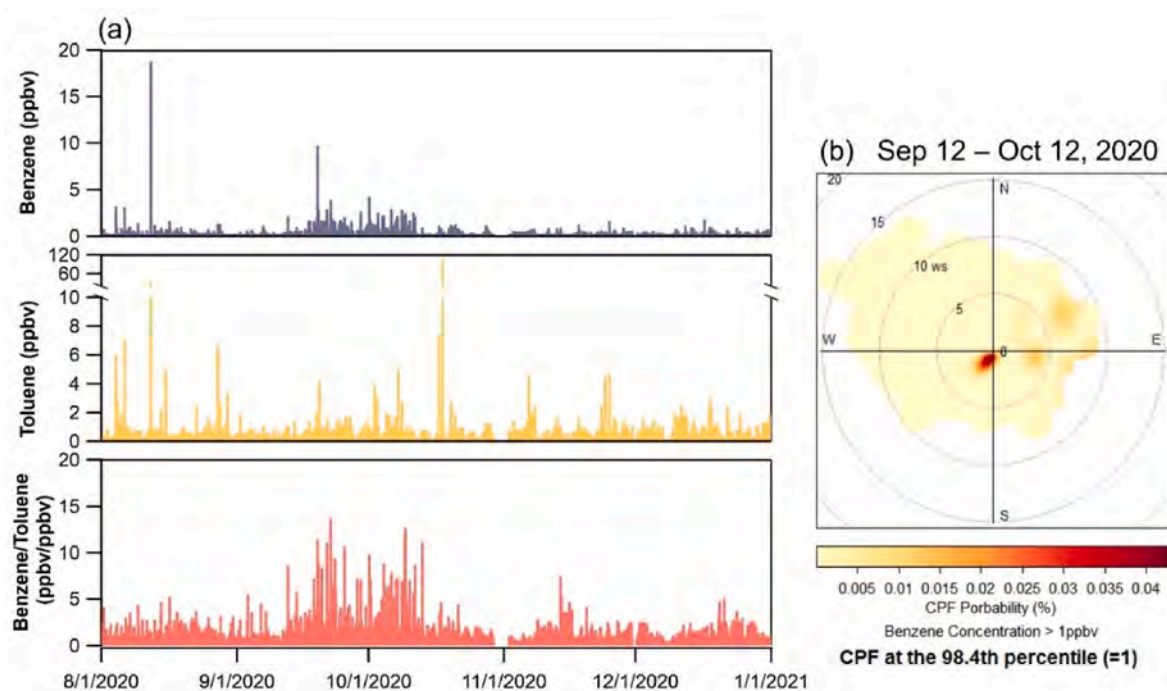


Fig. 6. (a) Timelines of benzene (top), toluene (center) and benzene to toluene ratio (bottom) from August to December 2020 measured with the PTR-MS at Soaring Eagle Park in Broomfield, CO. (b) Conditional probability function (CPF) plot for elevated benzene mixing ratios at Soaring Eagle Park from September 12 to October 12, 2020.

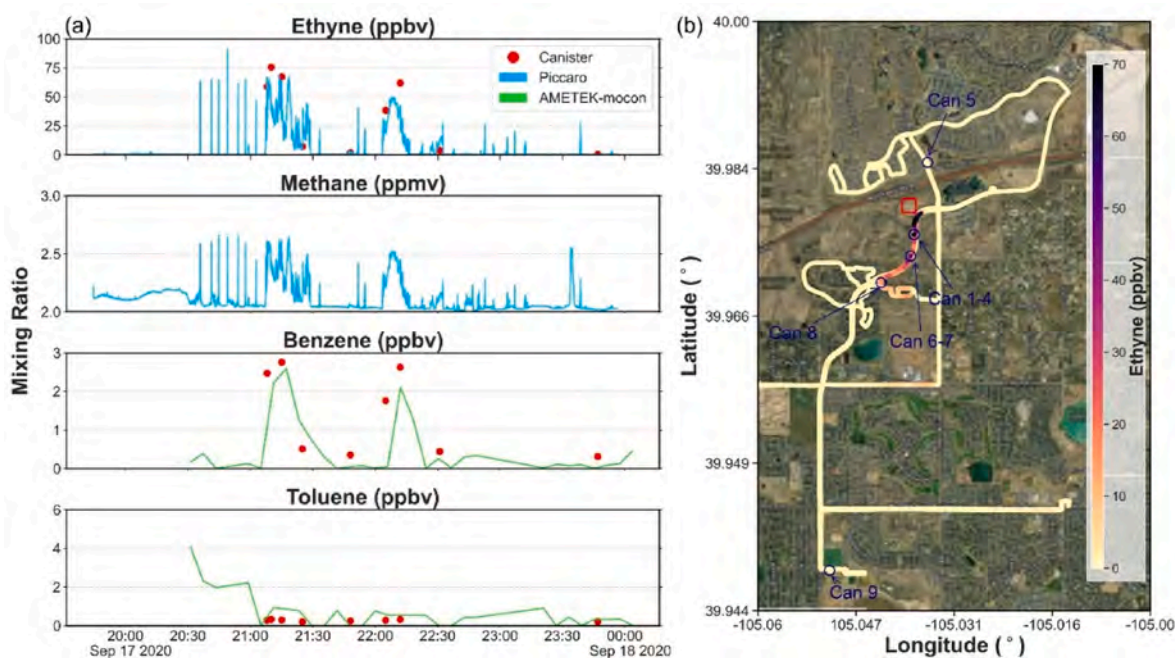


Fig. 7. (a) Time series of ethyne (ppbv), methane (ppmv), benzene (ppbv) and toluene (ppbv) measured during a plume tracker deployment on the evening of 17 September 2020. Mixing ratios measured in 9 grab canisters collected during the drive are shown as red dots. (b) Broomfield area map showing ethyne mixing ratios measured along the plume tracker driving route (base map is from ESRI: <https://www.arcgis.com/apps/View/index.html?appid=df7cee38677f479c8697026ebf920431>). Grab canister collection locations are labeled. The red square indicates the location of the Livingston pad.

in these mobile plume measurements, both propene and ethene levels were elevated in plume canister samples, consistent with a combustion signature. While the exact nature of the source of these emissions from the pad remains unknown, the presence of compounds commonly found

in natural gas flaring or combustion emissions, point to some sort of on-pad combustion source as a likely origin. Notably, this plume was no longer detected beginning in mid-October 2020 after its ongoing detection was reported to the well pad operator, an example of the value

of the Broomfield air monitoring program in helping to mitigate O&G emissions and their impacts on the surrounding community.

3.4. VOC plume observations

3.4.1. VOC levels and compositions in triggered canister samples

The network of PID sensors with triggered canister collection allows us to examine short-term (minutes to hours) periods of elevated VOC concentrations in Broomfield, both near well pads and in adjacent neighborhoods. We focus on VOC compositions in triggered canisters collected during specific O&G operations, including drilling, hydraulic fracturing, coil and production tubing operations, flowback, and production. Because some Broomfield well pads are close to each other, and different operations simultaneously occur on adjacent pads, we use well development records and local wind observations to identify emission sources influencing collection of each triggered canister. Only triggered canister samples attributed to emissions from a single operational activity on a nearby well pad are included in this analysis.

Fig. 8 presents frequency distributions of TVOC-49 and benzene mixing ratios from 91 triggered canister samples grouped by well development activity. Concentrations measured in weekly samples collected at the Commons background site are shown for comparison. A detailed data set of selected compounds measured in triggered canisters is shown in Table S7. TVOC and benzene mixing ratios measured in event-triggered canister samples were typically 1 to 3 orders of magnitude greater than mixing ratios measured in the Commons background samples, confirming successful capture of high concentration plumes during O&G operations. Triggered canister sample concentrations of TVOC-49 ranged from 36.6 ppbv to more than 140,000 ppbv; benzene ranged from 0.4 ppbv to 819 ppbv. The highest levels of each were seen in a sample collected near the United pad during flowback operations. The *i*/*n*-pentane ratios in the triggered canister data set were low, with an average value of 0.77, indicating strong influence from O&G emissions (see Fig. S7).

High concentration plumes of TVOC-49 and benzene were observed during all well development activities. Average TVOC-49 and benzene concentrations in captured plumes were highest during flowback and lowest during drilling operations. Because measured concentrations depend on factors beyond emission source strength, including distance from the pad, dispersion conditions, wind direction, and the level at which the PID sensor was set to trigger, we cannot readily relate emission strength to measured plume concentration. Given sensor location choice and varying transport conditions, one likewise should not immediately conclude that the activity with the largest number of triggered canisters would be the most frequent emitter of concentrated

plumes. Nevertheless, the data set collected here, covering nearly three years of measurements, represents a significant step forward in characterizing short-term elevated VOC concentrations that occur under real-world conditions near O&G drilling, completion, and production operations on large, multi-well pads. The VOC compositions measured in these concentrated, often transient, plumes also provide useful information concerning the chemical signatures of emissions from specific O&G operations.

Fig. 9 compares averaged VOC compositions measured in plumes emitted during various well development operations. Unsurprisingly, C₃–C₇ n-alkanes were the most abundant VOC group in the plumes across all operation types, with an average contribution of 84% (range 67–92%), followed by cyclic alkanes (mean: 5%, range 3–6%). High contents of light and cyclic alkanes have also been observed in other regions impacted by O&G-related emission sources (Gilman et al., 2013; Leuchner and Rappenglück, 2010; Pollack et al., 2021; Simpson et al., 2010; Swarthout et al., 2013; Thompson et al., 2014; Wilde et al., 2021). The contribution of C₈–C₁₀ n-alkanes in plumes associated with drilling activity is significantly enhanced, comprising an average of 11% of the measured VOCs vs. just 0.7–2% in plumes associated with other well pad operations. This is consistent with increases in C₈–C₁₀ n-alkane concentrations in weekly samples collected near the Livingston pad during drilling operations discussed above, highlighting the importance of drilling mud emissions as a VOC source. Since heavier n-alkanes associated with volatilization from synthetic drilling muds like Neoflo are more reactive with OH radicals than the lighter alkanes more prevalent in emissions from conventional petroleum-derived drilling fluids like Gibson D822, further study should evaluate possible tradeoffs between reduced odor (and aromatics content) and possible enhancements to ozone production when choosing a drilling fluid.

Only one clear plume sample was captured during hydraulic fracturing operations. Because hydraulic fracturing operations push material downhole, emission of subsurface hydrocarbons is considered less likely during this operation (Field et al., 2014; Hecobian et al., 2019). Significant on-site power generation is, however, typically required to pressurize and fracture wells, meaning that engine emissions of NO_x are important to consider where regional ozone levels are problematic.

3.4.2. Case studies of VOC-rich plumes

Here we highlight examples of VOC-rich plumes detected in the study. A concentrated VOC plume was observed at 01:16 LT on 29 July 2022. Two co-located sensors, United 02 and 03, simultaneously detected elevated VOC concentrations and triggered canister collection (see Fig. 10). This VOC-rich plume saturated both PID sensors and the triggered canister samples contained the highest TVOC-49

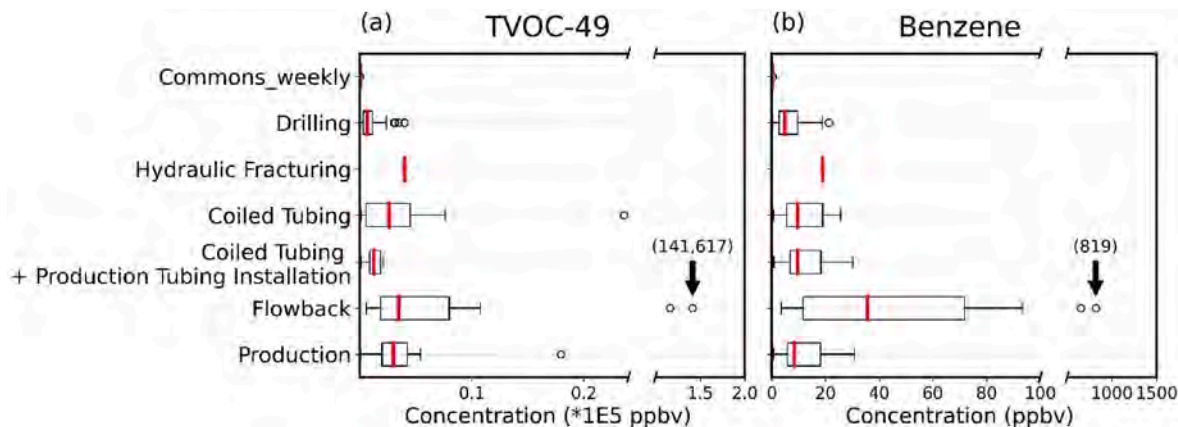


Fig. 8. Box and whisker plots (90th, 75th, 50th, 25th, 10th percentiles) of (a) TVOC-49 and (b) benzene mixing ratios measured in 91 15-s triggered canister samples during different O&G development operations from February 2020 to December 2022. The black arrows denote the highest TVOC-49 and benzene mixing ratios measured in triggered canister samples. Weekly canister data collected at the Commons (background) site are shown as a reference.

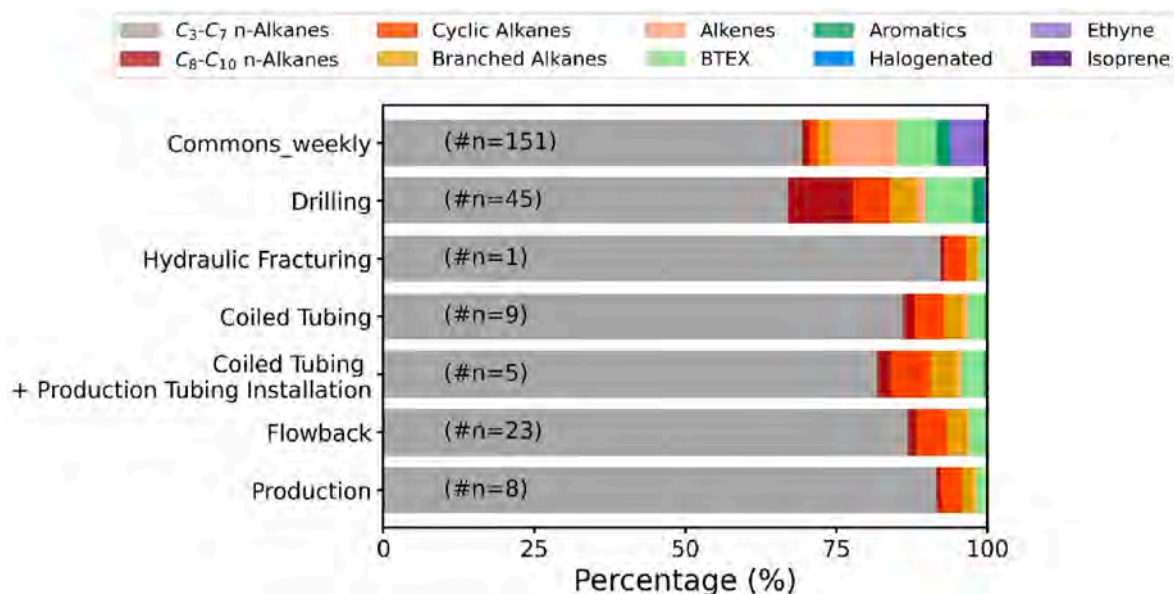


Fig. 9. Comparison of average VOC compositions in triggered canister samples that captured plumes emanating from different well pad operations. Weekly canister data collected at the Commons (background) site from February 2020 to December 2022 are shown here for comparison.

concentrations (142,000 and 116,000 ppbv) measured during Broomfield air quality monitoring. The plume persisted at the site for ~30 min. Winds were approximately 5 mph and shifted from N to NW prior to the trigger event, indicating the origin of the emission from the direction of the United pad. The two triggered canisters contained very high levels of methane (301 and 254 ppmv), ethane (79,600 and 50,400 ppbv), benzene (819 and 653 ppbv), and other typical O&G emission compounds. Low i/n-pentane ratios of 0.7 further indicate an O&G source of the plume. The United pad was in flowback during this event. While flowback operations have been reported as some of the biggest O&G VOC sources (Hecobian et al., 2019; Orak et al., 2021), flowback operations in Broomfield employed management practices to limit flowback emissions that appear to have successfully limited average increases in VOC concentrations around the pads, as discussed above. Sand cans, however, are required during early stages of flowback to capture sand particles and sediments coming up the well with flowback fluids. These canisters are opened and emptied, up to several times per day, to remove accumulated sand, allowing significant VOC venting to the atmosphere for short periods.

A second example VOC plume was observed ~04:00 to 05:00 LT on 4 December 2021. Four independent PID sensors at NWPKWY 02 and 03 and United 01 and 02 detected this plume and triggered canister collections (Fig. S8), including a sample containing 23,600 ppbv of TVOC-49. Enhanced VOC levels were captured by the PID sensors at 04:06 LT at NWPKWY02, at 04:11 LT at NWPKWY 03, and at 04:34 LT at United 01 and 02. Wind speeds were modest (2-3 mph) with wind direction consistent from the NW to SW, suggesting the plume originated from a source to the west. As shown in Fig. S8c, the 4 triggered canister samples contained highly elevated levels of compounds typical of O&G emissions including methane, C₃-C₇ n-alkanes, benzene and aromatics, with an average i/n-pentane ratio of 0.78, indicative of O&G emissions. Coil tubing/millout operations started at the NWPKWY pad A, to the west of the four monitoring sites, on 3 December 2021; emissions from this operation would be consistent with the timing and composition of the VOC plumes measured at the NWPKWY and United monitoring sites. The plume captured at United 02 had increased heavy alkane content compared to the plumes sampled at the other three sites. Drilling operations were underway at the United B well pad at this time, upwind of the United 02 monitor and downwind of the other three sites.

These two case studied represent emissions during pre-production

operations; a few substantial VOC plumes were also observed during maintenance activities after well pads went into production. For example, a triggered canister was collected on 26 April 2021, at Livingston 01 during a period of separator maintenance on the Livingston pad. The TVOC-49 level in the triggered canister was 5,440 ppbv, benzene was 30.9 ppbv, and the i/n-pentane ratio was 0.93. On 23 June 2021, the PID sensor at the Anthem 01 neighborhood site detected a VOC-rich plume transported from the direction of the Livingston pad where separator maintenance was underway. A triggered canister contained 3,870 ppbv TVOC-49, 14.8 ppbv benzene, and an i/n-pentane ratio of 0.75. This event is particularly noteworthy given the lengthy distance (~330 m) between the Livingston pad and the Anthem 01 neighborhood site. Production separators are used to separate mixed production fluids into constituent components (oil, gas, and water) before sending them to pipelines. Operated under pressure and exposed to the elements, regular maintenance is necessary to maintain proper separator performance. Separator maintenance in Broomfield involved isolating the separator from the well, with residual gas in the closed-loop system combusted through an enclosed combustion device (ECD) to purge the flowline. Afterward, a hydrovac (equipped with high-pressure hot water and high-volume vacuum) was used to clean out residual liquids inside the separator. An abundance of light alkanes and the low i/n-pentane ratio on the 23 June 2021 plume suggest the emissions probably derived from direct emission of petroleum hydrocarbons rather than emissions from the combustor.

4. Conclusions

This study provides a unique overview of concentrations of air toxics and other VOCs during more than two years of development of large, multi-well pads in suburban Broomfield, Colorado, USA. Measurements at short (seconds to minutes) and longer (weekly) timescales at locations close to and further from O&G well pads offer important insight into how VOC concentrations and both acute and chronic exposure potential vary in time and in space during well drilling and completions on into early stages of production. Key findings from this study include the following:

- Analysis of weekly samples collected near well pads, in adjacent neighborhoods and at a more distant background reference site

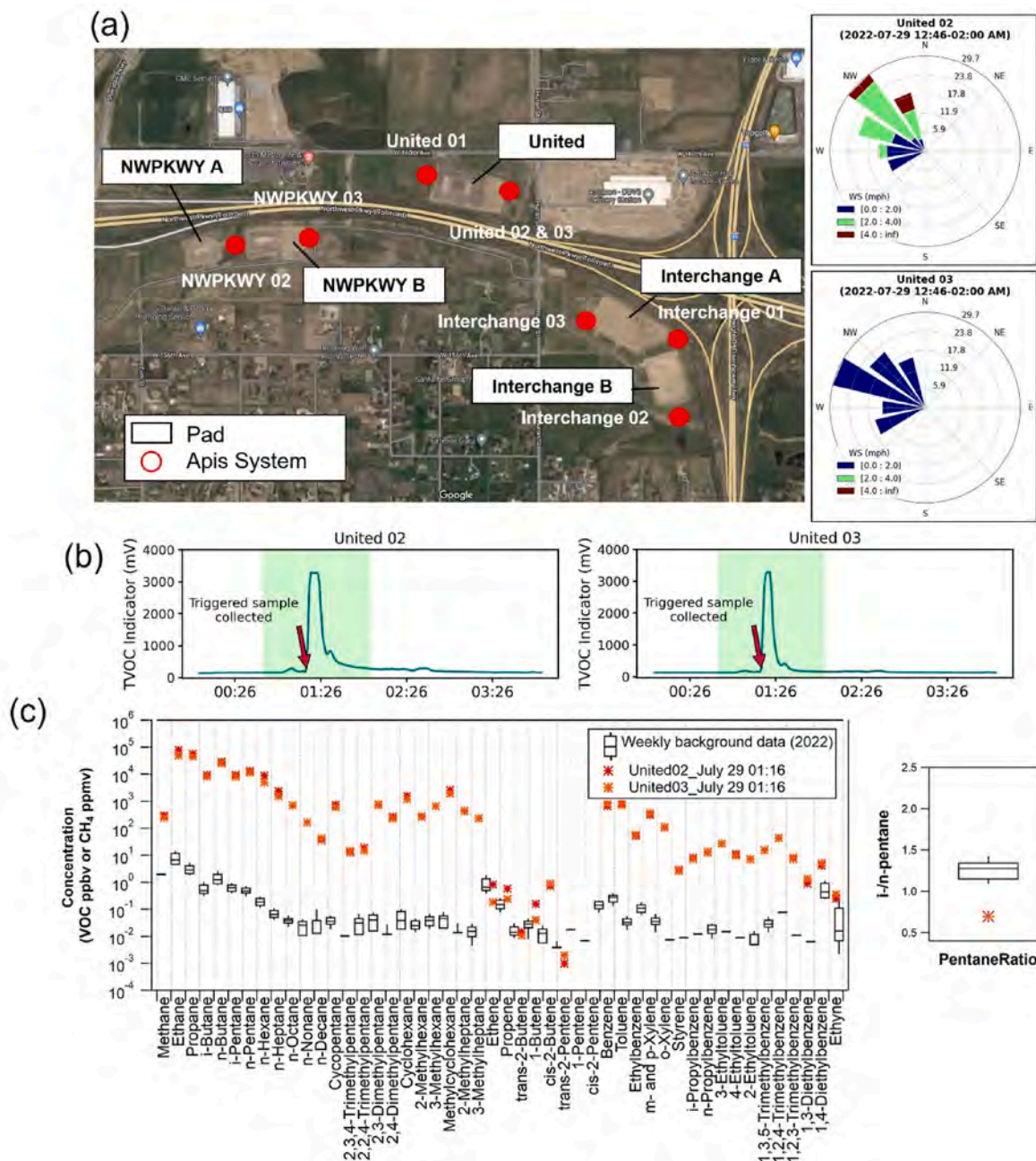


Fig. 10. (a) Wind information from 29 July 2022 at 00:46 to 02:00 LT (base map from Google map), and (b) Apis-PID response time series from the morning at the United sites. The green-shaded areas in (b) represent the time intervals of the wind data and the red arrows indicate the time triggered canister samples were collected. (c) Comparisons of VOC and i/n-pentane ratios for the triggered canister samples along with the distributions of weekly values measured at the Commons background site in 2022. The box and whisker plots show the 25th and 75th percentiles as the box, the 50th percentile as the line in the box, and the 10th and 90th percentiles as whiskers.

reveal increased concentrations of many VOCs, including alkanes and aromatics, near well pads during drilling, coiled tubing/millout and production tubing operations, and flowback.

- The use of grid-powered, electrified drill rigs in Broomfield eliminated a significant source of on-pad combustion emissions seen in previous studies (Hecobian et al., 2019), so that VOC increases near the pad bore a signature indicative of direct (uncombusted) hydrocarbon emissions, with low i/n-pentane ratios and an abundance of alkanes. Use of a synthetic, Neoflo-based drilling mud resulted in substantial increases in near-pad concentrations of C₈–C₁₀ n-alkanes during drilling operations, highlighting the importance of drilling mud handling and recycling operations to VOC emissions during

drilling. While use of the Neoflo-based drilling mud reduced odor complaints compared to a more traditional petroleum hydrocarbon-based drilling mud, emission of more reactive, long-chain alkanes should be further evaluated as precursors to photochemical ozone formation in this ozone non-attainment region.

- Previous O&G pre-production emission measurements in Colorado (Hecobian et al., 2019) found that emissions were typically largest during flowback operations. Comparison of findings from this study with those earlier measurements suggests that management practices utilized by the Broomfield O&G operator to reduce flowback emissions (e.g., use of closed-loop fluid handling systems and elimination

of permanent, on-site storage tanks from the pad) helped reduce average emissions during flowback.

- High time-resolution measurements included in the study revealed that even O&G operations that include many best management practices still emit concentrated VOC plumes, at least for short periods. The use of lower cost PID sensors that continuously monitor changes in ambient VOC levels, coupled with triggered collection of rapid-fill canister samples for offline VOC speciation, provided a powerful and cost-effective tool to permit detection and chemical characterization of short-duration VOC plumes emanating from well pads during O&G operations. Concentrated plumes were captured across a wide range of operations. The VOC compositions in these plumes provide important insight into the mix of VOCs emitted by different operations, while the timing of plume detection can help identify targets for future emission reduction strategies (e.g., concentrated plumes detected in conjunction with separator maintenance or the emptying of sand cans during closed-loop flowback operations). The short duration of detected plumes (79% were <30 min) means that fast measurement approaches are needed to adequately characterize these episodic emissions.
- Weisner et al. (2023) analyzed over 400 health surveys completed by Broomfield residents and found more frequent reports of upper respiratory and acute symptoms from adult residents living within 1.6 km (1 mile) of a well pad than those living further away (>3.2 km). We plan a future analysis to consider potential health risks associated with exposure to VOC levels observed in Broomfield. While all weekly average benzene mixing ratios, even at near-pad monitoring sites, remained well below the 3 ppbv chronic-duration inhalation minimal risk level (MRL), as defined by ATSDR (Wilbur et al., 2007), plumes captured using PID-triggered canisters contained benzene levels reaching as high as several hundred ppbv, compared to the ATSDR-defined acute-duration (14 days or less) inhalation MRL of 9 ppbv. While the acute exposure MRL has been considered by the State of Colorado as a benchmark for exposures as short as 1 h, direct comparison to air toxics concentrations in triggered canisters collected over a period less than 1 min is not appropriate. In a future study we will combine PID response timelines with measured plume VOC concentrations to extrapolate triggered canister concentrations to estimate 1-h average concentrations.

While the characterization of air quality changes associated with specific UOGD pre-production activities in this study is among the most comprehensive to date, a number of challenges remain to fully capture and describe such impacts. For example, one would ideally have even more complete measurements of emissions impacts in both space and time. As implemented, there are likely emission plumes that went undetected due to the limited number of monitoring systems around each well pad. For the many plumes that were captured, the characterization of those plumes was typically limited to a single canister sample. More continuous measurements would better characterize ranges of air toxics exposure over longer time periods, although resource and infrastructure limitations often make deployment of continuous VOC speciation monitors at numerous locations impractical. Some potentially important compounds such as formaldehyde, an air toxic and an important ozone precursor, were not measured in this study and should be a focus of future measurements. Finally, while available information about well pad operations during air monitoring was reasonably good in this study, even more detailed activity records and opportunities for on-pad monitoring could further inform interpretation of off-pad air quality measurements in future studies.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Dataset URL: <https://datadryad.org/stash/share/khttpNCg840Q05At9GdRh1FyQCqbKFsjra3G1QTz4yA>.

Acknowledgements

Funding for this work was provided by the City and County of Broomfield (CCOB). The findings, views and conclusions presented in this work are those of the authors and should not be interpreted as representing the CCOB. We are grateful to CCOB staff for providing information about well pad operations and to Detlev Helmig and Boulder AIR for housing the PTR-MS in the field and providing meteorological data used in the PTR-MS data analysis. Helpful discussions with Megan Weisner, Avesta Ehsan and Seongjun Kim have improved this manuscript.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.atmosenv.2023.120187>.

References

- Abeira, A., Pollack, I.B., Sive, B., Zhou, Y., Fischer, E.V., Farmer, D.K., 2017. Source characterization of volatile organic compounds in the Colorado Northern Front Range Metropolitan Area during spring and summer 2015. *J. Geophys. Res. Atmos.* 122, 3595–3613. <https://doi.org/10.1002/2016jd026227>.
- Akagi, S.K., Craven, J.S., Taylor, J.W., McMeeking, G.R., Yokelson, R.J., Burling, I.R., Urbanski, S.P., Wold, C.E., Seinfeld, J.H., Coe, H., Alvarado, M.J., 2012. Evolution of trace gases and particles emitted by a chaparral fire in California. *Atmos. Chem. Phys.* 12, 1397–1421. <https://doi.org/10.5194/acp12-1397-2012>.
- Atkinson, R., 1997. Gas-phase tropospheric chemistry of volatile organic compounds: 1. Alkanes and alkenes. *J. Phys. Chem. Ref. Data* 26, 215–290. <https://doi.org/10.1063/1.556012>.
- Atkinson, R., Arey, J., 2003. Atmospheric degradation of volatile organic compounds. *Chem. Rev.* 103, 4605–4638. <https://doi.org/10.1021/cr0206420>.
- Baker, A.K., Beyersdorf, A.J., Doeze, L.A., Katzenstein, A., Meinardi, S., Simpson, I.J., Blake, D.R., Sherwood Rowland, F., 2008. Measurements of nonmethane hydrocarbons in 28 United States cities. *Atmos. Environ.* 42, 170–182. <https://doi.org/10.1016/j.atmosenv.2007.09.007>.
- Bari, M.A., Kindzierski, W.B., Spink, D., 2016. Twelve-year trends in ambient concentrations of volatile organic compounds in a community of the Alberta Oil Sands Region, Canada. *Atmos. Environ. Int.* 91, 40–50. <https://doi.org/10.1016/j.envint.2016.02.015>.
- Benedict, K.B., Zhou, Y., Sive, B.C., Prenni, A.J., Gebhart, K.A., Fischer, E.V., Evansoski-Cole, A., Sullivan, A.P., Callahan, S., Schichtel, B.A., 2019. Volatile organic compounds and ozone in Rocky Mountain National Park during FRAPPE. *Atmos. Chem. Phys.* 19, 499–521. <https://doi.org/10.5194/acp-19-499-2019>.
- Brantley, H.L., Thoma, E.D., Squier, W.C., Guven, B.B., Lyon, D., 2014. Assessment of methane emissions from oil and gas production pads using mobile measurements. *Environ. Sci. Technol.* 48, 14508–14515. <https://doi.org/10.1021/es503070q>.
- Buzcu-Guven, B., Fraser, M.P., 2008. Comparison of VOC emissions inventory data with source apportionment results for Houston, TX. *Atmos. Environ.* 42, 5032–5043. <https://doi.org/10.1016/j.atmosenv.2008.02.025>.
- Buzcu, B., Fraser, M.P., 2006. Source identification and apportionment of volatile organic compounds in Houston, TX. *Atmos. Environ.* 40, 2385–2400. <https://doi.org/10.1016/j.atmosenv.2005.12.020>.
- Cheadle, L.C., Oltmans, S.J., Petron, G., Schnell, R.C., Mattson, E.J., Herndon, S.C., Thompson, A.M., Blake, D.R., McClure-Begley, A., 2017. Surface ozone in the Colorado northern Front Range and the influence of oil and gas development during FRAPPE/Discover-AQ in summer 2014. *Elem. Sci. Anth.* 5, 61–83. <https://doi.org/10.1525/elementa.254>.
- Choi, Y.-J., Ehrman, S.H., 2004. Investigation of sources of volatile organic carbon in the Baltimore area using highly time-resolved measurements. *Atmos. Environ.* 38, 775–791. <https://doi.org/10.1016/j.atmosenv.2003.10.004>.
- Colborn, T., Schultz, K., Herrick, L., Kwiatkowski, C., 2014. An exploratory study of air quality near natural gas operations. *Hum. Ecol. Risk Assess. Int. J.* 20, 86–105. <https://doi.org/10.1080/10807039.2012.749447>.
- Esswein, E.J., Snawder, J., King, B., Breitenstein, M., Alexander-Scott, M., Kiefer, M., 2014. Evaluation of some potential chemical exposure risks during flowback operations in unconventional oil and gas extraction: preliminary results. *J. Occup. Environ. Hyg.* 11, D174–D184. <https://doi.org/10.1080/15459624.2014.933960>.
- Evansoski-Cole, A., Gebhart, K., Sive, B., Zhou, Y., Capps, S., Day, D., Prenni, A., Schurman, M., Sullivan, A., Li, Y., 2017. Composition and sources of winter haze in the Bakken oil and gas extraction region. *Atmos. Environ.* 156, 77–87. <https://doi.org/10.1016/j.atmosenv.2017.02.019>.

- Field, R.A., Soltis, J., Murphy, S., 2014. Air quality concerns of unconventional oil and natural gas production. *Environ. Sci.-Proc. Imp.* 16, 954–969. <https://doi.org/10.1039/c4em00081a>.
- Ghosh, B., 2018. Impact of changes in oil and gas production activities on air quality in northeastern Oklahoma: ambient air studies in 2015–2017. *Environ. Sci. Technol.* 52, 3285–3294. <https://doi.org/10.1021/acs.est.7b05726>.
- Gilman, J.B., Lerner, B.M., Kuster, W.C., de Gouw, J.A., 2013. Source signature of volatile organic compounds from oil and natural gas operations in northeastern Colorado. *Environ. Sci. Technol.* 47, 1297–1305. <https://doi.org/10.1021/es304119a>.
- Gilman, J.B., Kuster, W.C., Goldan, P.D., Herndon, S.C., Zahniser, M.S., Tucker, S.C., Brewer, W.A., Lerner, B.M., Williams, E.J., Harley, R.A., Fehsenfeld, F.C., Warneke, C., De Gouw, J.A., 2009. Measurements of volatile organic compounds during the 2006 TexAQs/GoMACCS campaign: industrial influences, regional characteristics, and diurnal dependencies of the OH reactivity. *J. Geophys. Res.* Atmos. 114, 1–17. <https://doi.org/10.1029/2008JD011525>.
- Gkatzelis, G.I., Coggon, M.M., McDonald, B.C., Peischl, J., Aikin, K.C., Gilman, J.B., Trainer, M., Warneke, C., 2021. Identifying volatile chemical product tracer compounds in U.S. Cities. *Environ. Sci. Technol.* 55, 188–199. <https://doi.org/10.1021/acs.est.0c05467>.
- Halliday, H.S., Thompson, A.M., Wisthaler, A., Blake, D.R., Hornbrook, R.S., Mikoviny, T., Müller, M., Eichler, P., Apel, E.C., Hills, A.J., 2016. Atmospheric benzene observations from oil and gas production in the Denver-Julesburg Basin in July and August 2014. *J. Geophys. Res. Atmos.* 121, 11055–11074. <https://doi.org/10.1002/2016JD025327>.
- Hecobian, A., Clements, A.L., Shonkwiler, K.B., Zhou, Y., MacDonald, L.P., Hilliard, N., Wells, B.L., Bibeau, B., Ham, J.M., Pierce, J.R., Collett, J.L., 2019. Air toxics and other volatile organic compound emissions from unconventional oil and gas development. *Environ. Sci. Technol. Lett.* 6, 720–726. <https://doi.org/10.1021/acs.estlett.9b00591>.
- Helmig, D., Thompson, C., Evans, J., Boylan, P., Hueber, J., Park, J.-H., 2014. Highly elevated atmospheric levels of volatile organic compounds in the Uintah Basin, Utah. *Environ. Sci. Technol.* 48, 4707–4715. <https://doi.org/10.1021/es405046r>.
- Hildenbrand, Z.L., Mach, P.M., McBride, E.M., Dorreyatim, M.N., Taylor, J.T., Carlton Jr., D.D., Meik, J.M., Fontenot, B.E., Wright, K.C., Schug, K.A., 2016. Point source attribution of ambient contamination events near unconventional oil and gas development. *Sci. Total Environ.* 573, 382–388. <https://doi.org/10.1016/j.scitotenv.2016.08.118>.
- Hobbs, P.V., Sinha, P., Yokelson, R.J., Christian, T.J., Blake, D.R., Gao, S., Kirchstetter, T. W., Novakov, T., Pilewskie, P., 2003. Evolution of gases and particles from a savanna fire in South Africa. *J. Geophys. Res.* 108, 8485. <https://doi.org/10.1029/2002JD002352>.
- Holder, C., Hader, J., Avanas, R., Hong, T., Carr, E., Mendez, B., Wignall, J., Glen, G., Guelden, B., Wei, Y., 2019. Evaluating potential human health risks from modeled inhalation exposures to volatile organic compounds emitted from oil and gas operations. *J. Air Waste Manag. Assoc.* 69 (12), 1503–1524. <https://doi.org/10.1080/10962247.2019.1680459>.
- Jaroslowski, J., Pawlak, I., Guzowski, J., Pietruczuk, A., 2022. Impact of shale gas exploration and exploitation activities on the quality of ambient air - the case study of Wyzin, Poland. *Atmosphere* 13 (8), 1228. <https://doi.org/10.3390/atmos13081228>.
- Jobson, B.T., Berkowitz, C.M., Kuster, W.C., Goldan, P.D., Williams, E.J., Fehsenfeld, F.C., Apel, E.C., Karl, T., Lonneman, W.A., Riemer, D., 2004. Hydrocarbon source signatures in Houston, Texas: influence of the petrochemical industry. *J. Geophys. Res. Atmos.* 109, D24305. <https://doi.org/10.1029/2004jd004887>.
- Karl, T., Apel, E., Hodzic, A., Riemer, D.D., Blake, D.R., Wiedinmyer, C., 2009. Emissions of volatile organic compounds inferred from airborne flux measurements over a megacity. *Atmos. Chem. Phys.* 9, 271–285. <https://doi.org/10.5194/acp-9-271-2009>.
- Leuchner, M., Rappenglück, B., 2010. VOC source–receptor relationships in Houston during TexAQs-II. *Atmos. Environ.* 44, 4056–4067. <https://doi.org/10.1016/j.atmosenv.2009.02.029>.
- Lindaas, J., Farmer, D.K., Pollack, I.B., Abeleira, A., Flocke, F., Fischer, E.V., 2019. Acyl peroxy nitrates link oil and natural gas emissions to high ozone abundances in the Colorado Front Range during summer 2015. *J. Geophys. Res. Atmos.* 124, 2336–2350. <https://doi.org/10.1029/2018JD028825>.
- Macey, G.P., Breech, R., Chernaik, M., Cox, C., Larson, D., Thomas, D., Carpenter, D.O., 2014. Air concentrations of volatile compounds near oil and gas production: a community-based exploratory study. *Environ. Health* 13, 82. <https://doi.org/10.1186/1476-069X13-82>.
- McDuffie, E.E., Edwards, P.M., Gilman, J.B., Lerner, B.M., Dube, W.P., Trainer, M., Wolfe, D.E., Angevine, W.M., deGouw, J., Williams, E.J., Tevlin, A.G., Murphy, J.G., Fischer, E.V., McKeen, S., Ryerson, T.B., Peischl, J., Holloway, J.S., Aikin, K., Langford, A.O., Senff, C.J., Alvarez, R.J., Hall, S.R., Ullmann, K., Lantz, K.O., Brown, S.S., 2016. Influence of oil and gas emissions on summertime ozone in the Colorado Northern Front Range. *J. Geophys. Res. Atmos.* 121, 8712–8729. <https://doi.org/10.1002/2016jd025265>.
- McKenzie, L.M., Allhouse, W.B., Burke, T., Blair, B.D., Adgate, J.L., 2016. Population size, growth, and environmental justice near oil and gas wells in Colorado. *Environ. Sci. Technol.* 50 (21), 11471–11480. <https://doi.org/10.1021/acs.est.6b04391>.
- McKenzie, L.M., Blair, B., Hughes, J., Allhouse, W.B., Blake, N.J., Helmig, D., Milmoie, P., Halliday, H., Blake, D.R., Adgate, J.L., 2018. Ambient nonmethane hydrocarbon levels along Colorado's Northern Front Range: acute and chronic health risks. *Environ. Sci. Technol.* 52, 4514–4525. <https://doi.org/10.1021/acs.est.7b05983>.
- McMullin, T.S., Bamber, A.M., Bon, D., Vigil, D.I., Van Dyke, M., 2018. Exposures and health risks from volatile organic compounds in communities located near oil and gas exploration and production activities in Colorado (USA). *Int. J. Environ. Res. Publ. Health* 15 (7), 1500. <https://doi.org/10.3390/ijerph15071500>.
- Na, K., Kim, Y.P., Moon, I., Moon, K.-C., 2004. Chemical composition of major VOC emission sources in the Seoul atmosphere. *Chemosphere* 55, 585–594. <https://doi.org/10.1016/j.chemosphere.2004.01.010>.
- O'Dell, K., Hornbrook, R.S., Permar, W., Levin, E.J.T., Garofalo, L.A., Apel, E.C., Blake, N.J., Jarnot, A., Pothier, M.A., Farmer, D.K., Hu, L., Campos, T., Ford, B., Pierce, J.R., Fischer, E.V., 2020. Hazardous air pollutants in fresh and aged western US wildfire smoke and implications for long-term exposure. *Environ. Sci. Technol.* 54, 11838–11847. <https://doi.org/10.1021/acs.est.0c04497>.
- Orak, N.H., Reeder, M., Pekney, N.J., 2021. Identifying and quantifying source contributions of air quality contaminants during unconventional shale gas extraction. *Atmos. Chem. Phys.* 21, 4729–4739. <https://doi.org/10.5194/acp-21-4729-2021>.
- Peng, Q., Palm, B.B., Fredrickson, C.D., Lee, B.H., Hall, S.R., Ullmann, K., Campos, T., Weinheimer, A.J., Apel, E.C., Flocke, F., 2021. Observations and modeling of NOx photochemistry and fate in fresh wildfire plumes. *ACS Earth Space Chem.* 5, 2652–2667. <https://doi.org/10.1021/acsearthspacechem.1c00086>.
- Permar, W., Wang, Q., Selimovic, V., Wielgasz, C., Yokelson, R.J., Hornbrook, R.S., Hills, A.J., Apel, E.C., Ku, I.-T., Zhou, Y., Sive, B.C., Sullivan, A.P., Collett Jr., J.L., Campos, T.L., Palm, B.B., Peng, Q., Thornton, J.A., Garofalo, L.A., Farmer, D.K., Kreidenweis, S.M., Levin, E.J.T., DeMott, P.J., Flocke, F., Fischer, E.V., Hu, L., 2021. Emissions of trace organic gases from western U.S. wildfires based on WE-CAN aircraft measurements. *J. Geophys. Res.* 126, e2020JD033838. <https://doi.org/10.1029/2020JD033838>.
- Pétron, G., Frost, G., Miller, B.R., Hirsch, A.I., Montzka, S.A., Karion, A., Trainer, M., Sweeney, C., Andrews, A.E., Miller, L., Kofler, J., Bar-Ilan, A., Dlugokencky, E.J., Patrick, L., Moore Jr., C.T., Ryerson, T.B., Siso, C., Kolodzey, W., Lang, P.M., Conway, T., Novelli, P., Masarie, K., Hall, B., Guenther, D., Kitzis, D., Miller, J., Welsh, D., Wolfe, D., Neff, W., Tans, P., 2012. Hydrocarbon emissions characterization in the Colorado Front Range: a pilot study. *J. Geophys. Res. Atmos.* 117, D04304. <https://doi.org/10.1029/2011JD016360>.
- Pétron, G., Karion, A., Sweeney, C., Miller, B.R., Montzka, S.A., Frost, G.J., Trainer, M., Tans, P., Andrews, A., Kofler, J., Helmig, D., Guenther, D., Dlugokencky, E., Lang, P., Newberger, T., Wolter, S., Hall, B., Novelli, P., Brewer, A., Conley, S., Hardesty, M., Banta, R., White, A., Noone, D., Wolfe, D., Schnell, R., 2014. A new look at methane and nonmethane hydrocarbon emissions from oil and natural gas operations in the Colorado Denver-Julesburg Basin. *J. Geophys. Res. Atmos.* 119, 6836–6852. <https://doi.org/10.1002/2013JD021272>.
- Pollack, I.B., Helmig, D., O'Dell, K., Fischer, E.V., 2021. Seasonality and source apportionment of nonmethane volatile organic compounds at Boulder Reservoir, Colorado, between 2017 and 2019. *J. Geophys. Res. Atmos.* 126, e2020JD034234. <https://doi.org/10.1029/2020JD034234>.
- Prenni, A.J., Day, D.E., Evanowski-Cole, A.R., Sive, B.C., Hecobian, A., Zhou, Y., Gebhart, K.A., Hand, J.L., Sullivan, A.P., Li, Y., Schurman, M.I., Desyaterik, Y., Malm, W.C., Collett Jr., J.L., Schichtel, B.A., 2016. Oil and gas impacts on air quality in federal lands in the Bakken region: an overview of the Bakken Air Quality Study and first results. *Atmos. Chem. Phys.* 16, 1401–1416. <https://doi.org/10.5194/acp-16-1401-2016>.
- Roest, G.S., Schade, G.W., 2020. Air quality measurements in the western Eagle ford shale. *Elem. Sci. Anth.* 8, 18. <https://doi.org/10.1525/elementa.414>.
- Russo, R.S., Zhou, Y., White, M.L., Mao, H., Talbot, R., Sive, B.C., 2010. Multi-year (2004–2008) record of nonmethane hydrocarbons and halocarbons in New England: seasonal variations and regional sources. *Atmos. Chem. Phys.* 10, 4909–4929. <https://doi.org/10.5194/acp-10-4909-2010>.
- Rutter, A.P., Griffin, R.J., Cevik, B.K., Shakya, K.M., Gong, L., Kim, S., Flynn, J.H., Lefer, B.L., 2015. Sources of air pollution in a region of oil and gas exploration downwind of a large city. *Atmos. Environ.* 120, 89–99. <https://doi.org/10.1016/j.atmosenv.2015.08.073>.
- Ryerson, T.B., Trainer, M., Angevine, W.M., Brock, C.A., Dissly, R.W., Fehsenfeld, F.C., Frost, G.J., Goldan, P.D., Holloway, J.S., Hübler, G., Jakoubek, R.O., Kuster, W.C., Neuman, J.A., Nicks Jr., D.K., Parrish, D.D., Roberts, J.M., Sueper, D.T., Atlas, E.L., Donnelly, S.G., Flocke, F., Fried, A., Potter, W.T., Schaeffer, S., Stroud, V., Weinheimer, A.J., Wert, B.P., Wiedinmyer, C., Alvarez, R.J., Banta, R.M., Darby, L. S., Senff, C.J., 2003. Effect of petrochemical industrial emissions of reactive alkenes and NOx on tropospheric ozone formation in Houston, Texas. *J. Geophys. Res.* 108, 4249. <https://doi.org/10.1029/2002JD003070>.
- Schade, G.W., Roest, G., 2016. Analysis of non-methane hydrocarbon data from a monitoring station affected by oil and gas development in the Eagle Ford shale. *Texas. Elementa* 4, 000096. <https://doi.org/10.12952/journal.elementa.000096>.
- Schade, G.W., Roest, G., 2018. Source apportionment of non-methane hydrocarbons, NOx and H2S data from a central monitoring station in the Eagle Ford shale, Texas. *Elem. Sci. Anth.* 6, 35. <https://doi.org/10.1525/elementa.289>.
- Simpson, I.J., Blake, N.J., Barletta, B., Diskin, G.S., Fuelberg, H.E., Gorham, K., Huey, L. G., Meinardi, S., Rowland, F.S., Vay, S.A., Weinheimer, A.J., Yang, M., Blake, D.R., 2010. Characterization of trace gases measured over Alberta oil sands mining operations: 76 speciated C2–C10 volatile organic compounds (VOCs), CO2, CH4, CO, NO, NO2, NOy, O3 and SO2. *Atmos. Chem. Phys.* 10, 11931–11954. <https://doi.org/10.5194/acp-10-11931-2010>.
- Sive, B.C., Zhou, Y., Troop, D., Wang, Y., Little, W.C., Wingenter, O.W., Russo, R.S., Varner, R.K., Talbot, R., 2005. Development of a cryogen-free concentration system for measurements of volatile organic compounds. *Anal. Chem.* 77, 6989–6998. <https://doi.org/10.1021/ac0506231>.

- Sullivan, J.T., McGee, T.J., Langford, A.O., Alvarez, R.J., Senff, C.J., Reddy, P.J., Thompson, A.M., Twigg, L.W., Sumnicht, G.K., Lee, P., Weinheimer, A., Knote, C., Long, R.W., Hoff, R.M., 2016. Quantifying the contribution of thermally driven recirculation to a high-ozone event along the Colorado Front Range using lidar. *J. Geophys. Res. Atmos.* 121 (1), 377–310390. <https://doi.org/10.1002/2016JD025229>.
- Swarthout, R.F., Russo, R.S., Zhou, Y., Hart, A.H., Sive, B.C., 2013. Volatile organic compound distributions during the NACHTT campaign at the Boulder Atmospheric Observatory: influence of urban and natural gas sources. *J. Geophys. Res. Atmos.* 118, 10614–10637. <https://doi.org/10.1002/jgrd.50722>.
- Thompson, C.R., Hueber, J., Helmig, D., 2014. Influence of oil and gas emissions on ambient atmospheric non-methane hydrocarbons in residential areas of Northeastern Colorado. *Elem. Sci. Anth.* 3, 35. <https://doi.org/10.12952/journal.elementa.000035>.
- Warneke, C., Geiger, F., Edwards, P.M., Dube, W., Pétron, G., Kofler, J., Zahn, A., Brown, S.S., Graus, M., Gilman, J.B., Lerner, B.M., Peischl, J., Ryerson, T.B., de Gouw, J.A., Roberts, J.M., 2014. Volatile organic compound emissions from the oil and natural gas industry in the Uintah Basin, Utah: oil and gas well pad emissions compared to ambient air composition. *Atmos. Chem. Phys.* 14, 10977–10988. <https://doi.org/10.5194/acp-14-10977-2014>.
- Weisner, M.L., Allshouse, W.B., Erjavac, B.W., Valdez, A.P., Vahling, J.L., McKenzie, L.M., 2023. Health symptoms and proximity to active multi-well unconventional oil and gas development sites in the city and county of Broomfield, Colorado. *Int. J. Environ. Res. Publ. Health* 20 (3), 2634. <https://doi.org/10.3390/ijerph20032634>.
- Wilbur, S.B., Keith, S., Faroon, O., Wohlers, D., 2007. *Toxicological Profile for Benzene*. Wilde, S.E., Dominutti, P.A., Allen, G., Andrews, S.J., Bateson, P., Bauguitte, S.J.-B., Burton, R.R., Colfescu, I., France, J., Hopkins, J.R., Huang, L., Jones, A.E., Lachlan-Cope, T., Lee, J.D., Lewis, A.C., Mobbs, S.D., Weiss, A., Young, S., Purvis, R.M., 2021. Speciation of VOC emissions related to offshore North Sea oil and gas production. *Atmos. Chem. Phys.* 21, 3741–3762. <https://doi.org/10.5194/acp-21-3741-2021>.
- Yokelson, R.J., Bertschi, I.T., Christian, T.J., Hobbs, P.V., Ward, D.E., Hao, W.M., 2003. Trace gas measurements in nascent, aged, and cloud-processed smoke from African savanna fires by airborne Fourier transform infrared spectroscopy (AFTIR). *J. Geophys. Res.* 108, 8478. <https://doi.org/10.1029/2002JD002322>.
- Yokelson, R.J., Crounse, J.D., DeCarlo, P.F., Karl, T., Urbanski, S., Atlas, E., Campos, T., Shinozuka, Y., Kapustin, V., Clarke, A.D., Weinheimer, A., Knapp, D.J., Montzka, D. D., Holloway, J., Weibring, P., Flocke, F., Zheng, W., Toohey, D., Wennberg, P.O., Wiedinmyer, C., Mauldin, L., Fried, A., Richter, D., Walega, J., Jimenez, J.L., Adachi, K., Buseck, P.R., Hall, S.R., Shetter, R., 2009. Emissions from biomass burning in the Yucatan. *Atmos. Chem. Phys.* 9, 5785–5812. <https://doi.org/10.5194/acp-9-5785-2009>.
- Zheng, H., Kong, S., Xing, X., Mao, Y., Hu, T., Ding, Y., Li, G., Liu, D., Li, S., Qi, S., 2018. Monitoring of volatile organic compounds (VOCs) from an oil and gas station in northwest China for 1 year. *Atmos. Chem. Phys.* 18, 4567–4595. <https://doi.org/10.5194/acp-18-4567-2018>.
- Zhou, Y., Varner, R.K., Russo, R.S., Wingenter, O.W., Haase, K.B., Talbot, R., Sive, B.C., 2005. Coastal water source of shortlived halocarbons in New England. *J. Geophys. Res. Atmos.* 110, D21302. <https://doi.org/10.1029/2004jd005603>.