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Cumulative Human Health Risk Assessment of Regional Ozone and Volatile Organic Compounds from Unconventional Oil and Gas Sites in Colorado's Front Range

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Background: Most unconventional oil and gas (UOG) extraction in Colorado occurs within the Denver Metro/North Front Range (DMNFR) ozone Nonattainment Area (NAA). Previous UOG human health risk assessments do not consider cumulative risk from both volatile organic compounds (VOCs) and criteria air pollutants like ozone.

Methods: We conducted a cumulative human health risk assessment (CHHRA) using regulatory-grade 1- and 8-h ozone measurements from a DMNFR US Environmental Protection Agency (US EPA) monitoring station and weekly and short-term (15 s–1 min) VOC air quality monitoring data collected between 2018–2023 from 10 near-pad air monitoring sites, three community sites, and one background site. Acute and chronic noncancer hazard indices (HIs) for multiple health end points, as well as cancer risks, were calculated during well drilling, well completions, and production activity periods and compared between sites. VOC concentrations were compared between operations that used a petroleum-based drilling fluid vs. a synthetic drill fluid. Differences in weekly chemical concentrations between sites, UOG phases, and drill muds were analyzed using repeated measures analysis of variance with post hoc pairwise comparisons with Bonferroni adjustment.

Results: Acute HIs of VOCs and ozone ranged from 1.34×10^{-4} to 31.33 at the 95th percentile concentrations at all sites. One of the three community monitoring sites, Anthem, exceeded US EPA thresholds for respiratory, immunological, and developmental end points during production and for the immunological end point during well completions. At the near-pad sites, acute hazards exceeded US EPA thresholds during well completions for immunological, respiratory, reproductive, developmental, and neurological end points. Neurological and immunological HIs were above thresholds for the drilling phase at near-pad sites. Chronic HIs ranged from 8.43×10^{-4} to 0.47 at 95th percentile concentrations and, therefore, were below the HI threshold for all near-pad and community sites for all health end points. Cancer risks ranging from 209 to 335 in a million at 95th percentile concentrations were above US EPA thresholds for all sites, including the background site, which is more heavily influenced by Denver Metro traffic emissions.

Conclusions: Our results suggest that for communities located near UOG well pads in the DMNFR ozone NAA, acute health risks persist after the implementation of best management practices to reduce emissions. Greater protection to public health could be afforded by establishing policies that require drilling and well completions to be conducted outside the summer ozone season. Further research is needed to address potential health risks from the use of synthetic drilling fluid. https://doi.org/10.1289/EHP16272

Introduction

Unconventional Oil and Gas Development

United States crude oil exports set a record in 2023, averaging 4.1 million barrels per day.[1] Because of the technological advances in unconventional oil and gas (UOG) extraction, which includes methods such as hydraulic fracturing and horizontal drilling, newly drilled oil and gas wells in the United States are more productive despite a 69% decrease in the number of active drilling rigs since 2014, when the drilling boom surged to its highest level.[2] As of October 2023, the United States accounted for 16% of global crude oil production.[3]

UOG development and production emit volatile organic compounds (VOCs) into the air,[4] with plume compositions that are complex and vary depending on the specific phase of operation.[5–8] The process of UOG well development typically includes multiple phases of preproduction before a well is in production. Well development includes drilling and well completions (which includes hydraulic fracturing, coiled tubing/millout and installation of production tubing, and flowback). During the drilling phase, wells are drilled vertically for thousands of meters and then may be extended directionally or horizontally.[9] A synthetic or diesel-based hydrocarbon drill fluid, mixed to create a "drill mud," is used to lubricate the drill bit and achieve greater depths in the hydrocarbon bearing zones. Hydrocarbon-based drilling mud formulations may be used depending on the nature of the reservoir, or synthetic fluids may be used to reduce odors.[8] Each type of drilling fluid will have its own VOC composition to assist in moving rock cuttings up the wellbore. At the surface, cuttings are separated from the drilling mud, which is recycled, and disposed of in a timely manner to minimize air pollution impacts to the surrounding environment.[10] Hydraulic fracturing is then performed to create fractures in the hydrocarbon formation, allowing the oil and gas, fracturing fluid, and produced water to flow to the surface during the flowback phase. Prior to flowback, coiled tubing/millout and installation of production tubing occur.[8] Well development can take many months, because a single UOG site can host dozens of wells.

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Oil and Gas Development in Colorado's Ozone Nonattainment Area

The Denver-Julesburg (DJ) Basin, which produces oil and natural gas, lies beneath the major population center in the state, commonly referred to as the "Front Range." This region also falls within the Denver Metro/North Front Range (DMNFR) ozone Nonattainment Area (NAA).[11] Tropospheric ozone forms when VOCs and nitrogen oxides (NO_x) react in the presence of sunlight.[12] The Front Range is expected to grow by 2% each year, reaching 6.4 million people by 2050.[13] To reduce surface disturbances of overall UOG extraction, which can benefit the broader population, a single UOG well pad often houses dozens of wells.[14] However, this density of wells may increase cumulative exposure to hazardous air pollutants (HAPs) for those living near more intensive operations.

Colorado ranks among the top 10 in the nation for total energy production by state and fourth for crude oil production.[15] The increase of UOG well density within a growing population center presents challenges to reducing ozone. The DMNFR has been a violator of the of the US Environmental Protection Agency (US EPA) National Ambient Air Quality Standard (NAAQS) for ozone since 2007[16] and in 2022, was classified as a "severe" violator of the 2008 standard of 75 parts per billion (ppb).[17] During the 2024 summer ozone season, the region experienced 40 d where ozone levels surpassed either the 2008 or the 2015 ozone standard of 70 ppb.[18] Although the State Implementation Plan (SIP) outlines a path forward to ozone compliance for both the 2008 and 2015 standards,[19] the 2024 summer ozone season saw more exceedance days than 8 of the past 10 y, and monitors outside the NAA also saw an increase in ozone exceedance days.[18,20]

The oil and gas industry emits a significant portion of both NO_x and VOC precursors that drive formation of ozone and associated NAAQS violations during summer months.[4–6,21,22] It is well established that control of both VOC and NO_x emissions is imperative to reduce ozone levels and mitigate health outcomes.[23]

Health Impacts from VOCs and Ozone

Previous studies found that associations between oil- and gas-related noise[24] and air pollution and potential human health impacts occur at distances up to 1.6 km (1 mi) from UOG well pads.[24–27] Research has also demonstrated relationships between UOG sites and adverse human health outcomes including increased mortality risk in the elderly,[28] cardiovascular disease and atrial fibrillation exacerbations,[26,29–31] asthma exacerbations,[32,33] adverse birth outcomes,[34–42] congenital heart defects,[43] childhood hematological cancer,[44,45] heightened psychosocial stress, and increased reporting of upper respiratory and skin conditions.[27,46–49]

Human health risk assessments indicate increased risks from living near oil and gas well pads for cancer and respiratory, neurological, and hematological impacts from UOG-emitted VOCs, including benzene, toluene, ethylbenzene, and xylenes (BTEX).[25,50,51] According to both human and *in vivo* studies, benzene exposure has been associated with various forms of leukemia,[52–54] and exposure to xylenes may cause respiratory effects.[55] In addition, health effects from ozone are well documented and often impact health end points in ways that are similar to those of VOCs. Epidemiological studies find exposure to ozone can impact cardiovascular, respiratory and coronary diseases, hypertension,[56–58] inflammatory markers,[59] and asthma development in children.[60]

However, human health risk assessments, particularly noncancer assessments, do not address a chemical's ability to contribute to multiple health end points. Rather, they rely on assessment of risk from the most sensitive end point for the chemical because reference concentrations (RfCs) are based on this most sensitive end point.[61] These health effects that occur at higher concentrations than the most sensitive effect may be significant if considered in the context of cumulative exposures to multiple chemicals causing the same effects.[62] Previous work has used measured and modeled air data collected from UOG sites in western Colorado and the DJ Basin and applied the data to estimate human health risks for people living near UOG operations[50,51,63]; however, emissions have changed significantly since these studies,[8] and those risk assessments did not consider coexposure to ozone in the DMNFR ozone NAA.

The objective of this cumulative human health risk assessment (CHHRA) is to go beyond the standard risk assessment framework by quantifying cumulative cancer and noncancer health risks from short-term (acute) and long-term (chronic) exposure to ozone and VOCs during UOG drilling, well completions, and production. This research builds on two previous studies that assessed both the human health impacts[27] and changes in local HAPs resulting from oil and gas activity at the same UOG well pads in the DMNFR.[8] Our study design builds on this previous research but accounts for a more accurate picture of real-world exposure to multiple chemicals for communities living near UOG sites by considering multiple health risks from chemicals rather than only assessing risks to the most sensitive end point.

Methods

Study Area

The City and County of Broomfield (CCOB) is located within the DMNFR ozone NAA (midway between Denver and Boulder) and has a population of ~76,000.[64] During the period 2018–2023, an oil and gas operator developed more than 60 wells across 6 UOG well pads in a rapidly urbanizing area of north/central Broomfield (Figure 1). Number of oil and gas wells and location data were obtained from the Colorado Energy and Carbon Management Commission (ECMC).[65]

Colorado passed Senate Bill 19-181 in 2019, which paved the way for the adoption of more stringent oil and gas regulations across the state.[66] The bill increased the state setback distance to 610 m (2,000 ft) and gave greater power to local governments to regulate oil and gas activities. However, SB Bill 19-181 allowed operations to proceed at UOG sites already permitted by the State of Colorado at distances closer than 610 m, such as those in Broomfield. The nearest residences are ~300 m from the Livingston pad and are in an age 55 y and up community. Furthermore, approximately 2,000 residential parcels are located within a 1.6-km (1-mi) radius of the Livingston well pad. Because of concerns about air pollution and noise impacts, the local government established and funded its own oil and gas inspection program, with daily personnel visits to the well pads as well as an extensive air quality monitoring (AQM) program.[8,67] Despite the implementation of some of the most extensive best management practices (BMPs) to reduce emissions, numerous plumes of VOCs were released during UOG operations, such as drilling, flowback, and maintenance.[8]

VOC Data Source

VOC data from weekly and short-term ambient VOC concentrations measured at 14 different locations (see Figure 1) were used for our CHHRA.

VOC data at all near-pad, community, and background sites were collected from 2018 to 2023 by Ajax Analytics and the Colorado State University (CSU) Department of Atmospheric Science for the CCOB AQM program.[68] VOC air monitoring

data are made publicly available[69] and were provided to us in Excel format by CSU on behalf of CCOB. ArcGIS Pro version 3.1.0 was used to map locations of oil and gas pads, air monitors, and the closest distances to nearby residential communities that are located within the 610-m state setback and may experience oil- and gas-related air pollution events. Geospatial data for oil and gas locations were provided by the Colorado Energy and Carbon Management Commission.[65] Residential parcel data were sourced from the CCOB,[70] and air monitoring locations were provided by Ajax Analytics.[69]

VOC concentrations were measured at 10 near-pad AQM sites located at distances as close as 45 m from a UOG well pad. VOC concentrations were also measured at three community monitoring sites located 300 m to 900 m from the Livingston UOG well pad. Background VOC concentrations were measured at an AQM site about 5 km (3 mi) south of the Broomfield UOG well pads and away from other UOG activities. IonScience MiniPID2 sensors were used in both Apis AQ sensor systems and Sensit SPOD sensor systems. The sensor was polled every second to get a measurement, and these 1-s measurements were then averaged into 10-s or 15-s measurement time resolutions. All AQM analysis was performed against the raw millivolt (mV) signal and not influenced by user calibration settings.

Ozone Data Source

Hourly and 8-h ozone concentrations were sourced from the US EPA data repository for the years 2018 through 2023.[71] Data were extracted from Rocky Flats monitoring station site number 6, located 14.5 km (about 9 mi) from the study site and within the DMNFR ozone NAA. Figure 2 provides an overview of how data sources and sample intervals were used to inform our CHHRA. In brief, we used air monitoring data from two sources (VOC data collected by the CCOB AQM program and ozone data sourced from the US EPA). AQM data was sorted by sample interval time frame for both VOC and ozone datasets. All samples were then applied to the appropriate risk assessment (i.e., acute, chronic, cancer).

AQM Sample Collection

Details of sample collection and analysis are thoroughly described in Ku et al.[8] In brief, weekly integrated ambient air samples were collected in evacuated 6.0-L Silonite-coated canisters with flow-regulation systems. Each real-time monitoring system is equipped with a meteorological sensor to measure wind, temperature, humidity, and pressure and a Photoionization Detector (PID) sensor coupled with an automatic canister triggering system to detect changing levels of total VOCs and characterize the chemical

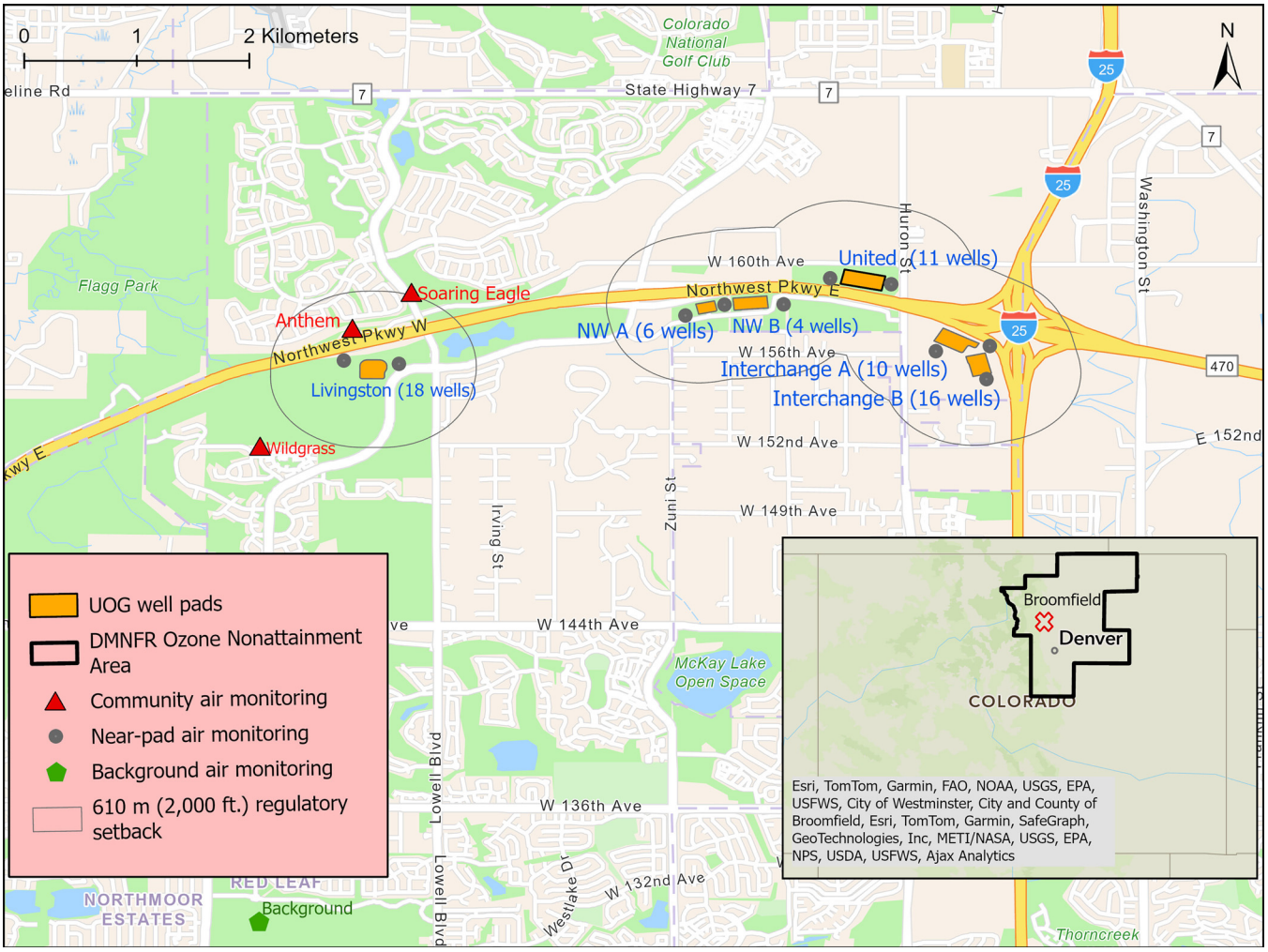

Figure 1. Locations of UOG well pads, number of wells, and community, near-pad, and background air quality monitors around the City and County of Broomfield, Colorado. Names of near-pad air monitors correspond with UOG well pad names. Gray outlines around well pads represent regulatory setback distance of 610 m (2,000 ft). The black outline in the insert represents the DMNFR ozone nonattainment area, and the red X represents the location of Broomfield, Colorado. Map image created with ArcGIS Pro version 3.1.0. Note: UOG, unconventional oil and gas.

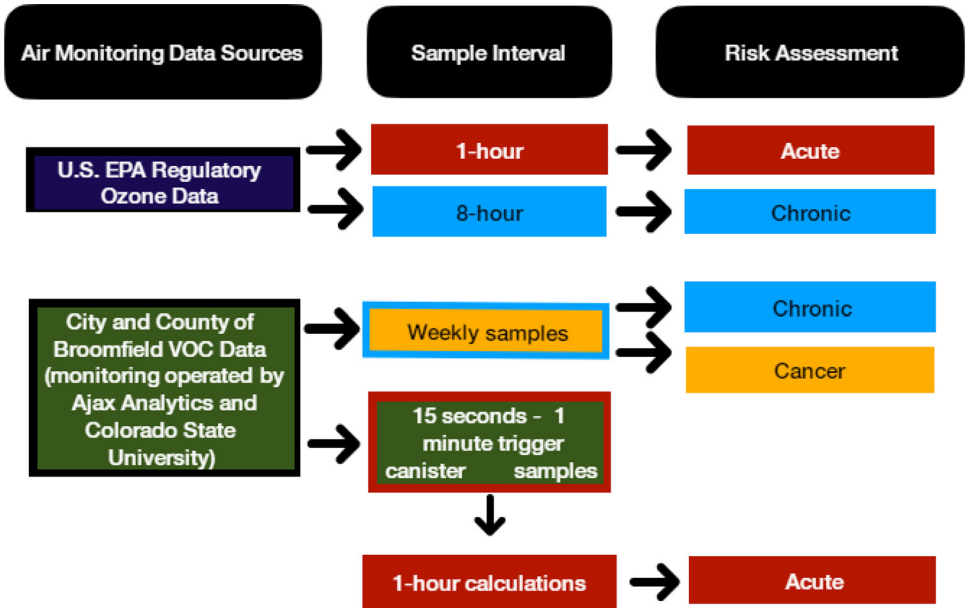

Figure 2. Flowchart demonstrating the data sources and sample interval lengths used in each portion of the CHHRA. The acute risk assessment used 1-h ozone data from the US EPA and 1-h VOC concentrations (extrapolated from 15 s–1 min trigger canister data) collected by the CCOB air quality monitoring program. The chronic risk assessment used EPA 8-h ozone data and weekly VOC data from the CCOB. The cancer risk assessment used weekly VOC data from CCOB. Note: CCOB, City and County of Broomfield; CHHRA, cumulative human health risk assessment; US EPA, US Environmental Protection Agency; VOC, volatile organic compound.

composition of detected elevated emission plumes. The triggered threshold was set between 300 and 1,500 mV (baseline signal ranged from 80 to 150 mV) at different locations to capture peak VOC plume concentration levels. When systems detected VOC-rich plumes, triggered canisters were filled quickly (~ 15 s) to collect air samples. The canisters were analyzed for methane and 50 VOCs, including C_2-C_{10} linear, branched, and cyclic alkanes; alkenes; alkynes; aromatics; and C_2 halocarbons by a custom multichannel gas chromatography system with five detectors (three flame ionization detectors, one electron capture detector, and one mass spectrometer). In total, 2,277 weekly samples and 88 triggered samples collected between October 2018 and December 2023 were considered for chronic and acute health risk evaluation, respectively.

One-Hour VOC Calculations

Numerous short periods of elevated VOC plume intercepts (typically lasting from minutes to hours, with a median duration of 15 min) were observed by the PID sensors during various UOG well-development and production operations. Triggered canister samples collected in these plumes provided information about the composition and concentration of VOCs in the air during these events. However, these short-term (15 s–1 min) measured concentration values are not directly comparable with published exposure guidelines or reference values from different organizations that generally assume continuous exposure for 1 h or longer. Therefore, we estimated 1-h mixing ratios of measured VOCs using a method developed by Ajax Analytics,[72] with some minor modifications including: *a*) using average weekly measurements to calculate background factors for consistency; *b*) removing background influence when calculating event factors; and *c*) replacing 1-h estimated values with background measurements for compounds that were not enhanced in the plumes. High time resolution PID signals and canister sample speciation data were used to estimate 1-h VOC mixing ratios during plume detect periods. This method provided a more accurate estimation of 1-h VOCs levels in comparison with assuming a single measured concentration represented the entire hour, which is crucial for evaluating community-level exposure in health risk assessments.[73]

Before conducting the estimation, we first examined the concentrations of all compounds in the triggered canister to identify species that did not exhibit higher concentrations in the plume than the weekly average concentration. For these species, the weekly average 1-h estimated value was assumed equal to the weekly average concentration. For VOCs that exhibited increased concentrations in the plume, we calculated ambient and event conversion factors species by species using Equations 1 and 2.

$$\textit{Ambient VOC}_x\textit{ Conversion Factor} = \frac{\textit{Weekly averaged VOC}_x\textit{ mixing ratio}}{\textit{Weekly average PID signal}} \quad (1)$$

$$\textit{Event VOC}_x\textit{ Conversion Factor} = \frac{\Delta\,\textit{VOC}_x\textit{ mixing ratio}}{\Delta\,\textit{PID signal}} = \frac{\textit{VOC}_x\textit{ mixing ratio in the triggered canister} - \textit{Weekly averaged VOC}_x\textit{ mixing ratio}}{\textit{PID signal at the canister trigger time} - \textit{Weekly average PID signal}}. \quad (2)$$

The ambient conversion factors were calculated by taking the VOC mixing ratios from the weekly canister collected at the same or nearby monitoring site during the same week of the emission event and dividing them by the weekly averaged PID signal. The event conversion factors were calculated by taking the excess VOC mixing ratios (the mixing ratio in the triggered canister minus the mixing ratio in the weekly sample) and dividing by the PID signal increase above the weekly average. These conversion factors were then applied to the time-varying PID signals during the VOC-rich plume detection event at the monitoring site. Minute-by-minute estimated VOC mixing ratios were calculated using Equation 3 or 4 for periods from 60 min before to 60 min after the triggered canister was collected. When the PID signal increased to at least 1.2 times the weekly average PID signal, Equation 3 with the event conversion factor was used to estimate in-plume VOC_x mixing ratios. Otherwise, Equation 4 was used to estimate ambient VOC_x mixing ratios. Finally, the 60-min moving averages were calculated for the estimating window, and the maximum 1-h average VOC_x mixing ratio was reported.

$$[VOC_{estimate\,x,t}] = [VOC_{weekly\,x}] + Event\ Conversion\ Factor \cdot PID\ Signal_t. \quad (3)$$

$$[VOC_{estimate\,x,t}] = Ambient\ Conversion\ Factor \cdot PID\ Signal_t. \quad (4)$$

Several assumptions and limitations must be considered when employing this method. First, this approach assumes that the relative chemical composition of the plume remains constant during a single plume detection period but that the absolute concentration level varies, likely due to the wind moving a single emission plume across the monitoring site with lower concentrations on the edge and higher concentrations toward the plume center. This assumption may not hold if plumes from multiple large emission sources reach the monitor during a single high VOC event. We have attempted to remove any such events during plume analysis. Last, we assumed consistency in background VOC composition throughout the week of the triggered event. However, changes in atmospheric conditions, including influences from anthropogenic sources such as rush-hour vehicle emissions or changes in dispersion conditions could impact VOC levels and compositions. For high concentration plume events, however, where plume concentrations are many times higher than in background air, changes in background VOC composition and concentrations will not have a material impact on estimates of 1-h concentrations.

Data Assessment

Oil and gas phases and drilling fluids. To associate weekly VOC measurements with nearby UOG activity, each weekly integrated-canister sample was assigned to a UOG operation phase (e.g., drilling, well completions, production), based on activity during the sample collection period at the nearest UOG well pad. Dates of each phase were recorded by the CCOB Oil and Gas Inspection Program. Although we recognized that some weekly samples may be influenced by UOG activities at farther locations due to varying wind directions throughout the sample collection period, characterizing aggregate, additive risks from exposure to pollution from multiple pads was outside the scope of this research.

For idle periods at a UOG site (i.e., wells were drilled, but many months passed before hydraulic fracturing commenced), we categorized those idle periods as "none" and excluded those samples from our chronic CHHRA. When an air monitor was located between two UOG well pads (e.g., between Northwest A site and Northwest B site), weekly samples were associated with the site that had an active phase occurring at the time of sample collection, because an active phase is more likely to influence the sample than an idle period. When two phases occurred within a weekly sample collection period (i.e., one phase ended and a new phase began in the same week), the phase that occurred first within that week was assigned to the nearest sampling location. For pads that had some wells in production and other wells in drilling or well completions phases at the same time, nearby air monitors were assigned drilling or well completions due to anticipated increased concentrations of VOCs during preproduction activities and the relatively shorter duration of preproduction. Measurements recorded at the three residential community sites (Anthem, Wildgrass, and Soaring Eagle) were assigned with phase activity from the nearest UOG well pad, the Livingston pad. We included a total of 1,521 weekly samples in our CHHRA.

The 15 s–1 min concentration data from 88 plume-triggered canisters were paired with UOG phases based on the well activity records and wind direction at the time of sample collection. For example, we examined the wind direction for 30 min prior to each triggered sample collection to identify the plume's origin. If a triggered sample was collected downwind of a pad undergoing a single operational activity, the canister sample was classified as influenced by emissions from that well pad. The sample composition and concentration levels were also checked to ensure they showed concentration levels well above background with a composition consistent with UOG VOC emissions (e.g., rich in light alkanes with an iso-pentane to n-pentane ratio <1).[8] The iso-pentane to n-pentane ratio has been established as a way to distinguish samples influenced by oil and gas vs. traffic/urban sources.[74] Samples from triggered canisters where emissions could not be attributed to a single UOG operation were excluded from the acute cumulative risk analysis to avoid significant influence from simultaneous operations occurring at nearby well pads.

Cumulative risks from drilling operations were analyzed separately from the rest of preproduction. Petroleum-based Gibson D822 drilling fluid was used to develop 16 wells on the Interchange B well pad (May–July 2019) and on the first well at the Livingston well pad (July 2019). Due to resident complaints about odor, the remaining 47 wells across five UOG well pads were drilled using the odorless Neoflo 4633 drilling fluid between 2019 and 2022 (drilling occurred July 2019–January 2020 and September 2021–June 2022).[8,69] Although the odor-reducing benefits to the surrounding communities are immediate, the potential differences between the impacts on human health are not well understood.

Cumulative risk assessment and characterization. To estimate acute and chronic noncancer and cancer risks, we considered short- and long-term exposures to VOCs and ozone. VOCs quantified in the assessment include benzene, toluene, ethylbenzene, xylenes, n-nonane, n-decane, aliphatic low hydrocarbons, aromatic medium hydrocarbons, styrene, trichloroethylene (TCE), tetrachloroethylene (PCE), propene, and ozone. VOCs included in the groupings of xylenes, aliphatic low hydrocarbon, and aromatic medium hydrocarbons are described in Supplemental Table 2. Compounds without toxicity values that were measured but not included in the CHHRA were methane, ethane, ethene, propane, i- and n-butane, ethyne, trans-2-butene, *cis*-2-butene, and 1-butene. Compounds detected below the detection limit were replaced with half the detection limit value for that compound and included in the analysis. For a full list of detection limits, see Supplemental Table S4 in Ku et al.[8] Descriptive statistics of all VOCs measured in the integrated weekly canister samples and ozone data by phase

are listed in Excel Tables S1 and S2 for UOG and community sites, respectively, and descriptive statistics of hourly VOC and ozone data by UOG site type and phase are listed in Supplemental Tables 1A and 1B, respectively. Seasonal variability was considered for our CHHRA. Although the distribution of weekly concentrations was somewhat varied across seasons, acute concentrations did not show seasonal variation. Chronic hazard indices and cancer risk calculations included median values in the time-weighted calculations, which removes much of the seasonal variability when looking at longer time periods (e.g., 30 y). Therefore, we did not calculate separate risks based on seasons.

For acute exposure, we used the 50th and 95th percentiles of 1-h VOC estimates and hourly ozone concentrations at associated time points to calculate acute risks. For chronic exposure, we used weekly VOC measurements and 8-h ozone data to calculate 50th and 95th percentile time-weighted averages (TWAs) for each site to calculate cancer and chronic noncancer risks. TWAs for each site were calculated by weighting 50th or 95th percentile concentrations for the length of time exposed during each UOG phase. The 50th or 95th percentile 8-h ozone values were calculated within durations of each UOG phase and associated with each phase at each site. For example, if drilling occurred over 4 wk, the 50th and 95th percentile calculated from all 8-h ozone values collected over 4 wk was calculated. Durations of drilling and well completions were simply the number of days it took to complete each phase (phase dates were made available by the CCOB on request), and duration of production was assumed to be 30 y. Therefore, TWAs for each site followed Equation 5, as recommended by the US EPA and California EPA Office of Environmental Health and Hazard Assessment,[75] with concentrations being either the 50th or 95th percentile of measured values in each phase.

$$TWA = \frac{[(Time_{drill} \times Conc_{drill}) + (Time_{pre} \times Conc_{pre}) + (30\,y \times Conc_{prod})]}{Time_{drill} + Time_{pre} + 30\,y}. \quad (5)$$

End point–specific chronic and acute RfCs for chemicals included in the CHHRA (Supplemental Table 3A) were derived using methods from Chiger et al. 2025.[76] In brief, human or animal points of departure (PODs) for chronic and acute noncancer end points were derived from the Agency for Toxic Substances and Disease Registry (ATSDR) Toxicological Profiles (ToxProfiles) and/or the US EPA CompTox Chemicals Dashboard (CompTox), which includes data on PODs or RfCs from the US EPA IRIS and Provisional Peer-Reviewed Toxicity Values (PPRTV) as well as the European Chemicals Agency (ECHA). Following the US EPA methodology[77] in its PPRTV for aliphatic low[78] and aromatic medium hydrocarbons,[79] RfCs were based on the most sensitive PODs for a representative compound, excluding PODs for naphthalene, a C_{10} polycyclic aromatic hydrocarbon. PODs were selected as described in Chiger et al.[76] based on the most sensitive

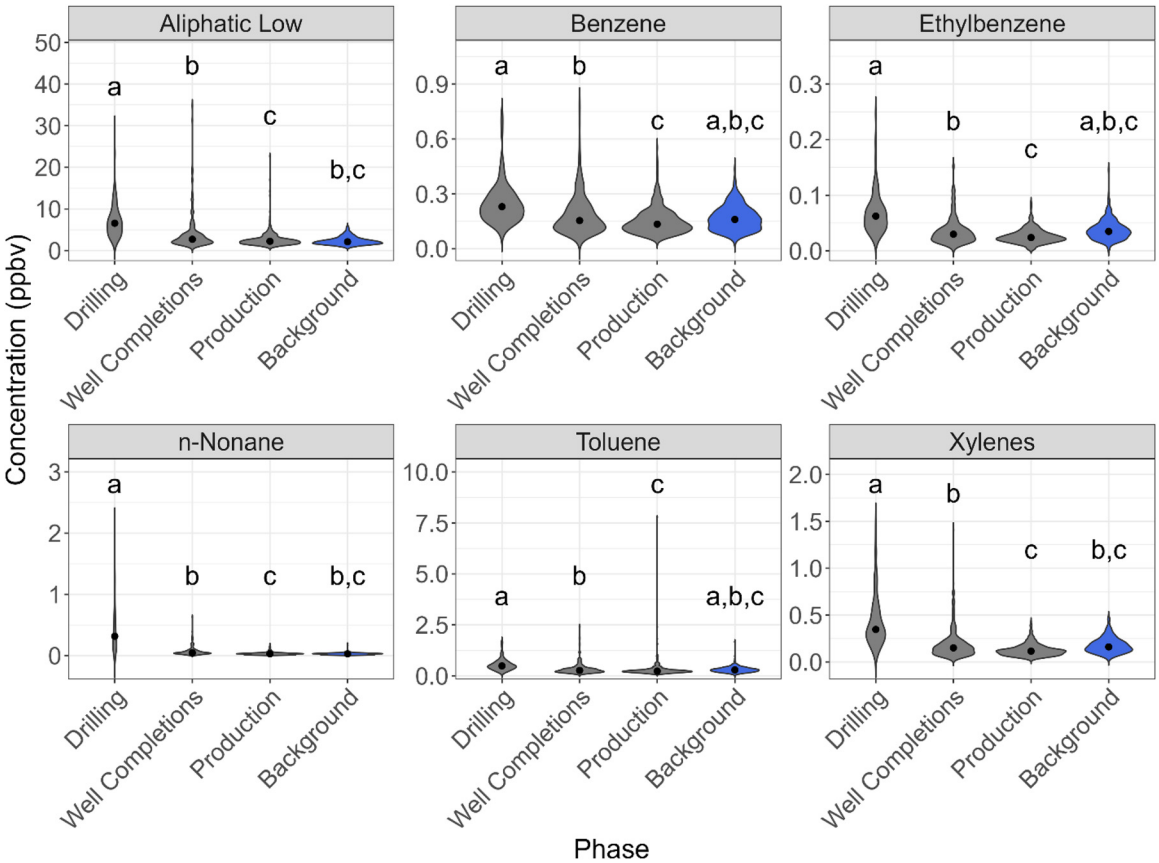

Figure 3. Distributions of select VOC concentrations by phases drilling ($n = 112$), well completions ($n = 236$), and production ($n = 502$) at near-pad UOG air monitoring sites in comparison with the background site ($n = 272$). Black dot represents median concentration, and the violin represents the full distribution of values. Letters a–d represent significant differences between means with different letters indicating the means are significantly different ($p < 0.05$, 95% CI) and matching letters indicating no significant differences. Significance was determined by repeated measures ANOVA after log-normalization with post hoc pairwise comparisons with Bonferroni adjustment. Summary data can be found in Excel Table S1, and statistical information in Supplemental Table 4A. Note: ANOVA, analysis of variance; CI, confidence interval; ppbv, parts per billion volume; UOG, unconventional oil and gas; VOC, volatile organic compound.

value for each end point. This selection process entailed prioritization of human studies over rodent studies, giving preference in order of existing RfCs, benchmark doses lower confidence limit (BMDLs), no observed adverse effect levels or concentrations (NOAELs or NOAECs), and lowest observed effect levels or concentrations (LOAELs or LOAECs). For chemicals and end points without existing RfCs, uncertainty factors (UFs) were used to derive "RfCs" by dividing the POD by the relevant UFs.[76,80] Ozone, however, had no UFs applied to PODs to ensure consistency with the ozone NAAQS and World Health Organization (WHO) air quality standards. The lowest RfC for ozone, therefore, was 60 ppbv for acute respiratory effects, as is consistent with the NAAQS and WHO standards.

To characterize acute and chronic noncancer risks, we used a hazard quotient/hazard index approach. Hazard quotients (HQs), defined as the ratio between the estimated exposure concentration and RfC, were derived based on acute or chronic exposure concentrations, described above. HQs for chemicals that contribute to the same adverse health end points were summed to create a hazard index (HI) for each health end point. Per US EPA guidance, adverse health effects are possible if any HQ or HI is above 1.[81,82] Because the HI is semiquantitative, it does not imply a multiplier, and therefore an HI of 4 is not twice the risk of an HI of 2. To determine HIs specific to UOG phases, the HI for each phase was averaged over either all near-pad sites or community sites. The lifetime excess cancer risk for each carcinogenic compound was derived by multiplying the estimated exposure concentration (TWA) by the inhalation unit risk (IUR) according to US EPA guidelines[83] (Supplemental Table 3B). Individual lifetime excess cancer risks for each chemical were then summed to derive the cumulative lifetime cancer risk near each site.

Statistical analysis. All data were analyzed using RStudio (version 4.2.3), and the code for this can be found in the supplemental R Markdown files. Differences in weekly chemical concentrations between phases and drill muds were analyzed using repeated measures analysis of variance (ANOVA). The degrees of freedom were calculated using the Kenward-Roger method to account for unequal variances and correlations inherent in the repeated measures design. Post hoc pairwise comparisons were performed using a Bonferroni adjustment to control for Type I error. Chemical concentrations were log-transformed before running ANOVAs to normalize data and increase homogeneity of variances as assessed by Shapiro-Wilk and Levene's tests, respectively. Statistical significance was determined by a p-value <0.05.

Results

VOC Concentrations by UOG Phase

Distribution of weekly concentrations for VOCs driving risk in the CHHRA were compared between for UOG phases for all oil and gas monitoring sites and the background site (Figure 3).

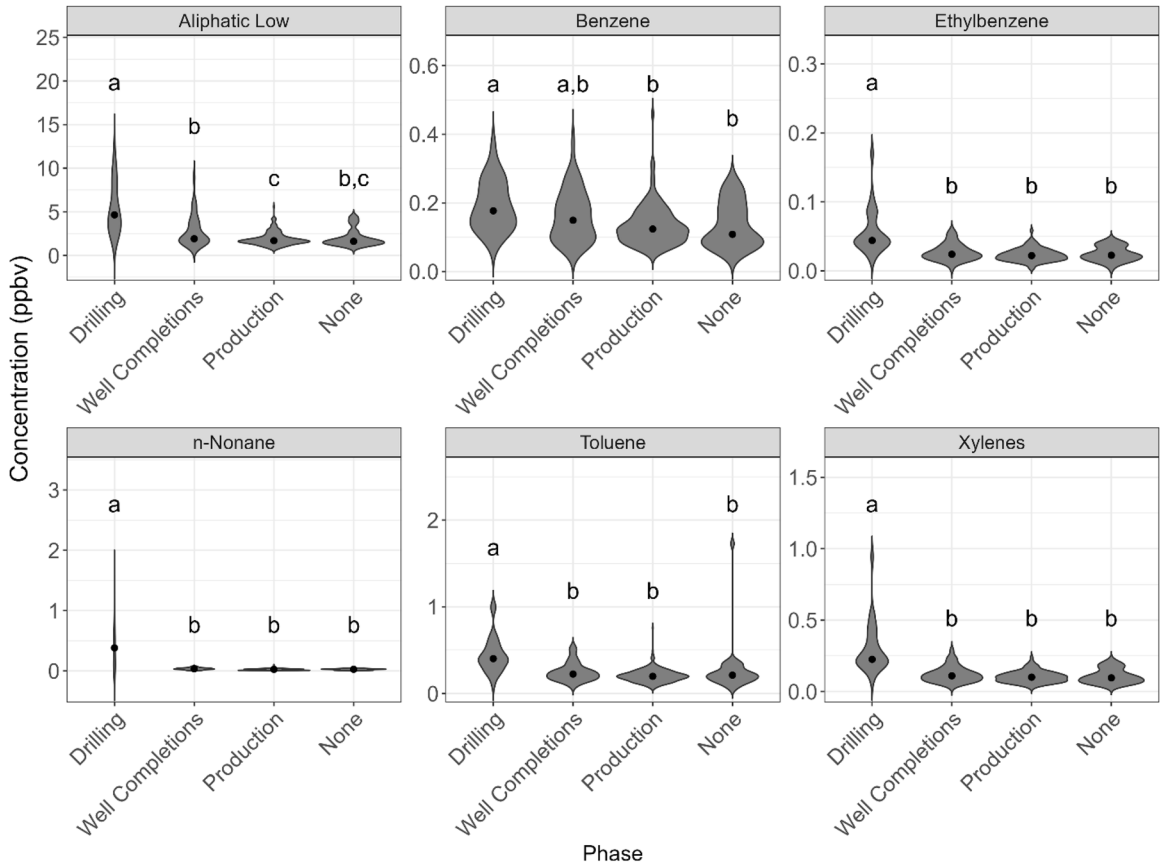

Figure 4. Distributions of select VOC concentrations by phases drilling ($n=29$), well completions ($n=44$), and production ($n=277$) at community air monitoring sites (Anthem, Wildgrass, Soaring Eagle) compared with idle, or "none" activity ($n=34$). Black dot represents median concentration, and the violin represents the full distribution of values. Letters a–d represent significant differences between means with different letters indicating the means are significantly different ($p<0.05$, 95% CI) and matching letters indicating no significant differences. Significance was determined by repeated measures ANOVA after log-normalization with post hoc pairwise comparisons with Bonferroni adjustment. Summary data can be found in Excel Table S2, and statistical information in Supplemental Table 4B. Note: ANOVA, analysis of variance; CI, confidence interval; ppbv, parts per billion volume; VOC, volatile organic compound.

When looking at the concentrations of these chemicals and chemical groupings (BTEX, n-nonane, and aliphatic low hydrocarbons), the highest median concentrations were observed in conjunction with drilling operations, which was significantly higher than well completions or production ($p < 0.05$). Well completions were also associated with statistically higher median concentrations of select chemicals in comparison with production operations ($p < 0.05$). Median ambient concentrations for xylenes, n-nonane, and aliphatic low hydrocarbons were significantly higher during drilling at near-pad sites than at the background site (Figure 3). However, there were no statistically significant differences between chemical concentrations when comparing well completions or production periods at near-pad sites with the background site (Supplemental Table 4A). In addition, weekly ambient VOC concentrations by phase of nearest UOG well pad were compared across the community monitoring locations (Anthem, Wildgrass, and Soaring Eagle) (Figure 4). All ambient VOC concentrations, except propene, were significantly higher ($p < 0.05$) during drilling at the community sites than during production (Supplemental Table 4B).

VOC Concentrations by Drilling Fluid Type

We also compared weekly concentrations of select ambient VOCs measured during drilling for all six UOG well pads between drilling fluid type (Figure 5). Because Neoflo is not formulated with BTEX[84] and Ku et al.[8] also reported lower BTEX volatile levels in lab studies of Neoflo drilling fluid, we expected to see lower ambient BTEX concentrations around operations using Neoflo- rather than Gibson-based drilling mud. When looking at distributions of BTEX and some other VOC concentrations used in the CHHRA, however, we found similar average ambient concentrations at monitors near drilling operations using Neoflo- and Gibson-based drilling muds (Supplemental Table 5). Because the number of samples collected during use of Gibson-based drilling mud was limited and differences in transport distance and meteorology can significantly affect ambient concentrations of emitted VOCs, further work is needed to evaluate whether the lower BTEX concentrations in Neoflo drilling fluids yield significant real-world reductions in exposures during drilling operations. We did, however, see significantly higher ($p < 0.05$) n-nonane concentrations in ambient air during drilling operations using Neoflo-based mud, consistent with its strong enrichment in the synthetic Neoflo drilling fluid.[8]

Acute Risks at Near-Pad Sites

Acute HIs at near-pad UOG sites were calculated for each health end point based on median (Figure 6A) and 95th percentile concentrations (Figure 6B) of 1-h VOC estimates at UOG monitoring sites and 1-h regional ozone concentrations (Supplemental Table 6A). Acute HIs at near-pad sites ranged from 1.1×10^{-4} to 1.42 for the median and 1.34×10^{-4} to 31.33 for the 95th percentile concentrations. At the 95th percentile concentrations, neurological and immunological HIs were >1 for the drilling phase. In addition to those two health end points, respiratory, reproductive and developmental HIs surpassed thresholds during well completions (Figure 6B).

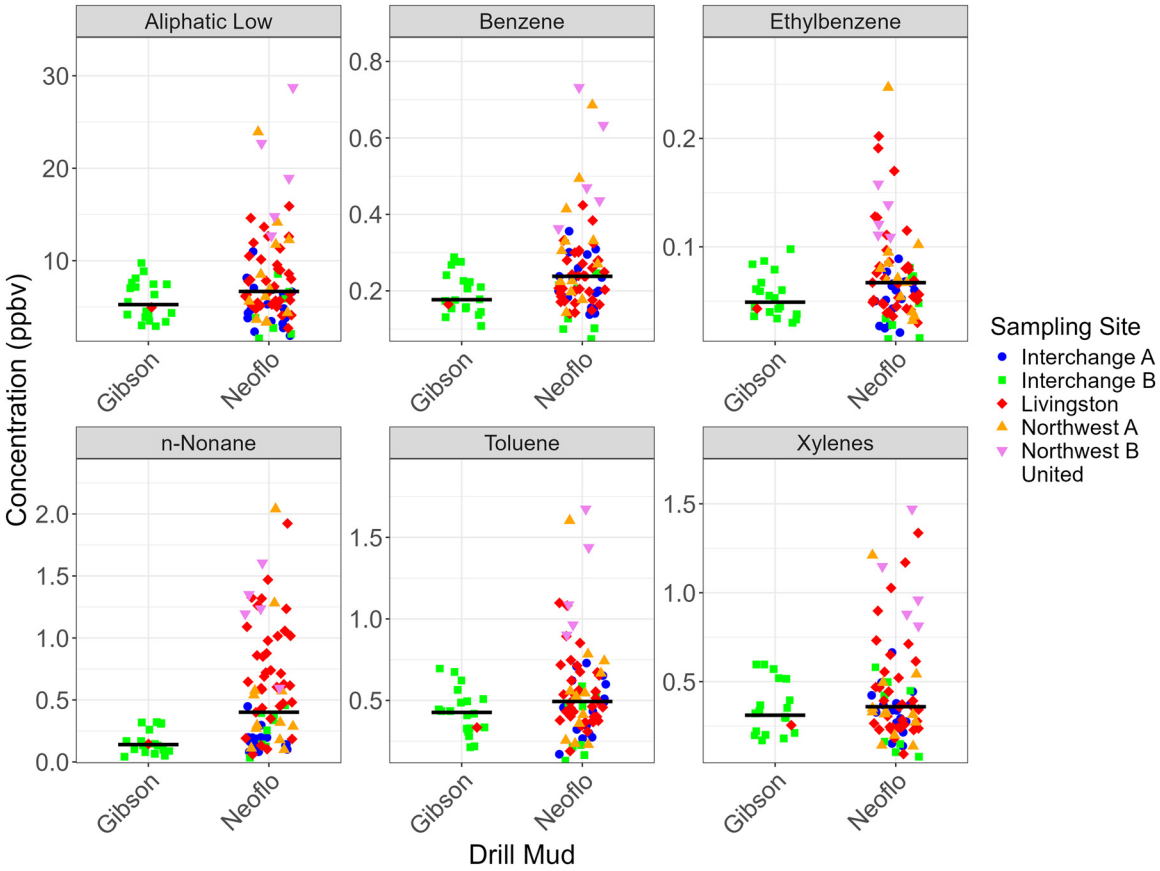

Figure 5. Distributions of select VOCs by drilling fluids Gibson ($n = 20$) and Neoflo ($n = 121$). Bar indicates median values. *Indicates statistically significant difference between means for *n*-nonane ($p = 0.047$). Significance was determined by repeated measures ANOVA after log-normalization with post hoc pairwise comparisons with Bonferroni adjustment. Summary and statistical data can be found in Supplemental Table 5. Note: ANOVA, analysis of variance; ppbv, parts per billion volume; VOC, volatile organic compound.

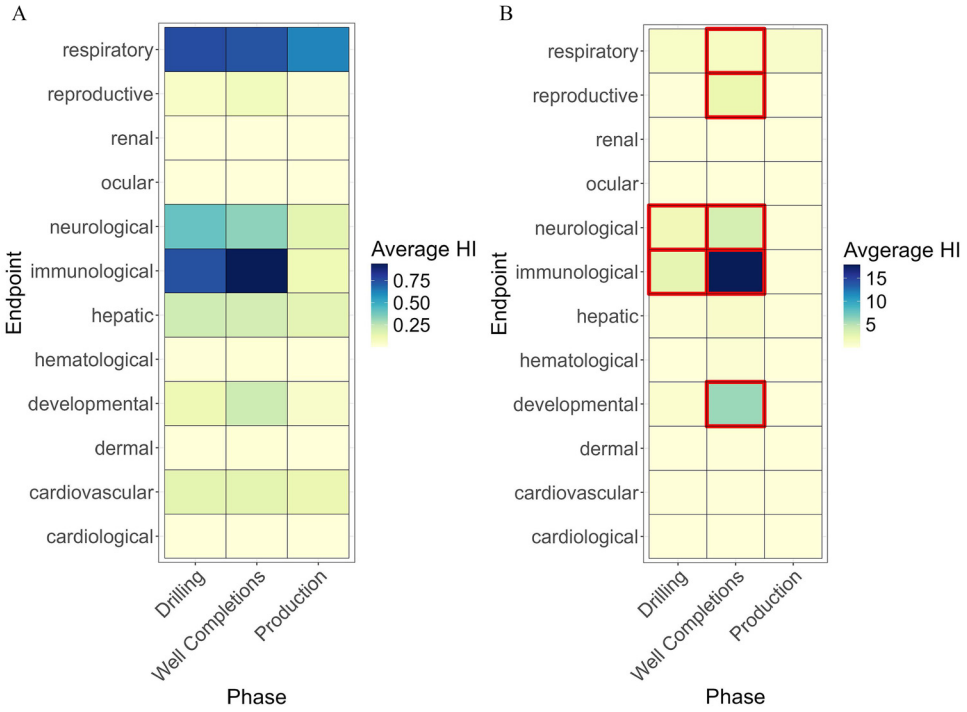

Figure 6. Acute HIs for (A) median chemical concentrations and (B) 95th percentile chemical concentrations by health end point for drilling ($n = 44$), well completions ($n = 35$), and production ($n = 5$) at UOG monitoring sites. Bolded, red border signifies HI > 1. Summary data can be found in Supplemental Table 6A. Note: HI, hazard index; UOG, unconventional oil and gas.

Chemicals contributing to HIs surpassing thresholds during well completions are presented in Figure 7. The aliphatic low hydrocarbons (see all chemicals included in Supplemental Table 2) were the main drivers for developmental (Figure 7A) and reproductive risks (Figure 7B). For the respiratory end point, ozone is the main driver of risk; however, the addition of oil- and gas-related VOCs, such as benzene, push the risk above 1 (Figure 7C). N-nonane, a compound found to be abundant in Neoflo drilling fluid volatiles,[8] is one of the main drivers of neurological risk (Figure 7D) during drilling and well completions along with the aliphatic low hydrocarbons. Immunological risk (Figure 7E) during drilling and well completions is driven primarily by toluene.

Acute Risks at Anthem Community Site

The Anthem community site, one of three community monitoring sites, was used solely to assess acute risks to communities due to limited or no hourly values at other community sites. Acute HIs near the Anthem community site ranged from 1.03×10^{-3} to 1.92 for the median and 1.95×10^{-3} to 3.17 for the 95th percentile concentrations, respectively. Figure 8 presents acute hazard indices by health end point based on median (Figure 8A) and 95th percentile (Figure 8B) concentrations of 1-h VOC estimates at the Anthem community monitoring site and 1-h regional ozone concentrations. Acute hazards were above 1 for the immunological end point for median chemical concentrations during well completions and production. For 95th percentile concentrations, HIs were above 1 for respiratory, immunological, and development end points during production, whereas the immunological HI was above 1 during well completions. Because there were no data for acute ambient air concentrations at the Anthem site during drilling (PID-triggered canister systems were deployed after drilling operations finished at the nearby Livingston pad), no acute risk was calculated during this phase. In addition, because there were limited data to calculate 1-h concentrations from the other community sites (Wildgrass and Soaring Eagle), we were unable to calculate acute risks for these sites.

Chemicals that contribute to HIs above thresholds for 95th percentile concentrations are presented in Figure 9. Toluene is the greatest contributor to the immunological health end point during well completions and production (Figure 9A), whereas the aliphatic low hydrocarbons and benzene are the main chemicals driving developmental risk during production (Figure 9B). Similar to the risk results at near-pad sites, ozone is the main driver of acute respiratory effects, with the addition of oil- and gas-related VOCs pushing the risk above 1 during production (Figure 9C).

Chronic NonCancer and Cancer Risks

Chronic noncancer HIs were calculated using median and 95th percentile chemical concentrations for the UOG, community, and background sites. All HIs were below 1 for all health end points, ranging from 7.05×10^{-4} to 0.29 for the median and 8.43×10^{-4} to 0.47 for the 95th percentile concentrations for all sites (Supplemental Figure 1A and 1B; Supplemental Table 6B).

Cancer risks were quantified based on hematological, hepatic, and renal cancers from exposure to benzene, ethylbenzene, PCE, and TCE. These cancers were the most sensitive cancerous effects from exposure to the four chemicals and served as the basis for derivation of the cancer hazard values.[85–88] Cancer risks were based on TWA weekly air monitoring concentrations from near-pad sites, community sites (Wildgrass and Anthem), and the background site. Interchange A was removed from the analysis due to lack of weekly data during production. Soaring Eagle weekly data were also removed from analysis because the monitor is located between multiple pads and assigning phases was not possible. The US EPA, consistent with the National Institute for Occupational Safety and Health (NIOSH),[89] typically uses a cancer benchmark between 1×10^{-4} and 1×10^{-6} (or between 100 and 1 in 1 million), with many programs opting to use the

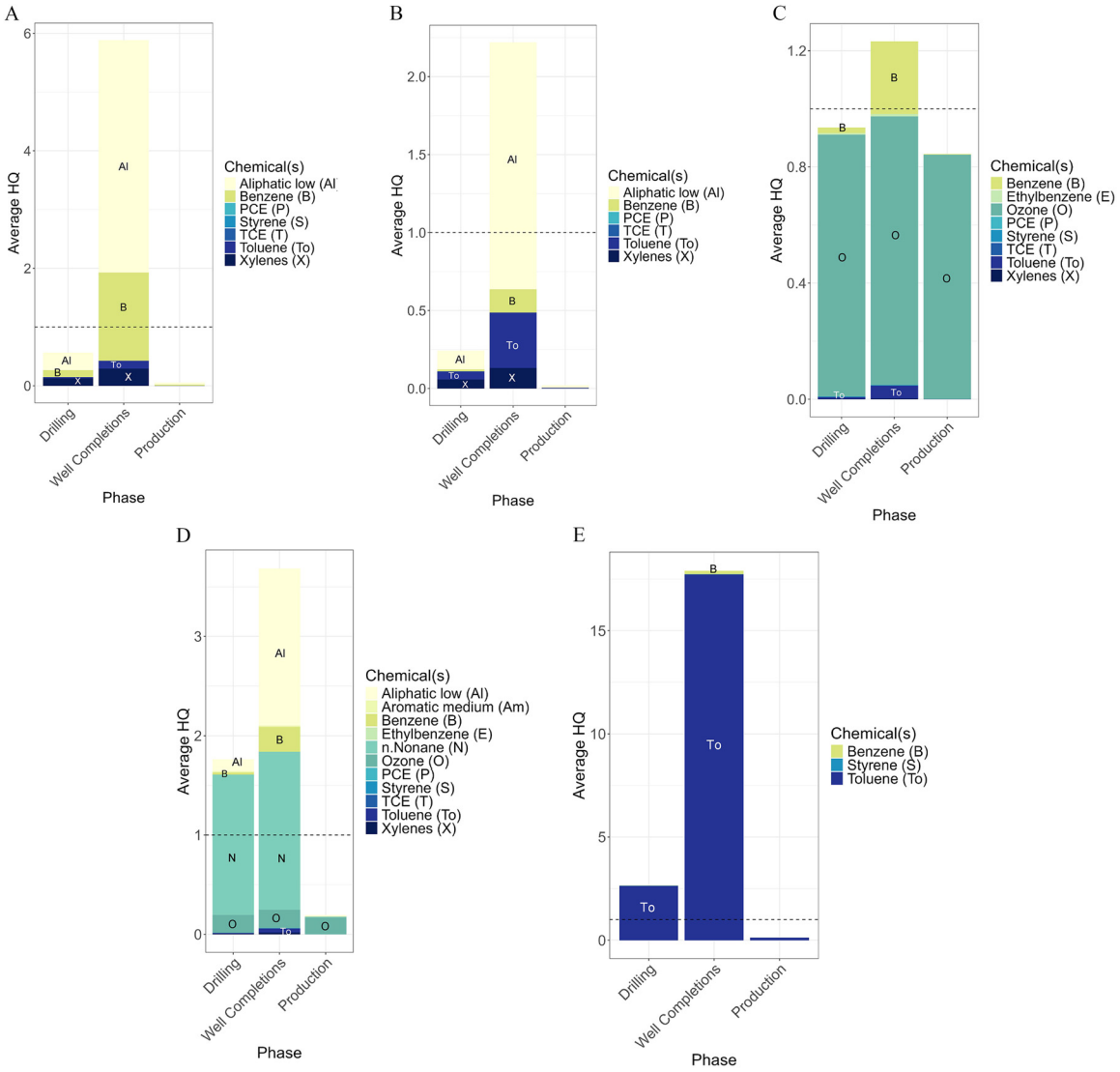

Figure 7. Acute HQs by phases for drilling ($n = 44$), well completions ($n = 35$), and production ($n = 5$) at 95th percentile chemical concentrations for oil and gas sites for (A) developmental, (B) reproductive, (C) respiratory, (D) neurological and (E) immunological end points. Dotted line represents the US EPA risk threshold of 1. Not all chemicals are visible in the bar graphs because some quantities are too low to appear. Summary data can be found in Excel Table S3. HQ, hazard quotients; US EPA, US Environmental Protection Agency.

more protective 1×10^{-6} benchmark for fenceline populations.[90] Cumulative cancer risks (from benzene, ethylbenzene, TCE, and PCE) ranged from 87.9 to 201 in a million for median and 209 to 335 in a million for 95th percentile concentrations. Median cumulative cancer risks were above the US EPA upper limit for acceptable risk (100 in a million) for all sites except Northwest B (Figure 10A). At 95th percentile concentrations, cancer risks for all sites were above thresholds (Figure 10B).

Discussion

Our results show that health risks persist after the implementation of best management practices to reduce emissions for communities located near UOG well pads in the DMNFR ozone NAA. Noncancer acute hazards exceeded thresholds at the Anthem community site for developmental and respiratory health end points during production. Although ozone is the primary driver of respiratory risk, the addition of VOCs pushed risk above acceptable thresholds. Accurately capturing risks requires multiple contaminants that affect the same health end points to be assessed. Thus, our results provide a more comprehensive picture of risks than previous risk assessments by assessing HAPs and a criteria air pollutant (CAP). Acute HIs at the Anthem community site were also above thresholds during well completions and production for the immunological end point, which can result in a decrease in the body's ability to fight infection[91] and may have greater impacts to the age 55 y and up Anthem community. For older individuals, the risk for atrial fibrillation (AF) has been found to increase during well development for those living within 2,059 ft of an oil and natural gas well site.[26] AF substantially increases the risk for heart failure and stroke,[92] and the increased respiratory risk from ozone and UOG-related activities may present additive impacts to elders with AF. We did not have sufficient data to calculate acute hazard indices at the other two community sites.

At near-pad sites, acute HIs exceeded thresholds for immunological, respiratory, reproductive, developmental, and neurological end points during well completions. In addition, immunological and neurological HIs were above thresholds during drilling. Weekly concentrations of VOCs captured during drilling with

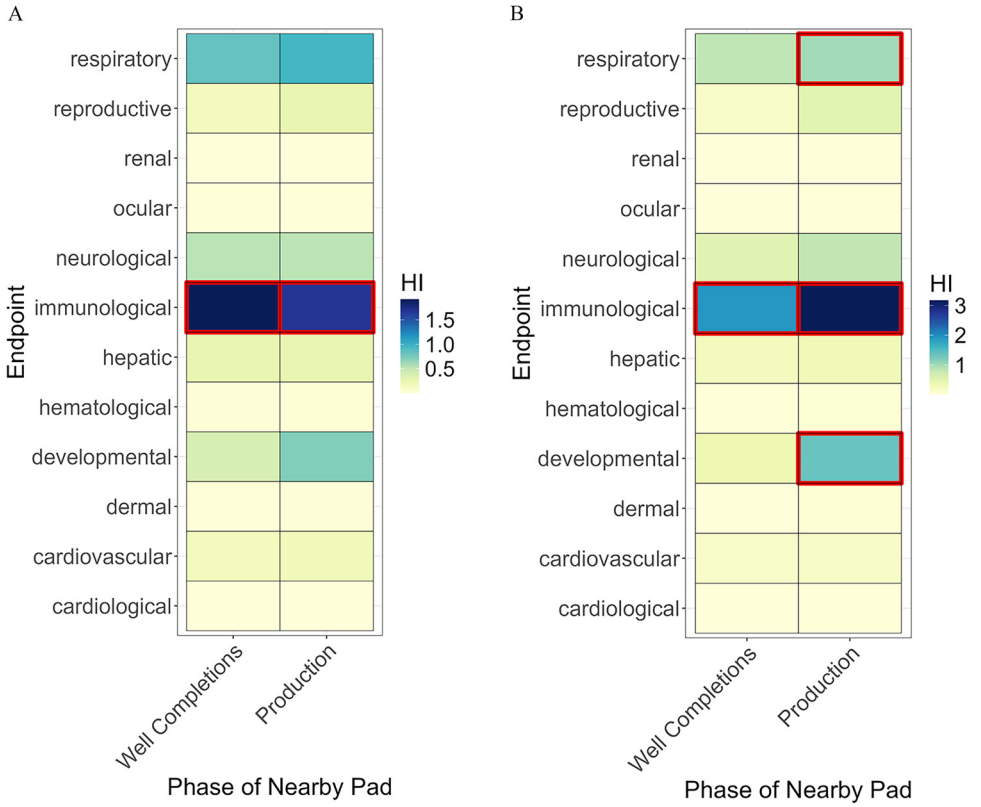

Figure 8. Acute HIs for (A) median and (B) 95th percentile chemical concentrations by health end point for well completions ($n = 1$) and production ($n = 2$) at the Anthem community monitoring site. Bolded, red border signifies HI > 1. Summary data can be found in Supplemental Table 6A. Note: HI, hazard index.

synthetic Neoflo 4633 are similar and in some cases greater than VOC concentrations from drilling with petroleum-based Gibson D822 fluid. According to CCOB inspection reports, all sites were drilled using electric drill rigs and no significant operational changes were observed between sites, except a change in drilling fluid. A significantly higher amount of n-nonane is associated with Neoflo than with Gibson drilling fluid volatiles, as previously confirmed by laboratory headspace analysis.[8] These heavier alkanes have higher reactivity with hydroxyl radicals than lighter alkanes and can, therefore, contribute to greater ozone formation[93] and increase the potential for acute health risks from increased ozone exposure, as well as additional health risks to the neurological,

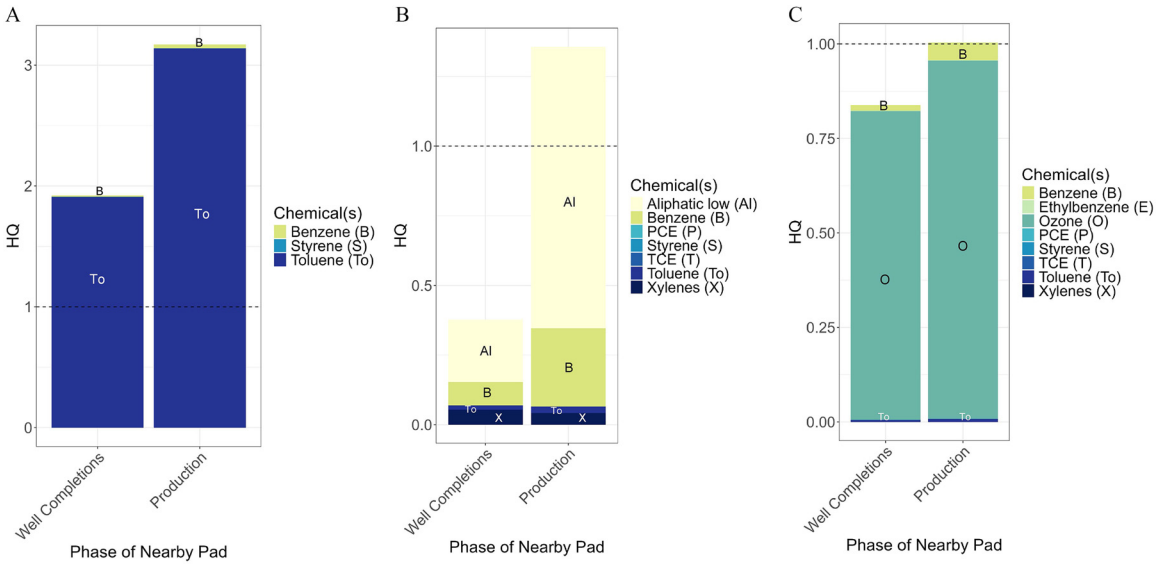

Figure 9. Acute HQs by phases well completions ($n = 1$) and production ($n = 2$) at nearest UOG well pad at 95th percentile chemical concentrations at the Anthem community site for (A) immunological, (B) developmental, and (C) respiratory end points. Dotted line represents the (EPA) risk threshold of 1. Not all chemicals are visible in the bar graphs because some quantities are too low to appear. Summary data can be found in Excel Table S3. HQ, hazard quotient; UOG, unconventional oil and gas; US EPA, US Environmental Protection Agency.

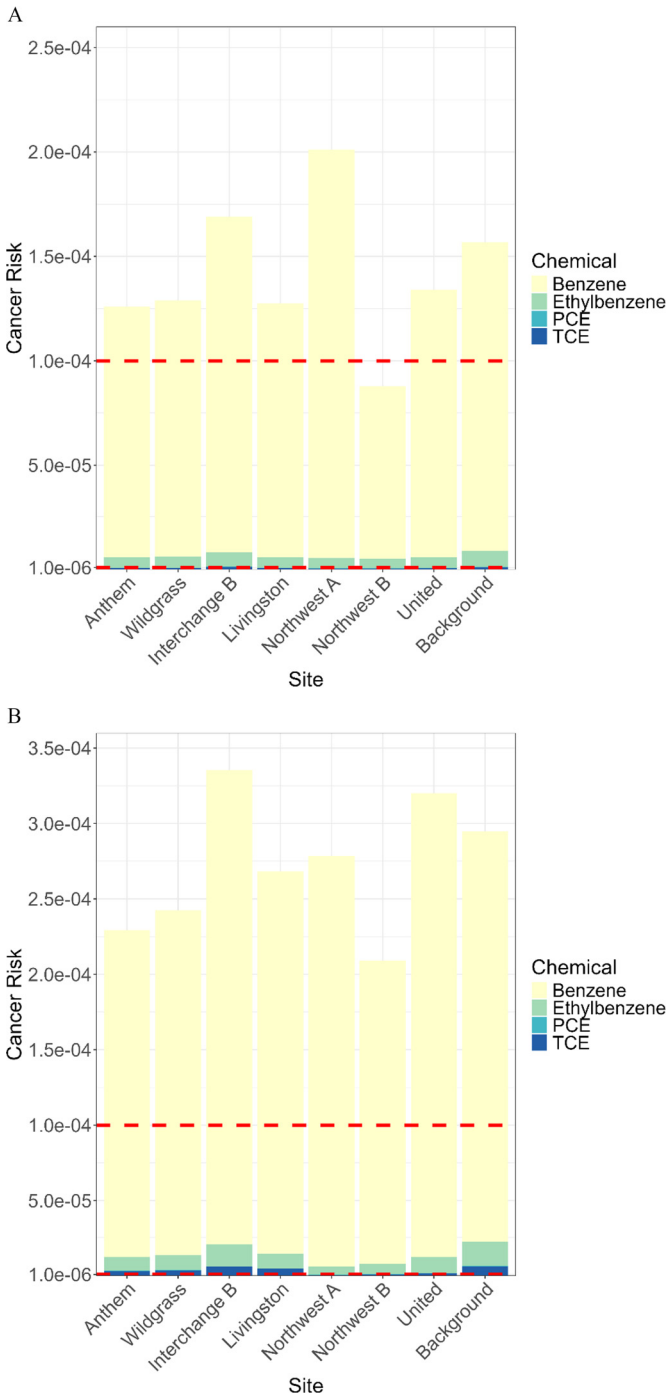

Figure 10. Cancer risks for near-pad, community, and background air monitoring locations based on (A) median and (B) 95th percentile weekly TWA concentrations. Dotted lines represent the range of cancer benchmarks, from 1×10^{-6} to 1×10^{-4}. Not all chemicals are visible in the bar graphs because some quantities are too low to appear. Summary data can be found in Excel Table S4. Sample sizes for each phase, which were used to calculated the TWA concentrations, are the following for each site: Anthem – drilling ($n = 18$), well completions ($n = 44$), production ($n = 154$); Background – no phase ($n = 256$); Interchange B – drilling ($n = 27$), well completions ($n = 67$), production ($n = 183$); Northwest A – drilling ($n = 12$), well completions ($n = 7$), production ($n = 4$); Northwest B – drilling ($n = 5$), well completions ($n = 16$), production ($n = 20$); United – drilling ($n = 15$), well completions ($n = 55$), production ($n = 35$); Wildgrass – drilling ($n = 11$), well completions ($n = 34$), production ($n = 107$). Note: PCE, tetrachloroethylene; TCE, trichloroethylene; TWA, time-weighted average.

developmental, and reproductive systems from HAPs exposure. Although switching from a petroleum-based fluid to a synthetic, odorless fluid has odor-reducing benefits to nearby communities, there may be unintended consequences for ozone formation and continued health risks.

All chronic hazards were below thresholds for all near-pad and community sites for all health end points. Because the nature of UOG releases from these six UOG well pads often occurred as short-term yet significant VOC plumes,[8] week-long concentrations are generally much lower than those exhibited in transient plumes. In addition, advancements in BMPs may result in emissions reductions during well completions, especially from the use of closed-loop, tankless fluid handling systems during well flowback. We recognize that seasonal variability may influence concentrations across the region and might mask some of the differences in the distributions of weekly concentration data. Ku et al.[8] found that UOG-related VOCs were elevated during wintertime due to atmospheric conditions that enhance accumulation of local pollutant emissions. For further analysis of seasonality and week-to-week differences in concentrations, see Ku et al.[8]

It is unclear how multiple acute exposures to increased levels of VOCs and ozone contribute to chronic effects over time. Therefore, chronic risk may be underestimated in this study. Although previous studies have suggested lowering the HI threshold or applying modifying factors to account for cumulative risks and nonchemical stressors,[94–96] this study focused only on risk from chemical stressors. The HI threshold was not adjusted in this study because cumulative chemical exposures were accounted for in the CHHRA.

Cancer risks were above the US EPA thresholds for all sites assessed, including the background site, which is located ~ 5 km from the Broomfield UOG well pads, closer to the Denver-Metro region and not close to any other UOG development. Previous research has established the background site to be heavily influenced by traffic emissions.[97] Although some of the near-pad monitoring locations are close to regional freeways, examination of traffic signatures in the CCOB VOC dataset shows the greatest influence at the Commons background measurement site. This site is closer to heavily trafficked surface streets in Broomfield and closer to higher traffic density associated with the core of the Denver Metro area to the south of Broomfield. Because our cancer risk analysis considered impacts from benzene and ethylbenzene, both which are emitted from vehicles, cancer risks present similar findings across all sites.

Aggregate Risks near Multiple UOG Sites

Numerous residences are located 300 m to 1.6 km from multiple UOG well pads. Due to few neighborhood air monitoring locations and reduced likelihood of capturing plumes as distance of monitors from the source increases, we were only able to calculate acute risk at one community site (Anthem). No residences in the Anthem community are located <300 m from multiple UOG well pads; however, many households in Colorado are found in such situations. Multiple residences are located ~ 300 m from the Northwest A and Northwest B pads, and adding together the risks from community air monitoring sites would provide a more realistic picture of risk. However, no air monitors were located within the communities near the Northwest pads, so we were unable to calculate aggregate risk in this study. We would expect HIs to be similar to or increased from the HIs calculated for the Anthem community site for households located 300 m from two well pads similar in design to the Livingston pad in the DMNFR ozone NAA.

Strengths and Limitations

Our study used precise air quality measurements to calculate cumulative risk, giving our results greater certainty than previous risk assessments that only used modeled data. However, because we did not apply air modeling to estimate cumulative risk at various distances (e.g., 1 km, 2 km) within communities surrounding UOG, we were unable to quantify aggregate cumulative risk to households living near numerous UOG well pads. Therefore, our acute, chronic, and cancer risks may be underestimated for some communities. Due to the HI risk assessment approach and lack of dose response quantification in this approach, we were also unable to quantitatively compare risks between sites.

The methods used in our CHHRA go beyond typical risk assessments by expanding consideration of health effects associated with chemicals beyond the most sensitive end point, which captured health risks that would not otherwise be identified. However, health risk assessments are only able to quantify risks for chemicals with existing toxicological or epidemiological data. Therefore, we could not include all VOCs analyzed in each canister sample in our assessment. In addition, we could not fully assess acute risks from Neoflo 4633 drilling fluid and Gibson D833 drilling fluid because no short-term canister data were collected during drilling with Gibson fluid. We recognize that Gibson fluid contains polycyclic aromatic hydrocarbons, which have carcinogenic and mutagenic effects[98] but were not measured in our dataset. Thus, risks during drilling with the use of Gibson fluid may be underestimated.

Policy Implications

This research finds that for communities located near UOG well pads in the DMNFR ozone NAA, acute health risks persist after the implementation of best management practices to reduce emissions. The results from this cumulative human health risk assessment further substantiate the findings from an epidemiological investigation in the same community[27] and studies such as this should be used to inform policymakers when making permitting decisions in populated areas.

Permitting UOG in Colorado should consider the ways preproduction, which includes both drilling and well completions, impact risks to public health during Colorado's summer ozone season (31 May–30 September).[99] Without greater advances in extraction technologies to reduce risks from air pollution, seasonal restrictions should be considered (i.e., limit dates of preproduction to outside the summer ozone season). In addition, revisions to Regulation 7[100] should require that oil and gas operators use more specific classifications to better characterize root causes of upset conditions when they see enhancements in their air monitoring data. For example, inspection records from the CCOB note that separator maintenance activities drove adverse air quality impacts in the Anthem community during production,[101] and our CHHRA finds this event increases acute health risks. Because production can last 30 y, it is important to consider how UOG can impact population health from repeated maintenance activities (e.g., separator maintenance) and upset conditions prior to the permitting process. Additional revisions to state regulations that direct UOG operators to monitor air quality beyond the current 6-month requirement would ensure greater protection to public health from upset conditions and routine maintenance activities that arise as equipment ages.

This study provides evidence of acute risks from UOG well pads in a local jurisdiction in Colorado, known to be a leader in oil and gas regulations.[67] The findings raise public health concerns for individuals living near oil and gas sites in ozone nonattainment areas across the United States with fewer regulations. Results from this CHHRA may be used more broadly to advocate for emissions-reduction technologies in such places. Future studies should aim to evaluate the aggregate risk from living near multiple UOG well pads. The inclusion of air modeling at various distances from nearby oil and gas activities will strengthen results.

Acknowledgments

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