10-5-321: DIRECTOR OF PUBLIC WORKS; SUBSIDENCE AND MONITORING PUBLIC RECORDS OF DRILL SITE AND WELL INSPECTIONS:

The director of public works, from time to time as he deems appropriate but no less often than once every two (2) years, shall determine if any adverse effect upon the surface of the city is occasioned or is in danger of being occasioned by reason of the removal of oil, gas, or other hydrocarbon substances from the subsurface of the city pursuant to a well regulated by the provisions of this article or pursuant to a well, no part of which is located within the city but which drains a subterranean oil or gas pool, part of which is in the city. In the event the director of public works observes any such adverse effect or danger, the director may order the immediate suspension of further production from such well or wells as may be located entirely or partly within the city, and, in the event of such an order, production on such wells shall be suspended by the permittee or other operator immediately upon receiving notice of such order. The permittee or other person lawfully producing oil or gas or oil and gas or any other hydrocarbon substance from any such well may appeal to the council. The council, upon good cause being shown by the permittee or such other person, may vacate or modify the order of the director of public works, or, if no part of the well is in the city, the council may direct the city attorney to immediately commence such actions or proceedings as may be necessary for the abatement, removal, and enjoining of further drilling operations which adversely affect property within the city in the manner provided by law and to take such other action and to apply to any court having jurisdiction to grant such relief as will restrain or enjoin any person from drilling or producing any such well.

The director of public works shall annually request from those agencies that inspect oil wells drilled beneath the city, and from those agencies that inspect the sites from which such wells are drilled, all public records relating to inspections or notices of violation created within the previous year. Upon compiling the records each year, the director shall provide to the city council a summary of their contents.

The city council may impose a regulatory fee on oil well operators to recover the cost of subsidence monitoring and the monitoring of public records pursuant to this section. (Ord. 13-O-2637, eff. 2-24-2013)

10-5-322: ENFORCEMENT:

Any well drilled or produced, and any building or structure erected, operated, or maintained, or any use of property contrary to the provisions of this article shall be and the same hereby are declared to be unlawful and a public nuisance, and the city attorney, upon an order of the council, shall immediately commence an action and proceedings for the abatement, removal, and enjoinment thereof in the manner provided by law, and shall take such other action, and shall apply to any court having jurisdiction to grant such relief, as will restrain and enjoin any person from drilling or producing any such well, or from erecting, operating, or maintaining such building or structure, or from using any property contrary to the provisions of this article. (Ord. 79-O-1720, eff. 2-15-1979)

10-5-323: CESSATION OF ACTIVITY:

A. Notwithstanding the provisions of chapter 3, article 41 of this title, all drilling, production, and extraction activities occurring from surface locations in the city, including controlled drill site no. 1, shall cease by December 31, 2016.

B. The city council may extend the date set forth in subsection A of this section for controlled drill site no. 1 upon application of the property owner and upon finding that an extension of time would be in the public interest. (Ord. 11-O-2614, eff. 11-18-2011)

NEW STATE ENERGY PRODUCTION REGULATIONS PROTECT THE ENVIRONMENT

In California, state and local governments work cooperatively in developing domestic energy supplies while protecting the environment. At the state level, California's landmark law SB 4 implements toughest-in-nation oil extraction regulations that protect the environment while still permitting essential energy production to move forward.

SB 4 Establishes the Nation's Most Transparent & Stringent Environmental Protections

California's SB 4 goes further than any other state in enacting safeguards to protect public health, safety, and the environment. Among other things, the new regulations require:

- Well Stimulation Permits Required. Operators must obtain a permit from DOGGR before performing a well stimulation treatment, including disclosure of all chemicals to be used.
- Neighbor Notification and Water Testing Required.
 Required notification to neighboring property
 owners before activities and neighbors may
 request baseline and follow-up water quality testing
 at operator's expense.
- Monitoring During Well Stimulation Treatment Required. Operators must monitor numerous benchmarks before, during and after each well stimulation and must terminate in event of a well breach.
- Seismic Monitoring Required. Operators must track seismic activity during and after well stimulation treatment.
- Monitoring After Well Stimulation Treatment Required. Operators must perform ongoing well monitoring after well stimulation treatment, take all measures to prevent contamination of water resources or loss of hydrocarbon resources, and provide reports to DOGGR.

"We have the most intelligent regulation on the drilling of oil in the country." Jerry Brown, Governor of California, 5/19/2014

- Disclosure Required. Within 60 days of well stimulation treatment, operators must report to DOGGR the source, volume, and composition and disposition of well stimulation fluids and this information will be made public.
- Post-Well Stimulation Treatment Report Required.
 Within 60 days of well stimulation treatment
 operators must submit report to DOGGR covering
 results, pressures encountered, and how operations
 differed from what was anticipated in treatment
 design.
- Evaluation Prior to Well Stimulation Treatment Required. Operators must study cement, pressure testing, well stimulation treatment area analysis, and well stimulation treatment design.
- Storage and Handling of Well Stimulation Fluids.
 Well stimulation fluids are subject to current law and regulations regarding reporting, response, and cleanup.

ENERGY INDEPENDENCE

Californians for Energy Independence is a coalition that supports state and local policies that allow for continued domestic energy production and opposes those policies – such as oil taxes and energy bans – that would hinder production and increase reliance on foreign oil. For more information, visit:

www.EnergyIndependenceCA.com

<u>Carson Oil & Gas Code Update:</u> <u>Changes In Regulatory & Information Landscape Since May 2014</u>

Date	Event
May 20, 2014	City Council directs staff to prepare an update to oil & gas code
Aug. 28, 2014	Independent Scientific Study Released: California Council on Science and Technology (CCST) independent scientific review of well stimulation technologies in California (commissioned by BLM) showing that environmental impacts of hydraulic fracturing and well stimulation are limited, water use is small, no potable water contamination has occurred, and the practices do not create seismic risks
Jan. 14, 2015	Senate Bill 4 Draft EIR Released: confirms that hydraulic fracturing and well stimulation would not pose significant impacts to water resources or seismic risks
Jan. 14, 2015	Independent Scientific Study Released: CCST independent scientific study on well stimulation in California (commissioned by Natural Resources Agency) showing that most hydraulic fracturing in the state takes place in the San Joaquin Valley, not in the Los Angeles Basin, and that water use associated with hydraulic fracturing in California is a tiny fraction of the statewide total
Feb. 24, 2015	Planning Commission Hearing
Apr. 14, 2015	Planning Commission Hearing
May 12, 2015	Planning Commission Hearing
June 4, 2015	Government Study Released: EPA study confirming that hydraulic fracturing nationwide has not led to widespread, systematic impacts on drinking water resources
June 9, 2015	Planning Commission Hearing
July 1, 2015	Senate Bill 4 Final EIR Certified: confirms that mitigation measures proposed in the Draft EIR will reduce most environmental impacts of hydraulic fracturing and well stimulation below the level of significance
July 1, 2015	DOGGR Permanent Regulations for Well Stimulation Treatments Effective: requiring permits for activities, disclosure of well stimulation fluid composition, extensive environmental monitoring before, during and after activities, and other regulations
July 9, 2015	Independent Scientific Study Released: Vols. II & III of CCST independent scientific study on California well stimulation (commissioned by Natural Resources Agency) presenting case studies on specific regions of the state and presenting recommended measures for preventing environmental impacts from well stimulation activities, including many measures already required by DOGGR's final regulations
July 28, 2015	Planning Commission Hearing





CARSON ESTATE TRUST
CARSON DOMINGUEZ PROPERTIES, L.P.
CARSON ENERGY LLC
www.carsoncompanies.com

August 11, 2015

BY E-MAIL

Members of the City Planning Commission City of Carson City Hall 701 East Carson Street Carson, California 90745

Re: Proposed Zone Text Amendments 19-15 and 20-15 re Petroleum Operations, Hydraulic Fracturing and Acidizing (collectively, the "Amendment")

Ladies and Gentlemen:

We are writing to address some of the comments made during the public comment portion of the Planning Commission meeting held on the Amendment on July 28, 2015. As you know well, one drawback to the public comment process is that it allows individuals to make statements with little or no opportunity for others to challenge their accuracy or relevance to the issue. Please let this letter serve as our attempt to correct a few, but far from all, of the misstatements that were made at that hearing. First, however, let us briefly explain why this issue is so important to us.

Importance of the oil ordinance to the Carson Companies

While Carson Estate Trust is a general partner of Dominguez Energy LP (DELP), the entity that owns the majority of the mineral rights in the Dominguez oilfield, Carson and the other general partner each only own 1% interests in DELP. Ninety-eight percent of the ownership in DELP, and thus most of the mineral rights in the Dominguez oilfield, are owned by hundreds of individuals, as well as a number of charities who have been gifted interests in DELP over the years. These charities include Good Samaritan Hospital, Union Rescue Mission, the Catholic Education Foundation, and many others. It's important to note that DELP does not own any of

CORPORATE OFFICE 100 Bayview Circle, Suite 3500 Newport Beach California 92660 949/725-6500 FAX 949/725-6550 RANCHO DOMINGUEZ OFFICE 18710 S. Wilmington Avenue, Suite 200 Rancho Dominguez, California 90220 FAX 310/884-5932 TEXAS OFFICE 9821 Katy Freeway, Suite 440 Houston, Texas 77024 713/360-7934 FAX 713/360-7952



the surface rights above its mineral interests, so if oil production is effectively banned, the City will have taken everything DELP owns.

There are at least 50 to 80 million barrels of recoverable oil in the Dominguez field. While today's low oil prices do not justify the very high cost and financial risk of extracting this oil at this time, it is clear that oil prices will someday rebound and production will once again make economic sense. Even at today's depressed prices, though, 50 to 80 million barrels is still roughly \$2.5 to \$4 billion worth of oil. If the City's ordinance effectively prevents oil drilling, clearly the huge amounts of money at stake would leave DELP with no option but to sue the City of Carson to recover just compensation.

Misstatement #1: The City of Carson is a "front line" city

The implication behind this comment was that siting oil wells in Carson is some sort of environmental injustice. The environmental justice movement makes sense when addressing decisions to locate prisons or landfills. But the one situation where environmental justice arguments make no sense at all is in the location of oilfields, since oilfields are necessarily located where the oil is. Thus, oilfields are found in places as diverse as Bakersfield, Beverly Hills, Newport Beach, Huntington Beach, Los Angeles, Santa Barbara, Signal Hill, etc.

Misstatement #2: We don't need oil and gas production

There seems to be a presumption amongst many of the outside environmentalist speakers that we don't need oil and gas in our lives. While it's true that wind and solar energy are contributing more to our energy needs than ever before (as much as 4% by some estimates), we are still a very long way away from eliminating fossil fuels from our lives. According to the California Energy Commission Energy Almanac (www.energyalmanac.ca.gov) California consumed 624 million barrels of oil during 2013, or roughly 1.7 million barrels per day. Of this amount, only about 37% was produced within California. This means that over 1 million barrels of oil are imported into California from Alaska or the Middle East every day. Oil can be imported by train or truck but the vast majority comes into the state by ship. Transportation of so much oil itself results in a huge amount of energy consumption and its resulting environmental impacts. Clearly, our need for oil will continue for some time, but we can lessen the environmental impact of our oil usage by producing it locally instead of shipping it from the Middle East and other distant sources.

Misstatement #3: Allowing oil production in Carson will give rise to another Carousel

We are very mindful of the tragic situation at the Carousel tract in Carson and the physical, emotional and financial harm that it has caused to the families that live there. It is important to keep in mind, though, that the Carousel problem arose from the 1960's decision to allow the construction of housing on the site of a 1924 tank farm, which was operated in accordance with



standards that would never be permitted under today's stringent environmental regulations. It's because of situations like Carousel that we have the extensive environmental and state oilfield regulations that exist today.

Misstatement #4: Oil production causes air pollution

At the Planning Commission meeting on the 28th, a number of people complained about poor air quality in Carson. As the speakers noted, the primary source of the air pollution they were talking about are the Carson refineries. While it's true that refineries are oil related, it's important to keep in mind that oil refining is an exceptionally complex industrial process in which huge quantities of petroleum products are heated under great pressure to produce gasoline and many different kinds of exotic petrochemicals, which unavoidably produces vastly more air pollutants and risk of explosion than could any modern oil well.

Crude oil itself is generally not considered particularly hazardous. In fact, it is the main ingredient in the asphalt with which we pave our roads and roof our homes. By contrast, even gasoline, the most widely used of the many chemicals produced in refineries, requires careful and special handling to maintain an acceptable margin of safety.

The impact to air quality from a drill site is generally limited to any exhaust from production machinery on site (pumps, separators, etc., in the limited instances where this machinery is not powered by electricity) and safety flares. These already minimal impacts are tightly regulated by the State of California and the Air Quality Management District. In other words, the air quality impacts of refineries are unavoidably significant, while the air quality impacts of oil wells are minimal—far less than most of the industrial operations carried on in and around the City.

As noted in the City of Carson's draft EIR for the now-shelved Oxy project, the production of oil in Carson actually *alleviates* air pollution because it reduces the need for truck, train or shipped crude into the Carson refineries and the other refineries in Torrance and surrounding areas.

Conclusion

We understand that the speakers at the hearings on the oil code have genuine fears and concerns. But for the most part those fears and concerns stem either from real problems caused by uses other than oil wells, such as refineries, or from misinformation provided by outsiders opposed to any oil production anywhere.

The result of this fear and misinformation is a draft oil code that goes far overboard, effectively preventing oil production in Carson and running afoul of both state law and the constitution. We believe that the City's oil code can be updated in a manner that balances the rational concerns of residents regarding the surface operation of oil wells with those of the oil industry and mineral owners. These interests coexist in a number of places throughout Southern California; Signal

Hill and Huntington Beach are good examples. The City of Carson, where oil production has continued without incident since the 1920's, can certainly find a way to balance these interests.

Sincerely,

Carson Estate Trust as general partner of DOMINOUEZ ENERGY, L.P.

John W Hawkinson

Senior Vice President, Finance

Saied Naaseh

From:

Alexandra Nagy <anagy@fwwatch.org>

Sent:

Monday, August 31, 2015 2:51 PM Saied Naaseh; Shannon Chaffin

To: Subject:

Dallas 1500ft setback

Hey Shannon and Saied,

I wanted to share with you the information on the Dallas 1500ft setback.

Here's an article from ThinkProgress: $\frac{http://thinkprogress.org/climate/2013/12/12/3053941/did-dallas-ban-fracking/$

Here's a link to the ordinance that was passed December 11, 2013 - starts on PAGE 1049: http://www3.dallascityhall.com/council_briefings/agendas/agendas 1213/FinalAgenda 12112013.pdf

Looking forward to the meeting on Wednesday at 8:30am.

All the best, Alex

Alexandra Nagy | Organizer Food & Water Watch anagy@fwwatch.org 323-843-8451 @realfoodnagy

Like us on Facebook!





Saied Naaseh

Subject:

From:

Alexandra Nagy <anagy@fwwatch.org> Sent: Monday, August 17, 2015 2:06 PM

To: Saied Naaseh; Shannon Chaffin

Attachments: Brown 2014_Understanding exposure from NG puts current air standards to the test.pdf;

Why 1500ft is legally defensible

Colborn 2012_ An Exploratory Study of Air Quality near Natural Gas Operations published version.pdf; Gilman 2013_Source Sig of VOCs for O&G operations in NE Colorado.pdf; Macey 2014_Air concentrations of VOCs near O&G production.pdf

Hey Shannon and Saied,

I wanted to share some background information on why a 1500 feet setback is just as defensible, or more so, than 1000ft. Basically, the fact that both SCAQMD and DOGGR use 1500ft, not 1000ft, gives you all the reason you need to use 1500ft as the setback limit. Just because others states have 1000ft setbacks doesn't mean much next to California law that already uses 1500ft for notification requirements. California law tends to "lead" on environmental issues anyway, and Carson is leading California.

- South Coast Air Quality Management District (SCAQMD) recognizes 1500ft as the sensitive receptor zone, meaning that people within 1500ft of an oil and gas well are at increased risk from pollution.
 - SENSITIVE RECEPTOR means any residence including private homes, condominiums, apartments, and living quarters; education resources such as preschools and kindergarten through grade twelve (k-12) schools; daycare centers; and health care facilities such as hospitals or retirement and nursing homes. A sensitive receptor includes long term care hospitals, hospices, prisons, and dormitories or similar live-in housing.
 - This can be found here for their rule 1148.2 that deals with oil and gas wells and well stimulation reporting. http://www.aqmd.gov/docs/default-source/Agendas/Governing-Board/2015/2015-jul10-039.pdf?sfvrsn=8
 - SCAQMD also notes that oil and gas wells can be a nuisance up to 3,000 feet
- SB4 required DOGGR to use a 1500 ft radius notification for residents within 1500ft of a fracking permit
- In evaluating whether 625 foot buffers around drilling sites served as an adequate safety measure, researchers at the West Virginia University School of Public Health found that there were elevated levels of particulate matter and benzene within that zone, at levels which could cause potential health effects. http://wvwri.org/wp-content/uploads/2013/10/A-N-L-Final-Report-FOR-WEB.pdf
- Hydrofluoric acid, a chemical used to corrode rock in acidizing treatments, turns into vapor at room temperature and is highly toxic and can cause severe skin and respiratory system burns. In filings submitted to the Environmental Protection Agency, BP and Marathon reported that accidental hydrofluoric releases from their refining facilities could vaporize and travel for over 20 miles. Even though the code will ban acidizing, acids will be used for "routine maintenance" and still pose a threat http://www.publicint egrity.org/2011/02/24/2118/use-toxic-acid-puts-millions-risk
- Studies have shown that proximity to well sites affects fetal development, increasing the prevalence of low birth weight and premature birth, as well as increasing the risk of fetal heart and neural tube defects.



- Elaine Hill, The Impact of Oil and Gas Extraction on Infant Health in Colorado(2013); Lisa McKenzie, Birth Outcomes and Maternal Residential Proximity to Natural Gas Development in Rural Colorado, Environmental Health Perspectives (2014)
- Texas study finding carcinogens at playgrounds roughly 500 2000 ft

http://www.shaletest.org/wp-content/uploads/2014/09/ProjectPlaygoundPatagoniaReport-2.pdf

- Brown 2014: survey of different air sampling done around the country. Includes McKenzie study that looks at elevated VOCs within a half mile attached
- Colborn 2012: sampling of air within a mile of 130 wells attached
- Gilman: Elevated VOCs 0.5 miles from 22 wells attached
- Macey: Formaldehyde at elevated levels up to 2,591 feet attahced

Please let me know if you have any thoughts or questions regarding all this material.

Looking forward to the next sit down.

All the best, Alex





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Article

Source signature of volatile organic compounds (VOCs) from oil and natural gas operations in northeastern Colorado

Jessica B. Gilman, Brian M. Lerner, William C. Kuster, and Joost de Gouw

Environ. Sci. Technol., Just Accepted Manuscript • DOI: 10.1021/es304119a • Publication Date (Web): 14 Jan 2013

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Source signature of volatile organic compounds from oil and natural gas operations in northeastern Colorado

J.B. Gilman,* B.M. Lerner, W.C. Kuster, and J.A. de Gouw

Cooperative Institute for Research in Environmental Sciences, Univ. of Colorado, Boulder, CO NOAA Earth System Research Laboratory, Chemical Sciences Division, Boulder, CO *corresponding author

Abstract

An extensive set of volatile organic compounds (VOCs) was measured at the Boulder Atmospheric Observatory (BAO) in winter 2011 in order to investigate the composition and influence of VOC emissions from oil and natural gas (O&NG) operations in northeastern Colorado. BAO is 30 km north of Denver and is in the southwestern section of Wattenberg Field, one of Colorado's most productive O&NG fields. We compare VOC concentrations at BAO to other U.S. cities; summertime measurements at two additional sites in northeastern Colorado; as well as the composition of raw natural gas from Wattenberg Field. These comparisons show that (i) the VOC source signature associated with O&NG operations can be clearly differentiated from urban sources dominated by vehicular exhaust, and (ii) VOCs emitted from O&NG operations are evident at all three measurement sites in northeastern Colorado. At BAO, the reactivity of VOCs with the hydroxyl radical (OH) was dominated by C2-C6 alkanes due to their remarkably large abundances (e.g., mean propane = 27.2 ppbv). Through statistical regression analysis, we estimate that on average 55 ± 18% of the VOC-OH reactivity was attributable to emissions from O&NG operations indicating that these emissions are a significant source of ozone precursors.



Introduction

Natural gas is a non-renewable fossil fuel that currently provides 25% of the total energy consumed in the United States.¹ Of the domestic natural gas produced today, 46% is from "unconventional" reserves (i.e., shale and tight sands). Since 2005, there has been an increase in "shale gas" production, which is expected to continue through 2035.¹ The recent and projected increase in oil and natural gas (O&NG) extraction from "unconventional" reservoirs has heightened environmental concerns regarding increased emissions of the greenhouse gas methane (CH₄),²⁻⁶ exposure to air toxics,⁷ and degradation of local air quality.^{4,8-9}

Raw, unprocessed natural gas is approximately 60-90% CH₄ by molecule. 10 The remaining fraction differs by reservoir, and is typically composed of a mixture of volatile organic compounds (VOCs) including alkanes (paraffins), cycloalkanes (napthenes). aromatics, non-hydrocarbon gases (e.g., CO₂, H₂S, SO₂, He, etc.), and water. ¹⁰ Certain by-products in raw natural gas will condense to the liquid phase depending on their vapor pressure and the conditions under which they are processed, transported, or stored. Natural gas condensate is a low-density, hydrocarbon solution composed of hydrocarbons with a range of boiling points similar to gasoline whereas crude oil is a higher-density fluid composed primarily of higher molecular weight, and less volatile hydrocarbons. 10 A single well may produce crude oil, raw natural gas, condensate and water depending on the reservoir. Specialized equipment located at each well site is designed to separate gases and oil from the liquid condensate and produced water. These by-products represent a small fraction of the raw natural gas or crude oil composition; however, they are often concentrated in storage tanks at each well site until the liquids are removed by tanker truck or pipeline. The industrial equipment required for O&NG operations includes diesel trucks, drilling rigs, power generators, phase separators, dehydrators, storage tanks, compressors, and pipelines. Each piece of equipment used to install, operate, or service a well is a known or potential emission source of CH_4 , VOCs, nitrogen oxides $(NO_x = NO+NO_2)$, and other gases or particulate matter (PM). Emissions of CH₄ and VOCs may occur at any stage of exploration and production by way of venting, flashing, flaring, or fugitive/non-permitted emissions. 11 When there are thousands of wells concentrated in a relatively small area, emissions

from these individual point sources can accumulate and represent a substantial area source of VOCs and other trace gases to the atmosphere. The focus of this study is to characterize the collective VOC emissions associated with O&NG operations in northeastern Colorado.

Enhanced levels of C₂-C₅ alkanes have been observed in ambient air samples collected near areas of O&NG production.^{2,4,13} These emissions were attributed to primary emissions from the oil and gas industry.^{2,4,13} Based on current U.S. emissions inventories, "natural gas and petroleum systems" are estimated to be the largest anthropogenic source of CH₄ (38%), and O&NG production contributes 11.3% of anthropogenic VOC emissions.¹⁴⁻¹⁵ Top-down estimates of CH₄ emission rates in Colorado and the southwestern U.S. indicate that current emission inventories of this potent greenhouse gas may be underestimated.^{2,4} This suggests that the co-emission of associated VOCs during the exploration for and the production of O&NG may also be underestimated.^{4,16}

Emissions associated with O&NG operations can affect air quality. For example, collocated emissions of VOCs and NO_x from oil and natural gas operations have been associated with high wintertime ozone levels (O₃ >150 ppbv hourly mean) in Wyoming's Green River Basin⁹ and Utah's Uintah Basin. As of 2007, portions of northeastern Colorado have been designated as a non-attainment area (NAA) for exceeding the 8-hour federal O₃ standard of 0.08 ppmv during the summertime. The NAA encompasses the Denver metropolitan area and surrounding cities where roughly one-half of Colorado's population resides, and Wattenberg Field where approximately 68% of the crude oil and 11% of the natural gas in Colorado is produced. Since 2008, the O&NG industry in northeastern Colorado has been subjected to much tighter regulations aimed at reducing emissions of CH₄, VOCs, and NO_x in concurrence with the State Implementation Plan to reduce ambient O₃ levels.

The primary objectives of this study are to (i) characterize primary VOC emissions from O&NG operations in northeastern Colorado, and (ii) estimate the relative contribution of VOC emissions from O&NG operations to OH reactivity, a metric that identifies the key reactive species that are involved in photochemical O₃ formation. This study expands on previous observations^{2,4} by providing a more detailed chemical



analysis of VOCs at higher temporal resolution. This enhanced level of detail is required to clearly distinguish the VOC source signature associated with O&NG operations from urban activities.

Methods

Measurement locations

Wintertime measurements were conducted at NOAA's Boulder Atmospheric Observatory (BAO, 40.05°N, 105.00°W) as part of NACHTT (Nitrogen, Aerosol Composition, and Halogens on a Tall Tower) experiment from 18 February to 7 March 2011. BAO is ~4 km east of Erie, Colorado and ~30 km north of the Denver metropolitan area, and is located within the southwestern section of Wattenberg Field of the greater Denver-Julesburg Basin (see map in Supplementary Information, Figure S1). At the time of these measurements, there were >15,000 active oil and natural gas wells within a 100 km radius and 22 wells within a 0.8 km (0.5 mile) radius from BAO. The nearest well pad was 300 m to the west.

Two summertime studies were also conducted in northeastern Colorado. . Measurements in Boulder, Colorado took place at NOAA's David Skaggs Research Center ~15 km west of BAO (39.99°N, 105.26°W) from 7-9 September 2010 during the Fourmile Canyon wildfire that was burning nearby and intermittently impacting the site (Figure S1).²¹ Measurements were conducted near Fort Collins, Colorado ~80 km north of BAO in an agricultural research field operated by Colorado State University (40.67°N, 105.00°W) from 20-24 July 2011.

For comparison, we include ship-borne measurements conducted in the Houston, Texas and Galveston Bay Area from August to September 2006 as part of TexAQS/GoMACCS 2006 (Texas Air Quality Study/Gulf of Mexico Atmospheric Composition and Climate Study)²² in addition to measurements conducted in Pasadena, California (34.14°N, 118.12°W) as part of CalNex 2010 (California Nexus) from 15 May to 15 June 2010.²³

Instrumentation

VOCs were measured in-situ by a custom-built, two-channel gas chromatograph-mass spectrometer (GC-MS). An unheated PFA inlet (20 m length, 4 mm i.d.) was continuously flushed with 7 SLPM of ambient air so that the inlet residence time was < 3 seconds. Inlet heights ranged from 8 m (at BAO) to 2.5 m (at Boulder and Fort Collins sites) above ground level. From the high volume inlet flow, two 350 mL ambient air samples are simultaneously collected for 5 min. During sample acquisition, water, CO_2 , and O_3 are removed prior to cryogenically trapping the VOCs. 12

The two samples collected in parallel are subsequently analyzed on their respective chromatographic columns. Channel 1 utilizes an Al_2O_3/KCI PLOT column ramped from 55°C to 150°C in 3.5 min to separate the C_2 - C_5 hydrocarbons. The C_5 - C_{11} hydrocarbons, oxygen-, nitrogen-, and halogen-containing VOCs are analyzed on Channel 2, which consists of a semi-polar DB-624 capillary column ramped from 38°C to 130°C in 11 min. The effluent from each column is sequentially analyzed by a linear quadrupole mass spectrometer (Agilent 5973N). The combined sample acquisition (5 min) and analysis (25 min) cycle repeats every 30 min. The limit of detection, precision, and accuracy are compound dependent, but are typically better than 0.010 ppbv, 15%, and 25%, respectively. Each compound reported is individually calibrated for using dynamic dilutions of several independent, multi-component gas-phase standards. 22

Results and discussion

Comparison of U.S. cities

Measurements of propane, benzene, and ethyne in northeastern Colorado are compared to other U.S. cities in order to highlight the influence of various emission sources on the observed mixing ratios of these compounds (Figure 1). Statistics for observations at BAO are summarized in Table 1 (see Supporting Information, Table S1 for statistics for all VOCs reported).

The mean mixing ratio of propane at BAO (27 \pm 1 ppbv, mean \pm standard error of mean) exceeds the range reported for 28 U.S. cities,²⁵ indicating the presence of a large propane source that is unique to the area. The mean propane level at BAO is 3-9 times larger than the observed means in the highly industrialized area of Houston, TX (6.7 \pm 0.8 ppbv),²² the large urban area of Pasadena, CA (2.92 \pm 0.03 ppbv), and the two other

Colorado sites (Boulder = 5.4 ± 0.5 ppbv, Fort Collins = 8.0 ± 0.5 ppbv) that lie outside of Wattenberg Field (Figure S1). Urban propane sources include the use of liquefied petroleum gas (LPG) and a minor source from fossil fuel combustion. Propane is produced during biomass burning (BB); however, the maximum observed value in Boulder was not associated with BB and there was no evidence of BB affecting the other datasets. Industrial sources of propane include raw natural gas processing and use as a feedstock in the petrochemical industry. The maximum propane level at BAO (304 ppbv) is most comparable to Houston (347 ppbv), where several fossil fuel refineries and petrochemical facilities are located.

Mean mixing ratios for benzene and ethyne for all datasets are within the range reported for 28 U.S. cities. Houston has the highest mean $(0.42 \pm 0.03 \text{ ppbv})$ and maximum (11.9 ppbv) benzene due to the industrial sources in the area. Pasadena has the highest mean ethyne $(1.27 \pm 0.01 \text{ ppbv})$ due to the preponderance of on road combustion sources. The maximum values for benzene (2.77 ppbv) and ethyne (8.36 ppbv) in Boulder were observed in biomass burning plumes. BAO and Fort Collins have elevated mean propane levels, but mean benzene and ethyne levels similar to other U.S. cities (Figure 1), indicating that both these sites are influenced by an area propane source that is unrelated to combustion.

At BAO, the C_2 - C_7 alkanes and C_5 - C_6 cycloalkanes are also highly abundant and are tightly correlated with propane (coefficients of determination, $r_{propane} > 0.90$) but less so with ethyne ($r_{ethyne} < 0.78$, Table 1). This is in accordance with long-term measurements at the top of the 300 m tower at BAO by Pétron et al. who showed that the C_3 - C_5 alkanes (i) are significantly enhanced compared to other measurements on tall towers in the U.S., (ii) strongly correlate with one another, but do not always correlate well with combustion tracers such as carbon monoxide and (iii) are enhanced by a factor of ~1.75 in the winter compared to summer due to longer photochemical lifetimes and more stable/stratified boundary layer conditions during the colder winter months.² In comparison, the 2011 wintertime propane levels at BAO are >3 times greater than the summertime levels in Boulder and Fort Collins suggesting that enhancements in propane at BAO cannot be explained by seasonal differences alone. The strong correlations of the C_2 - C_7 alkanes and C_5 - C_6 cycloalkanes with propane

suggest that these compounds (i) have a similar source as propane, and (ii) there was minimal photochemical processing during the wintertime study at BAO. One would expect to see greater variability (smaller r_{propane}) if there were other VOC sources with disparate emission ratios or from the preferential removal of the more reactive VOCs (e.g., heptane) as an air mass is photochemically aged.

Source signature of O&NG operations in Northeastern Colorado

The magnitude of observed VOC mixing ratios (Figure 1) will be affected by boundary layer conditions, the proximity to emission sources, and the extent of photochemical processing. In order to minimize these effects, we utilize the iso-pentane to n-pentane (iC_5/nC_5) enhancement ratio to identify the VOC source signature of O&NG operations. The iC_5/nC_5 enhancement ratio is equal to the slope of a linear 2-sided fit of an iso-pentane to n-pentane correlation plot (Figure 2). This ratio is largely independent of air mass mixing and dilution as both species are similarly affected;²⁸ therefore, the ratio will not be unduly influenced by the boundary layer conditions or the proximity to emission sources. The iC_5/nC_5 ratio will also be minimally affected by photochemical processing (which is minimal for the wintertime study) as both species have similar reaction rate coefficients with the hydroxyl radical.²⁹

In Figure 2, we compare the observed iC_5/nC_5 enhancement ratios for the same set of U.S. cities included in Figure 1. Pasadena has the highest iC_5/nC_5 ratio of 2.41 \pm 0.02 (r = 0.94). Literature values for the iC_5/nC_5 ratio for gasoline related sources range from 2.3 for the composition of liquid gasoline blended for wintertime use in California³⁰ to 3.80 for the composition of gasoline vapors.³⁰⁻³¹ The iC_5/nC_5 ratio in Pasadena lies within this range and most closely matches the values observed in a Los Angeles tunnel study $(iC_5/nC_5 = 2.45)^{32}$ indicating that emissions from gasoline fueled vehicles are the main sources of these compounds in Pasadena.

The iC_5/nC_5 ratios observed at BAO (0.885 \pm 0.002, r = 0.998), Fort Collins (0.809 \pm 0.008, r = 0.990), and Boulder (1.10 \pm 0.05, r = 0.91) are significantly lower than that observed in Pasadena indicating that gasoline is not the primary source of these compounds in these datasets. The iC_5/nC_5 enhancement ratio for raw natural gas in the Greater Wattenberg Area of the Denver-Julesburg Basin is 0.86 \pm 0.02 (r =

 $0.97)^{33}$, which is statistically equivalent to that observed in ambient air at BAO. The identical iC₅/nC₅ ratios observed in ambient air at BAO and raw natural gas samples collected in Wattenberg Field strongly suggest that O&NG operations in the area are the dominant source of these compounds. For Boulder, the individual data points lie on or between the iC₅/nC₅ ratios for Pasadena and BAO, indicating that both urban activities and O&NG operations impacted air masses in Boulder.³⁴ Our analysis shows that all three measurement sites in Colorado were influenced by VOC emissions from O&NG operations concentrated in Wattenberg Field of the greater Denver-Julesburg Basin.

The iC_5/nC_5 ratio appears to be similar for different O&NG reservoirs. For example, Gilman et al. reported intercepting an air mass influenced by natural gas activities on Russia's Kola Peninsula with an iC_5/nC_5 ratio of $0.89.^{24}$ Riaz et al. reported an iC_5/nC_5 ratio of 0.84 for natural gas condensate from a reservoir in the North Sea. The composition of the Macondo reservoir fluid that escaped into the Gulf of Mexico after the Deepwater Horizon explosion had an iC_5/nC_5 ratio of $0.82.^{36}$ Additionally, isopentane and n-pentane have similar boiling points, vapor pressures, and reaction rate coefficients with the hydroxyl radical so that the iC_5/nC_5 ratio will be less susceptible to perturbations during initial processing stages or photochemical oxidation upon release to the atmosphere. The iC_5/nC_5 ratio appears to be a robust indicator of the influence of O&NG operations.

Source apportionment of VOCs at BAO in northeastern Colorado

At BAO, the C_2 - C_7 alkanes and several of the cycloalkanes are tightly correlated with propane ($r_{propane} > 0.90$, Table 1), a predominant by-product in O&NG production, whereas the C_9 aromatics and ethene are more tightly correlated with ethyne ($r_{ethyne} > 0.90$), a combustion tracer associated with urban activities. We use these two species in a multivariate regression analysis to show that the variability in propane and ethyne can be used to explain the observed variability of the other VOCs. This allows us to (i) characterize the emission source profiles of various hydrocarbons associated with these sources and (ii) estimate the relative contribution of each emission source.

The expression used for the multivariate analysis is given by:

$$[VOC] = Bkgd_{VOC} + \left\{ ER'_{propane} \times [propane_{O}] \right\} + \left\{ ER'_{ethyne} \times [ethyne_{O}] \right\} \tag{1}$$



where [VOC] is the mixing ratio of the VOC to be fitted, and $Bkgd_{VOC}$, is equal to the minimum observed values (Table S1), [propane₀] and [ethyne₀] are the observed propane and ethyne mixing ratios minus the minimum observed values for propane (0.58 ppbv) and ethyne (0.30 ppbv), respectively. The expression (eq 1) is solved for $ER'_{propane}$, and ER'_{ethyne} , which represent the derived values of the VOC emission ratio relative to propane, and the VOC emission ratio relative to ethyne, respectively. Equation 1 does not include terms for photochemical production/loss as we assume photochemistry was negligible (see discussion above).

One limitation of this simplified source apportionment analysis is that $ER'_{propane} = 1$ and $ER'_{ethyne} = 0$ for propane and $ER'_{propane} = 0$ and $ER'_{ethyne} = 1$ for ethyne by definition. For explicit quantification of $ER'_{propane}$ and ER'_{ethyne} , the two variables ([propane₀] and [ethyne₀]) should be independent of one another. Raw and processed natural gas contains propane but not ethyne; however, combustion of fossil fuels often produces small amounts of propane relative to ethyne. Propane to ethyne emission ratios range from <0.10 for tailpipe emissions³² to 1.2-2.5 for urban areas that may include natural gas sources.³⁷ These ratios are significantly less than the observed propane to ethyne enhancement ratio at BAO ($ER_{ethyne} = 97$, see Table S1 and Table of Contents Figure) indicating that ethyne sources will have a small contribution to propane for the vast majority of the samples.

In Figure 3a-f, we compare the observed mixing ratios with those derived from the multivariate analysis for three example compounds: iso-butane, benzene, and ethene. The time series of the derived mixing ratios are colored by the contribution from each of the three terms of the multivariate fit, and the pie charts depict the mean contribution of each term. The variability of the three species is well represented by the multivariate fit ($r_{\rm fit} > 0.94$, Figure 3d-3f). For iso-butane, the correlation with propane is so strong ($r_{\rm propane} = 0.99$, Table 1) that the propane term ($ER'_{propane} \times [propane]$) completely dominates (Figure 3a). Benzene has significant contributions from both the propane and ethyne terms indicating benzene emissions are from more than one source (Figure 3b), similar to the findings of Pétron et al.² For ethene, the ethyne term dominates indicating combustion related sources are the primary source of this compound.

Results of the multivariate fit for all VOCs reported are compiled in Tables 1 and S1. The multivariate analysis using only propane and ethyne as variables adequately captures the observed variability ($r_{\rm fit} > 0.80$) in the alkanes, cycloalkanes, aromatics, and alkenes including isoprene (see Table S1). The other biogenic VOCs and oxygenated VOCs are not tightly correlated with either propane or ethyne resulting in a poorer fit ($r_{\rm fit} < 0.80$ and slope $r_{\rm fit} < 0.65$) indicating that these compounds have additional sources and/or natural variabilities that are independent of propane and ethyne emissions and will therefore be excluded from further discussion.

Figure 4 shows the comparison of the derived emission ratios (ER'propane and ER'ethyne) to various emission sources. ER'propane is compared to VOC to propane ratios determined from the composition of raw natural gas in the Greater Wattenberg Area³³ (ER_{propane} raw gas, Figure 4a) and for ambient air sampled downwind of an oil storage tank with a working oil well as reported by Katzenstein et al.4 (Figure 4b). The emission ratios for a majority of the compounds in all three datasets agree within a factor of 2; however, the derived propane source profile (i.e., the composite of the individual ER'propane) agrees more closely with the ambient air profile from Katzenstein et al. In Figure 4a, the derived ethane to propane emission ratio is lower in ambient air than expected from the raw natural gas composition (ER'propage < ERpropage raw gas), while the derived emissions of the C₄-C₅ alkanes relative to propane are higher than ER_{propane} raw gas. This suggests that the C2-C5 alkanes observed in ambient air at BAO may not be only from direct venting of raw natural gas to the atmosphere, but from the emission of raw natural gas components after some stage of initial processing where the lighter, more volatile components have been partially separated from the heavier, less volatile components; a common industry practice called condensate stabilization.³⁸ These findings are consistent with previous observations by Pétron et al. at BAO.2 We note that the iC₅/nC₅ ratio (see previous discussion) would not be affected by condensate stabilization because they have similar vapor pressures.

The derived ER'_{ethyne} are compared to published VOC to ethyne emission ratios measured in gasoline-powered motor vehicle exhaust²⁷ (Figure 4c) and in urban Los Angeles²³ (Figure 4d). For the C₃-C₅ alkanes, ER'_{ethyne} derived for BAO is 0 because the fit is overwhelmed by the propane source term; therefore, these compounds do not

appear in Figures 4c-4d due to the logarithmic scale. The ER'_{ethyne} for the majority of the C_6 - C_{11} alkanes, C_6 - C_9 aromatics, and C_2 - C_3 alkenes agree with literature values for ambient air in the urban area of Los Angeles. The derived ethane to ethyne emission ratio is greater than that expected for vehicle exhaust and in Los Angeles (ER'_{ethyne} > ER_{ethyne}) suggesting that we are overestimating the urban emission ratio of ethane at BAO by more than a factor of 2.

From these comparisons, we conclude that a large fraction of the VOC variability observed at BAO can be explained by a linear combination of two emission sources. The first source is proportional to propane, has a composition that is similar to that of natural gas itself and to emissions from condensate tanks in Texas and Oklahoma, and is therefore attributed to O&NG operations in the area surrounding BAO. The second source is proportional to ethyne, has a composition similar to that of urban emissions and is therefore attributed to traffic-related sources in the area. The relative contribution of O&NG operations to the observed mixing ratios can now be estimated from Equation 1 by a ratio of the three components of the multivariate analysis as shown:

$$O\&NG\ Fraction = \frac{\{ER'_{propane} \times [propane_0]\}}{Bkgd_{VOC} + \{ER'_{propane} \times [propane_0]\} + \{ER'_{ethyne} \times [ethyne_0]\}}$$
(2)

The mean O&NG fractional contributions for those VOCs included in the subsequent analysis section are compiled in Tables 1 and S1. From this analysis, O&NG operations in northeastern Colorado during the wintertime study at BAO are identified as the dominant source of C_2 - C_8 alkanes and C_5 - C_8 cycloalkanes and a minor source of C_6 - C_8 aromatics and alkenes compared to urban emission sources.

OH reactivity

The primary source of O_3 in the lower troposphere is the photolysis of NO_2 that has been produced from peroxy radical (ROO•) oxidation of NO. In typical urban air masses, a complex, photo-initiated oxidation sequence that involves reactions between NOx ($NOx = NO+NO_2$) and reactive VOCs provides the peroxy radicals required for the fast and efficient photochemical formation of O_3 . Oxidation of VOCs by the hydroxyl radical (•OH) is the initial step in the process. OH reactivity is a simple metric that identifies the key reactants that most readily form ROO•, and therefore, are most likely

to play a key role in the potential formation of O_3 . The actual amount of O_3 produced is dependent on the relative abundances of NOx and VOCs, which affect the overall oxidation mechanism.

The OH reactivity for the VOCs measured at BAO was calculated using:

$$R_{OH+VOC} = \sum (k_{OH+VOC} \times [VOC]) \tag{3}$$

where R_{OH+VOC} is the sum of the products of the temperature and pressure dependent reaction rate coefficient, k_{OH+VOC} , and the VOC concentration, [VOC], in molec cm⁻³. The campaign mean and median R_{OH+VOC} for the wintertime measurements at BAO are $3 \pm 3 \text{ s}^{-1}$ and 2 s^{-1} , respectively. We compare this to the Texas study where the median R_{OH+VOC} ranged from 0.28 s⁻¹ in the remote marine boundary layer to 3.02 s⁻¹ near Houston in the summertime.²²

The diurnal profile of the mean and median R_{OH+VOC} (Figure 5a) shows that the OH reactivity is greater in the first half of the day (00:00-12:00 MST). The decrease around 12:00 MST is associated with an increase in both wind speed and boundary layer depth, which effectively dilutes the reactants resulting in a reduction of R_{OH+VOC} . The fractional contribution of each VOC class to R_{OH+VOC} (Figure 5b) is independent of the boundary layer dynamics. R_{OH+VOC} is dominated by the alkanes, which account for 60% of the OH reactivity on average. Reactivity of the oxygenated VOCs (OVOCs), which is dominated by acetaldehyde and ethanol, accounts for 27% of the VOC reactivity. Alkenes, cycloalkanes, and biogenics are generally more of reactive than alkanes; however, their relatively low abundances compared to the alkanes make them only minor contributors to R_{OH+VOC} .

We can estimate the contribution of hydrocarbons emitted from O&NG activities by applying the O&NG fraction from the combination of Eqs 2 and 3.

$$R_{OH+VOC} O\&NG = \sum (k_{OH+VOC} \times [VOC] \times O\&NG \ fraction) \tag{4}$$

The mean contribution of VOCs attributed to O&NG activities (R_{OH+VOC} O&NG) is 55 ± 18% (1 sigma deviation) for the BAO dataset. This large contribution directly pertains to the elevated concentrations of the light alkanes, which are known byproducts of and are attributed to O&NG production. The fraction of reactivity due to emissions from O&NG emissions varies strongly between different air masses. The distribution of calculated R_{OH+VOC} O&NG values is included in Figure S2 as well as a



wind directional analysis. Samples with the highest R_{OH+VOC} O&NG occur when winds arrive at BAO from the northeast sector where the majority of the O&NG wells are located (Figure S2). Only 4% of all samples at BAO had high R_{OH+VOC} O&NG and were from the western sector where the nearest wells are located indicating that they were not the dominant O&NG source at BAO.

The results of this analysis indicate that VOC emissions from O&NG production in northeastern Colorado are a significant source of O₃-precursors in this region. The contribution from O&NG operations is expected to decrease somewhat during the summertime "O₃ season" as the relative importance of biogenic VOCs may increase. We have recently conducted summertime measurements at BAO in order to investigate the relative role of biogenic VOCs and investigate the products formed during active photochemistry in order to identify the important VOC precursors, which will be detailed in a forthcoming analysis.

Associated Content

Supporting Information

Data from the 2011 wintertime study at BAO (NACHTT) is available at http://www.esrl.noaa.gov/csd/groups/csd7/measurements/2011NACHTT/Tower/DataDownload/. An expanded table of statistics and analysis results for all 53 VOCs reported in included in Table S1. Additional figures include a detailed map of the measurement sites in northeastern Colorado (Figure S1) and the distribution of calculated R_{OH+VOC} O&NG values and associated wind rose frequency plots (Figure S2). This material is available free of charge via the Internet at http://pubs.acs.org/.

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Notes

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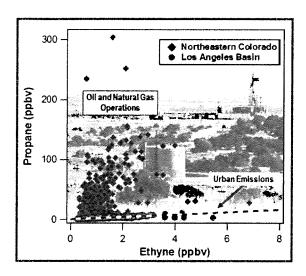


Figure 1. Box and whisker plots (maximum, 75th, 50th, 25th percentiles, and minimum) including mean values (open circles) for a) propane, b) benzene, and c) ethyne. Range of mean values for 28 U.S. cities (Baker et al.) is indicated by red dashed lines.

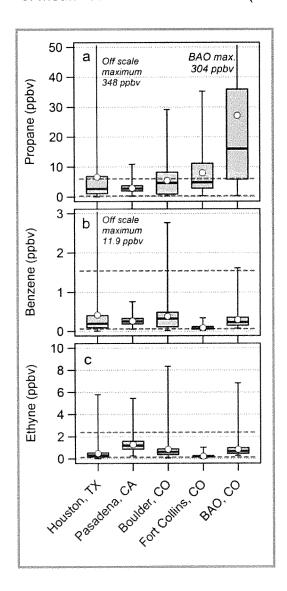


Figure 2. Correlation plots of iso-pentane versus n-pentane for BAO, Fort Collins, and Boulder measurement sites in northeastern Colorado. Data from other U.S. cities including Houston, Texas (TexAQS 2006, individual data points not shown) and Pasadena, California (CalNex 2010) are included for comparison. Raw natural gas samples from the Greater Wattenberg Area of the Denver-Julesburg Basin are plotted as mole percent. Enhancement ratios (ER) are determined by linear 2-sided fits. Inset shows the full range of ambient observations.

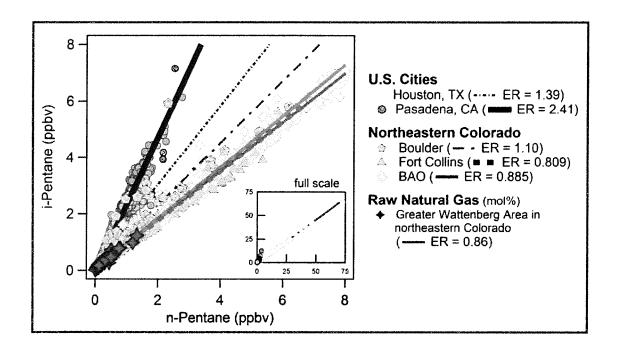


Figure 3. The left column shows the time series of the measured mixing ratios at BAO and mixing ratios derived from the multivariate fit for a) iso-butane, b) benzene and c) ethene. The time series of the derived mixing ratio and the pie charts are colored by the contribution of each term of the multivariate fit analysis. The pie charts depict the mean contribution of each term. The right column shows correlation plots of the derived versus the measured mixing ratios for d) iso-butane, e) benzene and f) ethene where r_{fit} is the linear correlation coefficient and S_{fit} is the slope of the linear 2-sided fit.

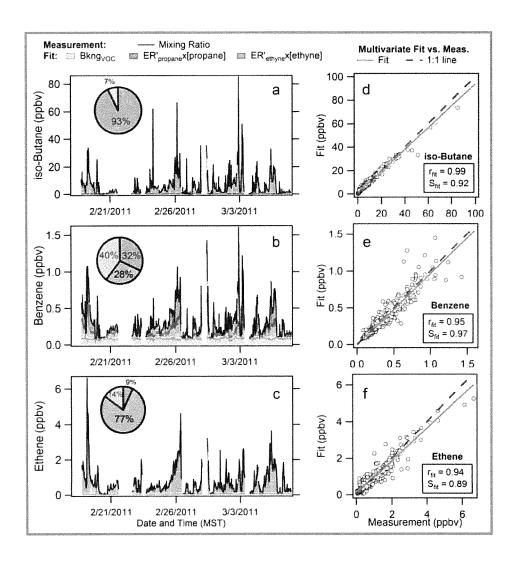


Figure 4. Comparison of VOC-to-propane emission ratios derived from the multivariate fit (*ER'*_{propane}) versus VOC-to-propane ratios a) for raw natural gas in the Greater Wattenberg Area of the Denver-Julesburg Basin and b) reported by Katzenstein et al. for a sample downwind of an oil storage tank with a working oil well. Comparison of the VOC-to-ethyne emission ratios derived from the multivariate fit (*ER'*_{ethyne}) to the VOC-to-ethyne emission ratios published by c) Schauer et al. for gasoline-powered motor vehicles and d) Borbon et al. for urban Los Angeles, California. The 2:1, 1:1, and 1:2 lines are shown in all panels, where the shaded area represents a factor of 2 from unity. Each marker represents a different VOC. Alkanes are colored maroon and are identified by carbon number (e.g., C2 = ethane, iC4 = iso-butane). Aromatics are colored purple (Bz = benzene, Tol = toluene, and 135tmbz = 1,3,5-trimethylbenzene). Alkenes and ethyne are colored pink and are identified by empirical formulas (e.g., C2H₂ = ethyne).

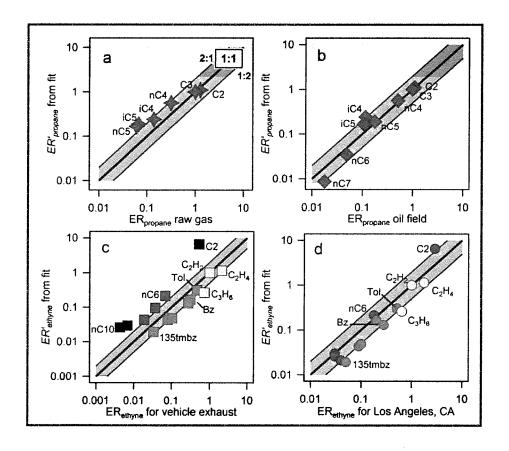
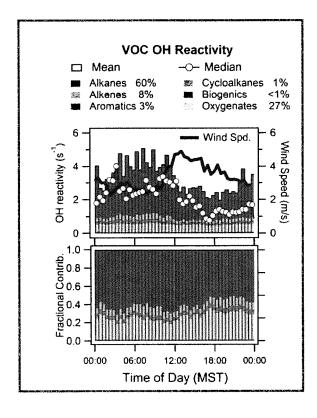


Figure 5. a) Diurnal profile of the VOC OH reactivity at BAO. The mean VOC OH reactivity is represented by the height of bar and is colored by the contribution from each compound class. Diurnal profiles of the median VOC OH reactivity is given by the markers and mean wind speed is given by the thick black line. b) The average fractional contribution of each VOC compound class as a function of time of day. The campaign integrated contributions for each compound class are listed as percentages in the figure key.



Compound	Mean	St.Dev.	Median	⊠in.	Мах.	^r propane ^r ethyne	^r ethyne	Bkng	ER' propane	ER' ethyne	Mean O&NG
	vdqq	1 sigma	vddd	vadd	vdqq			nqdd	ppbv [ppbv C ₃ H ₈] ⁻¹	ppbv [ppbv C ₂ H ₂] ⁻¹	Contrib. (%)
Alkanes											
10 11 Ethane	35	38	22	1.6	300	96.0	0.61	1.6	1.090	9.9	72
Propane	27	33	17	0.58	304	1.00	0.56	0.58	(0	06
12 13 i-Butane	0.9	8.5	2.9	0.078	85	0.99	0.55	0.078	0.243	0.00	93
14 n-Butane	14		7.3	0.11	184	0.99	0.54	0.11	0.563	00.0	9.5
15i-Pentane	4.2	5.9	2.0	0.038	64	0.97	0.55	0.038	0.168	0.00	95
16n-Pentane	4.7	6.7	2.2	0.028	73	0.97	0.54	0.028	0.190	0.00	96
17 n-Hexane	1.1	1.3	9.0	0.014	12	0.95	0.60	0.014	0.0348	0.213	78
18n-Heptane	0.32	0.35	0.19	<10D	2.8	0.92	0.63	0	0.0087	0.096	73
19 Cycloalkanes											
20 21 Methylcyclopentane	1.3	1.2	1.0	0.030	6.7	0.97	0.78	0.030	0.028	0.28	99
2 Cyclohexane	0.30	0.28	0.20	0.0063	1.4	0.97	0.78	0.0063	0.0062	0.069	67
23 Methylcyclohexane	0.28	0.34	0.17	0.0045	5.6	0.91	69.0	0.0045	0.0074	0.065	72
24 Aromatics											
25 Benzene	0.29	0.21	0.23	0.075	1.6	0.88	0.79	0.075	0.00428	0.166	32
26Toluene	0.30	0.29	0.21	0.016	2.2	92.0	0.85	0.016	0.0038	0.308	31
27 m&p-Xylenes	0.11	0.10	0.075	0.005	0.61	0.75	98.0	0.005	0.00099	0.130	23
28 o-Xylene	0.03	0.03	0.023	<10D	0.19	0.71	0.87	0	0.00026	0.0488	20
23 Alkenes and Alkynes											
Ethyne	0.84	0.61	0.67	0.30	8.9	0.56	1.00	0.3	0	Н	0
32 Ethene	0.74	0.79	0.49	0.052	9.9	09.0	0.94	0.052	0.0025	1.14702	8.6
33 Propene	0.16	0.19	60.0	0.012	1.5	0.47	0.83	0.012	0.0001	0.26195	1.8
34 35	<lod below="" detection<="" limit="" of="" td=""><td>nit of dete</td><td>rtion</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></lod>	nit of dete	rtion								
	r Coefficient of		rmination	for obser	Vod VO	10 010	dae each	determination for observed VOC to propage ephancement ratio	ci t ic		
	propane COCIIICIO			יים המסום	אבר אבר אבר	5 5 0 1	מוע עווי	מורבוובוור	ario		
	rpropane Coefficient of	int of deter	rmination	for obser	ved VO	C to ethy	ne enhar	determination for observed VOC to ethyne enhancement ratio	tio		
ER	ER ' propone Emission ratios derived from the multivariate regression analysis for each VOC relative to propane	າ ratios der	ived from	the mult	ivariate	regressi	on analys	is for each	VOC relative to	propane	
13	ER' ethyne Emission	Emission ratios derived from the multivariate	ived from	the mult	ivariate						
IVIEAN O&IVG CONTRID.	<i>ontrib.</i> IVlean co	Mean contribution of VOC emissions from O& expressed as a percentage	ution of VOC emission. essed as a percentage	nissions 1 entage	rom O8						
19					!						
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40											



David Brown*, Beth Weinberger, Celia Lewis and Heather Bonaparte

Understanding exposure from natural gas drilling puts current air standards to the test

Abstract: Case study descriptions of acute onset of respiratory, neurologic, dermal, vascular, abdominal, and gastrointestinal sequelae near natural gas facilities contrast with a subset of emissions research, which suggests that there is limited risk posed by unconventional natural gas development (UNGD). An inspection of the pathophysiological effects of acute toxic actions reveals that current environmental monitoring protocols are incompatible with the goal of protecting the health of those living and working near UNGD activities. The intensity, frequency, and duration of exposures to toxic materials in air and water determine the health risks to individuals within a population. Currently, human health risks near UNGD sites are derived from average population risks without adequate attention to the processes of toxicity to the body. The objective of this paper is to illustrate that current methods of collecting emissions data, as well as the analyses of these data, are not sufficient for accurately assessing risks to individuals or protecting the health of those near UNGD sites. Focusing on air pollution impacts, we examined data from public sources and from the published literature. We compared the methods commonly used to evaluate health safety near UNGD sites with the information that would be reasonably needed to determine plausible outcomes of actual exposures. Such outcomes must be based on the pathophysiological effects of the agents present and the susceptibility of residents near these sites. Our study has several findings. First, current protocols used for assessing compliance with ambient air standards do not adequately determine the intensity, frequency or durations of the actual human exposures to the mixtures of toxic materials released regularly at UNGD sites. Second, the typically used periodic 24-h average measures can underestimate actual exposures by an order of magnitude. Third, reference standards are set in a form that inaccurately determines health risk because they do not fully consider the potential synergistic combinations of toxic air emissions. Finally, air dispersion modeling shows that local weather conditions are strong determinates of individual exposures. Appropriate estimation of safety requires nested protocols that measure real time exposures. New protocols are needed to provide 1) continuous measures of a surrogate compound to show periods of extreme exposure; 2) a continuous screening

model based on local weather conditions to warn of periodic high exposures; and 3) comprehensive detection of chemical mixtures using canisters or other devices that capture the major components of the mixtures.

Keywords: acute toxic actions; toxic materials; unconventional natural gas development (UNGD).

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Introduction

Recent and projected growth in the oil and gas production sector has underscored the need for EPA to gain a better understanding of emissions and potential risks from this industry sector. Harmful pollutants emitted from this industry include air toxics such as benzene, toluene, ethylbenzene, and xylene; criteria pollutants and ozone precursors such as $\mathrm{NO_x}$ and VOCs; and greenhouse gases such as methane. These pollutants can result in serious health impacts such as cancer, respiratory disease, aggravation of respiratory illnesses, and premature death. However, EPA has limited directly-measured air emissions data on criteria and toxic air pollutants for several important oil and gas production processes. [These] limited data, coupled with poor quality and insufficient emission factors and incomplete NEI data, hamper EPA's ability to assess air quality impacts from selected oil and gas production activities.

 US Environmental Protection Agency (EPA) Office of Inspector General (1)

The question we, and others, have asked is: do the levels of exposure to the mixture of unconventional natural gas development (UNGD) emissions constitute a potential human health hazard to those living very near UNGD activities (2–7)? The answer hinges on the emissions themselves, their synergistic effects, the methodology used for collecting and analyzing data, and the standards for gauging human health risk. More specifically, the answer hinges on whether the methodology used is designed to

capture the important features of episodic and fluctuating emissions and exposures that characterize UNGD activity.

In this article, UNGD refers to the complete process of extracting, processing and transporting natural gas, including all associated infrastructures, such as flare stacks, flowback pits, compressors, and condensate tanks. Each stage of UNGD produces a different combination of emissions and the levels of release are also variable. Colburn et al. (8) collected air samples weekly for 1 year and reported that emissions were highest during the drilling phase of development. However, estimates provided by industry for the New York State Revised Draft SGEIS (9) suggest that VOC emissions may be greater during the production phase. In any case, emissions vary at each well pad because of several factors, including the type of gas being extracted, the mixture of fluids used, the quality of equipment, as well as the methods of extraction and processing. For example, flowback fluids may be trucked off a well pad or held in impoundments onsite, whereas in the finishing process, gases may be flared or vented.

Another variable in terms of human exposure risk is state setback regulations. Among the states that have them, each has different requirements for well setbacks from buildings and/or water sources. A survey on setback regulations for natural gas drilling reports that, for buildings, the setback distance can vary from 100 to 1000 feet, with an average of 308 feet (10). Water source setbacks can vary from 50 feet (Ohio) to as much as 2000 feet (Michigan). This same report finds "extensive regulatory heterogeneity among the states" for those with active gas production (10).

Toxicity of a chemical to the human body is determined by the concentration of the agent at the receptor where it acts. This concentration is determined by the intensity and duration of the exposure. All other physiological sequelae follow from the interaction between agent and receptor. Once a receptor is activated, a health event might be produced immediately or in as little as 1 to 2 h (11, 12). Alternatively, future exposures might compound the impact of the first one, eventually producing a health event. In some instances where there is a high concentration of an agent, a single significant exposure can cause injury or illness. Federal and state health standards for water and air, which are applied to UNGD emissions, ought to reflect and be evaluated in reference to these physiological realities; currently they do not. Thus, in order to understand and define the gap between air standards and the process by which UNGD exposures cause health effects, we examined the literature on UNGD emissions and exposures and then evaluated widely accepted health standards in light of environmental data we have collected.

Our interest in closing the gap between standards and the mechanisms of environmental health effects stems from the work we do in communities in southwest Pennsylvania, USA. Individuals in these communities have taught us a great deal about their health concerns and their unease with the air in and outside of their homes. There are similar issues with the potential for well water contamination from UNGD in the region. In this paper, we specifically address the risks posed by episodic, high concentration air exposures. Commonly used standards and benchmarks are particularly ill-equipped to consider this set of exposures.

Standards and monitoring protocols

The air standards and guidelines often used by the federal government, state governments, and by many independent researchers are those set by the National Ambient Air Quality Standards (NAAQS). These standards approach, but do not meet, the physiological criteria for how exposures cause damage at the individual level. This is not, however, a failure of the NAAQS. The standards have been designed to benchmark regional air quality, which refers to whether the overall pollution level in a region, over time, is within the ambient air target zone EPA deems safe. The standards are a tool for the regulatory system, which requires averaging of samples taken. How these data are collected, averaged, and interpreted varies by pollutant. It should also be noted that one of the criteria for determining standards is that the targeted level must be measurable, that is, if a chemical is not readily measurable at a given level, its use cannot be monitored, regulated or enforced. This criterion precludes standards being set to a very low level.

As seen in Table 1, the form (i.e., application) of the standard varies by compound. However, regardless of the substance, each standard relies on averages of exposures, sometimes over long periods of time. By seeking to provide overall regional air quality guidance, NAAOS and other air quality benchmarks have the following critical weaknesses when applied to individuals or very local areas: 1) current NAAQS do not address the interactions of the chemical agents in the air and then in the body; 2) long-term averages fail to capture the frequency or magnitude of very high readings; and 3) with periodic data collection, important spikes or episodic exposures (common in UNGD) can be missed. In those few cases where shortterm or hourly ambient air levels are measured, the purpose is generally to avoid poisoning from catastrophic releases (13).



Table 1 National ambient air quality standards.

Pollutant		Primary/secondary	Averaging time	Level	Form
Carbon monoxide		Primary	8 h 1 h	9 ppm 35 ppm	Not to be exceeded more than once per year
Nitrogen dioxide		Primary Primary and secondary	1 h Annual	100 ppb 53 ppb	98th percentile, averaged over 3 years Annual mean
Ozone		Primary and secondary	8 h	0.075 ppm	Annual fourth-highest daily maximum 8-h concentration, averaged over 3 years
Particle pollution	PM ₂ · ₅	Primary Secondary Primary and secondary	Annual Annual 24-h	12 μg/m³ 15 μg/m³ 35 μg/m³	Annual mean, averaged over 3 years Annual mean, averaged over 3 years 98th percentile, averaged over 3 years
	PM_{10}	Primary and secondary	24-h	150 μg/m ³	Not to be exceeded more than once per year on average over 3 years
Sulfur dioxide		Primary	1-h	75 ppb	99th percentile of 1-h daily maximum concentrations, averaged over 3 years
		Secondary	3-h	0.5 ppm	Not to be exceeded more than once per year

Adapted from: www.epa.gov/air/criteria.html.

In addition, researchers use other guidelines for determining whether an exposure is within or beyond safe limits. Some researchers and regulatory agencies, for instance, use EPA's Integrated Risk Information System (IRIS), a database of research on human health exposures. Guidance provided through IRIS covers hundreds of chemicals and their possible effects on humans. The database assists researchers with hazard identification and dose-response assessment as well as with oral reference doses (RfDs), inhalation reference concentrations (RfCs), and carcinogenicity assessments. The RfD or RfC reflects an estimate of the highest daily exposure across a lifetime, which is likely to be without significant risk of health effects. The science underlying these reference levels, however, does not necessarily apply to the risk circumstances brought about by UNGD. Furthermore, RfDs and RfCs have no direct regulatory application and no legal enforceability. Researchers have also evaluated the wisdom of looking at peak exposures as compared to averages over longer periods of time. Delfino et al. (14) posited that maxima of hourly data, not 24-h averages, better captured the risks to asthmatic children, stating, "it is expected that biologic responses may intensify with high peak excursions that overwhelm lung defense mechanisms". Additionally, they suggest that "[o]ne-hour peaks may be more influenced by local point sources near the monitoring station that are not representative of regional exposures".

Similarly, Darrow (15) writes that peak exposures can sometimes better capture relevant biological processes. This is the case for health effects that are triggered by short-term, high doses. They write, "Temporal metrics that reflect peak pollution levels (e.g., 1-h maximum) may

be the most biologically relevant if the health effect is triggered by a high, short-term dose rather than a steady dose throughout the day. Peak concentrations ... are frequently associated with episodic, local emission events, resulting in spatially heterogeneous concentrations".

To give just one example, we know that 1 to 2 h of a diesel exhaust exposure can cause, for instance, reduced brachial artery diameter and exacerbation of exercise-induced ST-segment depression in people with pre-existing coronary artery disease; ischemic and thrombotic effects in men with coronary heart disease (16); and is associated with acute endothelial response and vasoconstriction of a conductance artery (17).

Given that episodic high exposures are not typically documented and analyzed by researchers and public agencies, health complaints in the area are not being correlated with industry emissions. However, examination of published air emission measurements in gas extraction and processing sites, along with collected health data from the Environmental Health Project (EHP) and others, show very real potential for harm from industry emissions (18). Reports of acute onset of respiratory, neurologic, dermal, vascular, abdominal, and gastrointestinal sequelae near natural gas facilities contrast with research, which suggests that there is limited risk posed by UNGD. By extension, we believe the contrast points to the inadequacy of using current federal standards.

For public agencies to protect human health, they need standards that are sensitive to and consistent with the known routes of exposure, the duration and frequency of exposures, the nature of chemical mixtures, tissue repair rates, plausible target organs, and the increased



sensitivity of susceptible populations. Monitoring efforts must be complex enough to account for the actual mechanisms at work in the exposure-receptor relationship. They must also be sufficiently robust to measure fine-grained, hour-to-hour variability in air concentrations.

The objectives of this paper are to illustrate the shortcomings of the available data as well as the inadequacy of the standards by which they are evaluated. We present new protocols for air monitoring based on the observed health effects produced by exposures and on documented emissions patterns from the industry. The protocols are directed at the needs of the local residents who must be able to determine the safety and welfare of their families. The protocol reflects the following central requirements: 1) continuous measures of a surrogate compound to show periods of extreme exposure, 2) a continuous screening model based on local weather conditions to warn of periodic high exposures, and 3) comprehensive detection of chemical mixtures using canisters or other devices that capture the major components of the mixtures.

Background

Documented emissions¹

Researchers have begun to document the content and quantities of emissions from UNGD sources, such as engine exhausts, condensate tanks, production equipment, well-drilling and completions, and transmission fugitives. Emissions identified have included four of the five NAAOs pollutants (excluding ozone) and a wide range of volatile organic compounds (VOCs) and other air toxics (19). Research conducted in the Fort Worth, Texas area documented the variation in emissions among locations and forms of UNGD activity. Point source research found a total of 2126 emission points in one 4-month UNGD field study. Pneumatic valve controllers were the most frequent emission sources at well pads and compressor stations. Emissions from storage tank vents proved to be one of the most significant polluters, accounting for 2076 tons of VOCs per year (20).

Among others, Earthworks has found air contaminants in areas, and in combinations, which one would not expect to find outside of industrial activity (21, 22). However, not every chemical in the 2012 Earthworks study

was found at every site monitored. That said, there were notable consistencies across sites. For instance, 94% of the samples tested for 2-butanone detected it; 88% of those testing for acetone and 79% of those testing for chloromethane detected it. Moreover, 1,1,2-trichloro-1,2,2trifluorethane, carbon tetrachloride, and trichlorofluoromethane were also frequently found. Specific emissions were not found uniformly across all locations, indicating that emissions themselves vary from site to site. In addition, there are different emissions recorded in the literature partly due to variations in researchers' ability to capture and document those emissions.

Some studies around UNGD activities have found benzene, particulate matter (PM), formaldehyde, and other chemicals at levels in exceedance of state or federal limits. The Texas Commission on Environmental Quality, for instance, reports that at one source, 35 chemicals were detected above "appropriate short-term comparison values". At some sites, multiple chemicals (carbon disulfide, ethane, isopentane, and 1,2-dibromoethane) exceeded short-term health-based comparison values. Benzene was also detected above the long-term healthbased comparison value at 21 monitoring sites (3).

The federal government has not, as yet, gathered the quantity and quality of emissions data that are necessary to properly characterize the environmental conditions around UNGD sites. The Inspector General's Office of the EPA confirms the inadequacy of data in reporting the following: EPA has 1) not developed default emission estimates for oil and gas nonpoint sources, 2) not ensured state submission of nonpoint sources oil and gas data as required by the EPA's air emissions reporting requirement (AERR), and 3) some states' failure to collect emissions data from smaller (i.e., nonpoint) oil and gas production facilities due to a lack of permitting requirements. The Inspector General's Office concludes that, although resource intensive, developing a robust emissions inventory could cover these numerous small, unregulated sources (1).

Connections between emissions and health

Two important obstacles prohibit researchers from comprehensively assessing the health risks posed by UNGD activities. The first obstacle has to do with the incomplete list of chemicals used and air emissions generated by the industry. Companies and their sub-contractors are not mandated by the federal government to disclose the complete list of chemicals used in the hydrofracking process; nor are they required by state or local governments to provide a full accounting of the chemicals used at a given site. Second,



¹ Other research confirming emissions are presented in our review of research in the Findings section of this paper.

there is a problem of assessing risk of known chemicals. Many of the chemicals that have been identified at UNGD sites or nearby do not have established comparison values by which to measure their potential health effects. Furthermore, chemicals are released into the air contemporaneously and there is little to no information on the toxicity of these mixtures. This is not a unique problem posed by UNGD. What is unusual is the proximity of emission sources to people's homes and to places where they carry out their daily activities. To provide a sense of the urgency of addressing this issue, in a study of 290 households in Washington County Pennsylvania, collected as a convenience sample, we found that 707 unique, "active" wells or compressor stations were identified as located within three miles of all residences combined (Unpublished). It has been reported in the Wall Street Journal that as many as 15 million people live within one mile of a natural gas wellhead (http://stream. wsj.com/story/latest-headlines/SS-2-63399/SS-2-365197/).

Despite the limitations in data, some studies have been conducted on correlations between health risks and UNGD emissions. For instance, based on toxicity values for six carcinogenic contaminants in one Garfield County, Colorado study, researchers found low but increased risk of developing cancer in residents living near UNGD activity. Additionally, based on the presence of noncancer hazards, close proximity to UNGD activity was associated with low but increased risk of developing acute noncancer health effects; however, the authors report that insufficient data makes this finding inconclusive. Many air contaminants surrounding UNGD had no established toxicity levels so researchers could not identify and include those risks in their report (23).

Another Colorado study found that a noncancer chronic Hazard Index was greater for residents living ≤ 0.8 km from wells than it was for those more than 0.8 km out. Cumulative cancer risks were also greater for residents within 0.8 km of wells than for those living further out. Benzene and ethylbenzene were the primary contributors to cumulative cancer risk for residents living in close proximity to UNGD facilities (24).

An assessment of Pennsylvania birth outcomes, released as a working paper, compared birth outcomes for infants born to mothers living within 2.5 km of a permitted but not yet built gas well site and those within 2.5 km of an active gas well site. Results suggest that exposure to UNGD before birth increases the overall prevalence of low birth weight and the overall prevalence of small for gestational age; in addition, exposure reduces 5 min APGAR scores compared with births to mothers living near sites that have not yet been developed (25). In Colorado, a similar study found an increased prevalence of congenital heart

defects, and possibly of neural tube defects in neonates for mothers residing within a 16 km radius of natural gas wells, based on density and proximity (26).

While not including all substances used or emitted from UNGD sites, the EPA's IRIS provides data on known heath effects from exposure to toxic contaminants. The database contains information on more than 550 chemicals, including VOCs such as acrolein and formaldehyde, which are known to be emitted from UNGD sites. IRIS also provides information concerning acute toxicity.

Rationale

The Southwest Pennsylvania EHP examined whether UNGD emissions data collection, analysis, and comparison to standards reflect real-time exposures and their known pathophysiological mechanisms. EHP aimed to investigate the assumptions driving existing research and how such assumptions might mislead researchers in ways that undermine, even invalidate, their findings.

An initial appraisal of the literature led us to hypothesize that the application of federal standards to research on health impacts from industry air pollution failed to sufficiently address the periods of highest risk for people living near UNGD sites. We found a disconnection between the standards that do not address short-term exposure peaks, and how those actual exposures might put people at risk. In addition to examining existing research, we used data from real-time exposure measurement to shed light on the relationship between exposure measurement and the standards by which they are deemed safe or unsafe. These data came from monitoring efforts previously conducted by EHP in the homes of residents living near UNGD sites in Washington County, Pennsylvania. We measured PM because it poses well understood health risks, serves as a surrogate for other UNGD exposures, and is a synergist that intensifies the risks of other airborne toxins.

Materials and methods

We undertook analyses in three areas. First, we assessed the emerging literature on health risks posed by UNGD. Then, we analyzed EHP's previously collected data on PM, and PM, micron levels in homes near UNGD activity as a proxy to assess real-time air pollution exposures. Finally, we created a simple weather screening model to capture the role of meteorological conditions on the dispersion of air emissions from industry sources. All three were aimed at understanding the relationship between actual human exposures and the standards by which they were deemed safe or unsafe.



Based on what we suggest as the necessary monitoring protocols for determining hazards to human health, we analyzed whether current methods of data collection, as revealed in published articles and reports, provide adequate measures. Our recommended protocols included the following: 1) continuous measures of a surrogate compound to show periods of extreme exposure, 2) a continuous screening model based on local weather conditions to warn of periodic high exposures, and 3) comprehensive detection of chemical mixtures using canisters or other devices.

Our examination of the aptness of federal ambient air standards began with a review of relevant standards and their rationales. We then reviewed the sampling methodologies and data analyses in a subset of emissions research on UNGD emissions and their associated health risks. For this review (Tables 2a–f) we selected six studies

Tables 2a–f Review of sampling methods and averaging times in six shale gas development air emissions studies. A Glossary of abbreviations is in Appendix A.

Research article (27)	Purpose of study	Sampling method and time per location	Averaging time	Tested chemicals and reference values
Michael McCawley, WVU School of Public Health (27)	Measurements of air contaminants were taken to characterize levels that might be found at 625 feet from the well pad center at unconventional gas drilling sites during the activities at those sites.	- Summa canisters (24-h) - Flame ionization detector and gas chromatograph (FID -GC) - Two-hour average OC and EC concentrations: aerosol carbon field analyzer - TEOM for PM (24-h) - PID photoionization detector	Minutes – 1 min averages for four criteria pollutants Hours Days	Range of averages given for PM _{2,5} , O ₃ , NO _x , CH ₄ , SO ₂ and benzene ³ . Used RfC, HQ and HI

Comments: High levels of fluctuation found: "The duration of the specific activity of interest at each of the sites was a week or less". Authors note that more appropriate sampling periods than the 3-year averaging period required for the NAAQS are needed, as is a health effects study. Weather and topography are also considered important factors. The HQ for benzene was above MRL – of 9.5 μ g/m³ for chronic (>365 days), 19 μ g/m³ for intermediate (14 to 364 days) and 28.5 μ g/m³ for acute (1–14 days) exposure. PM_{2.5} dust levels at the 625 foot setback distance had 1-h average values above the annual NAAQS limit occurring over the course of several days at all but one site.

Table 2b

Research article (23)	Purpose of study	Sampling method and time per location	Averaging time	Tested chemicals and reference values
Health Consultation Garfield County (2010)	Evaluation of 2008 sampling data to identify public health implications	 Four sites for 1 year: well sites <1.5 miles from sample sites Summa canisters (24-h) weekly (SNMOC) DNPH-coated cartridges (24-h) once every 2 weeks 	Day Year	90 speciated non- methane organic compounds (SNMOC) and carbonyls Used EPA and ATSDR values

Comments: "It cannot be determined if breathing ambient air in the monitored areas of Garfield County could harm people's health ... because the cancer risks and noncancer hazards for 65 of the 86 contaminants cannot be quantitatively estimated due to limited toxicological information and/or the unavailability of accepted inhalation toxicity values". Authors note that the current state of the science is unable to assess exposures to complex mixtures of air toxics, especially synergistic and antagonistic interactions at low levels, and that insufficient data are available to evaluate intermittent short-term peak exposure.

Table 2c

Research article (24)	Purpose of study	Sampling method and time per location	Averaging time	Tested chemicals and reference values
McKenzie et al. (24)	Isolated health risks to residents living near wells during the flowback stage of UNGD using air quality data collected at the perimeter of wells	 Ambient air once every 6 days Summa canister (24-h) near wells during short-term UNGD stages 14 homes within a 0.5-mile range of a UNGD site 	Day Year	Tested for up to 78 hydrocarbons; used RfCs HQ and HI for carcinogens used IUR

Comments: The greatest risk corresponds to the relatively short, subchronic but high emissions during well completion: "[Could] not consider health effects from acute (<1 h) exposures to peak hydrocarbon emissions because there were no appropriate measurements". The authors call for the use of more specific sampling periods.



Research article (20)	Purpose of study	Sampling method and time per location	Averaging time	Tested chemicals and reference values
City of Fort Worth Natural Gas Air Quality Study (20)	Assess air pollution from UNGD in Fort Worth	 Two-month study period, eight sites Ambient air-once every 3 days with (DNPH) cartridges, Summa canisters (24-h) Mass flow control system, two sites Also screened for fugitive emissions 	Day Year	139 pollutants considered; reported 59 VOCs, methane carbonyls; used LCLs for cancer and noncancer values; used TCEQ ESLs and AMCVs, EPA limits

Comments: No pollutant concentration exceeded any short-term health benchmark of the Texas Commission on Environmental Quality (TCEQ), EPA, or the Agency for Toxic Substances and Disease Registry (ATSDR). "It is only appropriate to compare annual average concentrations, not individual measurements, to long-term health benchmark values such as the EPA NATA values". The authors consider specific wind effects, but not topography.

Table 2e

Research article (28)	Purpose of study	Sampling method and time per location	Averaging time	Tested chemicals and reference values
Southwestern Pennsylvania Marcellus Shale Short- Term Ambient Air Sampling Report (28)	Short-term screen for ambient air concentrations of target pollutants near certain Marcellus Shale gas drilling operations; assess potential air quality impacts; assess potential health risks from exposure to ambient concentrations	 OP-FTR open path sampler: six seven-hour sampling sessions within 1 week GC/MS: 5 min each hour for six seven-hour sampling sessions within 1 week Summa canister (24-h) Infrared camera for screening fugitive emissions 	Hours Days	48 VOCs; used RfC, REL, AEGL and ERPG standards; HQ and HI, NAAQS OP-FTR 2-min maximum used as a 1-h average for HQ

Comments: Nothing above NAAQS or other reference points. Concentrations of acetone, benzene, n-heptane, propene, and toluene were close to levels detected in the DEP monitoring network sites. The authors note that combined effects from operations in an area, along with other sources, may contribute to exceedance of the NAAQS. We also note that 33 of the 45 target compounds have an associated RfC.

Table 2f

Proposed Research Protocol (29)	Purpose of study	Sampling method and time per location	Averaging time	Tested chemicals and reference values
Technical Support	One year of monitoring to	– EPA-based analysis	Hours	VOCs, Carbonyl,
Document for	determine any chronic or	– Five NAAQS pollutants, continuous or	Days	Ozone, NOx, CO, PM, 5,
Long-Term Ambient	long-term risks to the public	semicontinuous measurement	Month	methane/nonmethane
Air Monitoring	from individual or multiple	- Methane/nonmmethane compounds, FLIR	Three to	Hydrocarbons, H ₃ S
Project, (29)	shale gas sources, including	- Summa canisters; HAP, VOC and carbonyls,	Five years	USEPA TO-15 method
	HAPs and criteria pollutants	sample once every 6th day for 24 h		ref. values; PA DOH HQ

Planned analysis: NAAQS and arithmetic means used for VOCs and HAPs below MDL. Cumulative excess cancer risk will trigger more review, cumulative noncancer risk HQ >1 will trigger more review: "This comparison will be a direct comparison of estimated mean concentrations of pollutants ... observed mean concentration estimates will be compared to 3-year average pollutant concentrations".

that focused on air contamination and health impacts of UNGD. The studies had a wide geographic range and were conducted by a variety of organization types. The studies were located in West Virginia, Colorado, Texas and Pennsylvania, and were conducted or commissioned by Schools of Public Health, a state Department of Public Health, independent consulting firms, and state Departments of Environmental Protection. Given that emissions factors and monitoring practices may have improved since the early years of UNGD, we selected studies published from 2010 to 2013 in peer-reviewed journals and from public access sites in different states. We paid particular

attention to how researchers grappled with the problem of multiple exposures and how hazard indexes were effectively employed.

To compare real-time fluctuations in air contamination to the results and conclusions found in the studies, we analyzed previously collected data on $PM_{2.5}$ exposures in homes near UNGD sites. From June 2012 to August 2013, EHP placed DylosTM air particle monitors (Dylos Corporation, Riverside, CA, USA) in 14 homes near UNGD sites. The data from these homes constitute an opportunity sample, because the homes were self-selected. The residents had approached EHP for assistance in determining whether their health might be



affected by their proximity to UNGD sites. The $Dylos^{TM}$ monitor measures and records levels of $PM_{2.5}$ and $PM_{0.5}$ every minute for up to 24 h. The data are downloaded daily and readings can continue indefinitely. In the research presented here, indoor air was monitored between 44 and 353 consecutive hours in homes near drilling-related activities. PM is of interest not only because of its association with health risks, but also because it is a surrogate for other substances to which people may be exposed. The $Dylos^{TM}$ particle monitor measures counts of particles per meter cubed and is sensitive to humidity. EPA measures the mass of particles and sets a standard based on 30% humidity. Counts are not directly comparable to mass; therefore scaling factors are needed to compare the data.

Weather patterns and other atmospheric conditions have a well documented effect on the dispersion of air emissions (30). Based on the work of Frank Pasquill, D.Sc., EHP developed a targeted air pollutant dispersion screening model using the following: 1) estimates of UNGD source emissions documented in the literature and from 2012 Pennsylvania Department of Environmental Protection (PADEP) oil and gas inventory reports (31), 2) distance to a hypothetical residence, and 3) the impact of local (Pittsburgh) weather patterns. This resulted in a situationally relevant assessment of the dispersion of emissions in areas around UNGD activity (32).

Findings

In reviewing the selected studies on air emissions and health impacts from UNGD, we looked at the methods used to collect air samples and the averaging time used to analyze the sampling results. In studies a–d (Table 2), results were compared primarily to federal and state standards and guidelines to determine the impact of air emissions on human health. EHP found evidence of inadequate sampling protocols for capturing meaningful data. We also found inconsistencies between researchers' interpretations of findings on exposures based on current standards and their potential impact on health.

Sampling and averaging methods

A typical method of air sample collection is the use of Summa canisters. These canisters collect air emissions over a 24-h period. Levels of pollutants are thus averaged over the 24-h period. Spikes in emissions within that period cannot be quantified.

The research in West Virginia and in Pennsylvania had (or will have in the case of one PA study) some shorter-term averaging. McCawley, in West Virginia, reported 1-min average samples for four criteria pollutants, 1-h averages for PM samples and 2-h averages for organic carbon and elemental carbon samples. These shorter-term results allowed McCawley to determine high levels of fluctuations in emissions. Unfortunately, there are few meaningful standards to which his results can be

compared because current federal standards do not accurately address periods of short-term peak exposures.

In its 2010 Southwestern Pennsylvania study, the Pennsylvania DEP used 7-h sampling periods (six periods within a week at each of the five sites). The gas chromatography/mass spectrometry (GC/MS) instrument sampled 5 min/h for each 7-h period. The open path sampler (OP-FTR) reported the highest 2-min value of any detected compound per sampling period (reported as approx. 8 h). If the compound was detected at a high enough level during the sampling session to produce an average greater than the method detection limit (MDL), that average was also reported.

For the Health Consultation in Garfield Co. (2010), Summa canisters and 2,4-dinitrophenylhydrazene (DPNH)-coated cartridges were used for 24-h collection periods. McKenzie et al. collected 24-h samples with Summa canisters and sampled ambient air once every 6 days. The City of Fort Worth (2011) sampled once every 3 days with (DNPH) cartridges and Summa canisters for 24-h periods and screened for fugitive emissions.

The proposed PA DEP long-term study in Southwestern Pennsylvania will collect data for 1 year. Periodic sampling with 24-h canister samplers will be used for hazardous air pollutants (HAP), VOCs, and carbonyls. Methane and nonmethane compounds will be detected with Forward-looking infrared (FLIR) VOC imaging technology. Continuous or semi-continuous samplers will be used for ozone, NO_x, CO, H₂S, and PM₂₅ for comparison to NAAQS. The review above illustrates the variety of measurement approaches and reference values used by researchers. In studies a to d, the authors refer to difficulties in assessing health risks for various reasons (Table 2). McCawley (2013) referred to the variability in exposures, the short-term duration of specific activities, and the long-term averaging period for NAAQS. In the Garfield County Study (2010) the researchers found that some of the necessary chronic inhalation toxicity values were not available and that complex mixtures could not be adequately assessed. Both McKenzie et al. (2012) and the City of Fort Worth (2011) found no appropriate method for assessing acute exposures. This will be addressed in the discussion section, but it is worth noting here that there is no relationship among the form of data collection, the standards applied, and the physiological effects of exposure to toxins.

The problem of risk assessment of mixtures (Hazard quotient/Hazard index)

To date, most studies on health risks associated with UNGD rely on 24-h canister samples to calculate a Hazard index



(HI). Acute effects most often occur after a few minutes or an hour of exposure. In fact, the 24-h average exposures are not even predictive of the 24-h maximum exposure. The 24-h averages underestimate exposures by a factor of two to three times (see Figure 1). The problem is further complicated by the interactions among multiple agents in the body that can produce greater than additive effects.

An illustration of the problem using published data

For this example, we chose four of the chemicals used in the UNGD industry that were measured at one site, at multiple times, and reported to the PA DEP. They included acrolein, benzene, toluene, and chloromethane (28). When we attempted to evaluate the interaction using the Hazard quotient (HQ) and reported average, the effect of omitting the highest values became apparent.

The HQ for each chemical can be established by taking the chemical measurement and dividing it by the level at which no adverse effects are expected (referred to here as the standard and derived from standards or guidance values found in IRIS). The HQs are added together to form the HI. If the sum is \leq 1.0 the mixture is not considered to produce a harmful interaction.

Example

$$\frac{acrolein}{standard} + \frac{benzene}{standard} + \frac{toluene}{standard} + \frac{chloromethane}{standard} \le 1.0$$

Using a sample of averaged canister data from the PADEP Marcellus Shale Short-Term Air Sampling Report, the calculation is as follows (measurements in $\mu g/m^3$) (28):

3.7/6.9+0.35/28.8+0.94/3770+1.40/1030=0.55.

Measured chemical amounts are reported in Appendix A, p. 36. RfCs are found in Appendix E, p. 45.

The result is <1.0, which would lead to the conclusion that it is not likely to result in pathophysiologic effects. However, this calculation is not an accurate way to measure acute toxicity. The standards used are relevant to acute exposures but the measurements are of 24-h average emissions. These averages underestimate the acute exposures by a factor of 2 to 3. The correct HI is much greater than can be determined using the conventional approach.

Evidence of short-term high values of air contaminants: particulate matter

EHP used Dylos™ air particle monitors to assess indoor air quality in homes near UNGD. The air monitor records real-time levels of PM₂₅ and PM₀₅ each minute for up to 24 h. The DylosTM monitor records counts of PM_{25} and above or PM_{0.5} microns and above. By contrast, EPA measures the mass of PM, microns and below to avoid having heavier particles distort the data. Given that the Dylos™ monitor counts particles, a few larger particles will not affect the data. In both cases relative humidity is a factor to control. The houses in which data were collected represent an opportunity sample near UNGD sites. In the data, we saw intervals with extremely high values. To understand the frequency of these high PM counts, we established a standard for "peak exposure" by taking the median reading for each house (Table 3) and from that found the median for all houses. The original data came from 14 homes (a total of 2117 h).

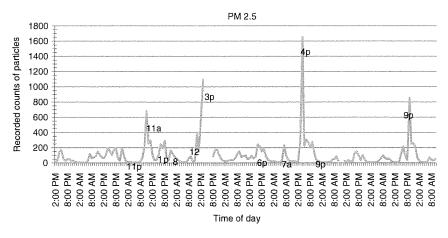


Figure 1 PM, 5 Measurements collected in House 7 from March 7, 2013 to March 14, 2013 (counts/0.01 cubic feet). Dylos Readings for PM 25 from March 7, 2013 to March 14, 2013. a, am; p, pm.



Table 3 Number of hours monitored and the median number of PM, counts per house (counts/0.01 cubic feet).

House	Number of hours monitored	Median PM _{2.5} counts
1	141	54
2	215	65
3	120	40
4	168	4
5	308	51
6	142	45
7	353	38
8	190	30
9	71	69
10	72	75
11	44	49
12	138	57
13	69	38
14	166	78

We found that the median value for all houses combined was 50. This median value was then multiplied by three to establish the criterion for a "peak" exposure. The minimum "peak exposure" value for this study was established at 150 counts of $PM_{2.5}$. We then calculated the number of peaks at each house and the percent of hours with peak exposures. The particle monitor data in Table 4 show that peaks over 150 counts can occur over 30% of the time in a given house (33).

Table 4 Peak PM $_{2.5}$ count values for each house, number of hours,% total hours, times of day, and maximum peak value (counts/0.01 cubic feet).

House		% of total hours with peaks		Maximum peak value of PM _{2.5} counts	Median value of PM _{2.5} counts
1	12	8.5	N	2711	54
2	11	5	M, N	756	65
3	3	2.5	M	171	40
4	1	0.5	N	201	4
5	8	2.5	A, E	556	51
6	11	7.7	A, E, N	576	45
7	31	8.7	M, A, E	1654	38
8	29	15	M, A, E	991	30
9	9	12.6	M, E, N	1057	69
10	23	32	M, A, E, N	844	75
11	7	16	M, E	3846	49
12	2	1.4	E	203	57
13	3	4.3	M	164	38
14	57	34.3	M, A, E, N	1761	78

^aTimes of day: Morning: 6:00 a.m. to 12 noon; Afternoon: 12 noon to 6:00 p.m.; Evening: 6:00 p.m. to 12 midnight; Night: 12 midnight to 6:00 a.m.

Attempts to capture these peaks with 24-h Summa canisters, through periodic or one-time spot sampling (under 24 h) or after a complaint has been filed, will most often miss times of peak exposure. Even with continuous monitoring such as ours, averaging of the peaks with the lower levels of PM obscures the most important feature of the data from a public health perspective because high level exposures can cause the most physiological harm (14). Only through continuous, real-time monitoring with short reporting periods, will peaks likely be captured.

Fluctuations in indoor PM levels are expected, regardless of outside activity, and can be the result of cooking, vacuuming, and children at play. The duration, magnitude, and timing of some of the peaks seen in this study, however, could not be readily explained by normal daily activity.

Research on indoor and outdoor PM levels near highways confirms the relationship between outside and indoor particle pollution. Fuller et al. found both indoor and outdoor particle levels to be the highest <100 m from the highway, whereas both indoor and outdoor levels were lowest in and around homes more than 1000 m from the highway (34). The researchers concluded that outdoor particle pollution was "the most important predictor of indoor [particle number concentration]" (34). Other significant predictors of indoor particle levels cited by the authors included temperature, weekday, time of day, wind speed, and wind direction.

Air pollution dispersion model estimates

The EHP model looks at the estimated impact of one emissions source, while in many cases a residence may have more than one source within a radius of two to three miles.

In order to estimate the effect of local weather conditions on ground level exposures, 2012 hourly weather data reported at the Pittsburgh International Airport (wind speed, wind direction, and cloud cover) were applied to the air screening model developed by EHP (32). A single VOC emission level of 300 g/min from a compressor station was used for the point source. The influence of local air movement and vertical dilution (mixing depth) on the levels of ambient air emissions one mile from a surface source in part explained periods of peak exposures.

The modeled findings shown in Table 5 indicate that ambient VOC concentrations are underestimated when averages are used to evaluate the health risk associated with a source (as is recommended in the "Form" of the



Table 5 Effects of averaging the variability of exposures that occur in 6 h increments, for each month of the year.a

Month	Monthly average ^b	Six-hour average for the 75th percentile	Six-hour average for the 90th percentile
January	43	50	132
February	58	85	123
March	58	88	137
April	52	75	148
May	81	124	189
June	66	103	155
July	59	115	157
August	89	147	206
September	85	136	177
October	80	131	189
November	80	111	167
December	74	111	157
Yearly average	68.5		

^aBased on Pittsburgh, PA weather data in 2012. ^ball 6-h periods for each month.

NAAQs air monitoring strategy). When the "midnight to midnight" 24-h periods were divided into 6-h intervals, the scale and frequency of this underestimation of exposure risk became apparent. About 10% of the intervals for downwind locations will produce exposures two to three times higher than the value estimated using the NAAQs form (Table 5). If VOC concentrations were averaged over a 1-h rather than a 6-h period, the discrepancy would be even greater.

The projected effect on indoor air

A house with one air change per hour would experience 75% of the outdoor ambient air after 3 h and 98% after 6 h. Further, even if the ambient air is reduced to the unlikely level of zero, it would require 3 h for the indoor concentration to fall to 25% of the maximum. Thus, for a significant portion of each month, residents downwind from pollution sources experience levels of pollution inside their houses that are higher than the monthly averages. These are potentially significant exposures from a physiological standpoint. The uptake of outdoor pollutant into house air is determined by assuming that the house has one air change per hour with instantaneous mixing, such that at the end of 1 h, the concentration inside of the house will be 1/2 the outside concentration. After 2 h, the concentration will be 75% of the outside and each hour the indooroutdoor difference is reduced by one half. The clearing of the pollutant follows the same assumption.

Discussion

When evaluating acute responses to air toxics, it is important to understand the physiological and cellular responses to short-term exposures because inhalation or ingestion of a toxic agent can cause effects within minutes (35). The health sequelae seen near UNGD sites include respiratory, neurologic, and dermal responses as well as vascular bleeding, abdominal pain, nausea, and vomiting. Given the pathophysiologies of these acute toxic responses, it is apparent that current monitoring protocols at UNGD sites are inadequate to ensure safety.

When air emission levels are highly variable, the following typically collected measurements are not relevant to individual health impacts: periodic collection of 24-h samples, tons released per year, and hourly averages per day, per week, or per year. Instead, real-time measures of patterns of exposures are needed, and these must include peak levels, durations, and components of mixtures. The NAAQS compliance monitoring criteria (Table 1) do not provide sufficient information to assess human health risks from acute episodes of exposures. A relevant example of appropriate, real-time monitoring at industrial sites that abut residential areas is The Benzene and other Toxics Exposure (BEETEX) Study developed by the Houston Area Research Center (HARC) (36). The purpose of the study was to identify exposure to air toxics in nearby residential areas and to attribute air toxics to specific sources. The methodology for monitoring and data analysis are in development for the 2014 study, with the goal of identifying "cost-effective, state-of-the-art neighborhood scale monitoring networks the improvement of emissions inventories, the conduct of epidemiological studies for air toxics, and ultimately the enforcement of regulations" (36).

Others have demonstrated the mismatch between typical environmental compliance monitoring on the one hand, and health risk evaluation on the other. The Minnesota Department of Health (MDH), in particular, has addressed this problem with respect to ground water utilized for drinking. MDH has revised its Health Risk Limits (HRL) protocol as part of a concerted effort to provide conservative, health protective guidelines that respond to sensitive and highly exposed populations. The Minnesota HRLs respond to the relationship between the timing and duration of exposure as well as the potential adverse effects. The HRLs are intended to be protective for a range of adverse effects for a given duration of exposure. In addition, MDH's revised risk limits address the problem of multiple exposures whether exposure from several pathways or from multiple chemicals - by using an exposure decision tree in conjunction with site-specific information. In the revised rules, MDH

includes methods that risk managers can use to sum up the risks from multiple chemicals that share a common health endpoint in order to assess the combined health risk at the site being evaluated. MDH typically utilizes this approach, but if specific data about a mixture are available, other more targeted approaches are likely to be preferable (37).

The form of current standards

The central problem identified in this paper is that at sites where it appears that health effects are produced by UNGD, toxic emissions are often not being measured or not detected at levels deemed dangerous. Our concern is that this may be an artifact of the sampling methodologies and analyses currently being used today. An example of how appropriate monitoring and sampling can reveal otherwise hard to capture variations can be found in a study of woodsmoke emissions in the Adirondack region of New York State (38). This rural region has a very limited air quality monitoring network, yet residents can experience multi-day and/or sub-daily pollution loading that can be intense. Given that monitoring sites are so widespread, and local hourly impacts cannot be captured, these populated areas have significant public health pollution threats that the regulatory system does not respond to or understand. However, when researchers used the appropriate equipment and methods, they instantaneously discovered serious air quality problems. In this example, a model that identified likely "hotspots" using geographic and demographic data was employed. Then mobile monitoring equipment and procedures as well as stationary monitoring sites were used to collect real-time data.

When we examine the research summarized in Tables 2a–f, we find a common deficiency in the data collection, that is, the inability of commonly used methods to capture episodic or significant variability. Specifically, as we have already noted, many sampling methods fail to characterize and quantify peaks in emissions and potential exposures. Looking at Tables 3–5 as well as Figures 1 and 2, it becomes apparent that exposures do, in fact, become quite high relative to median or mean values. These spikes are inconsistent with the characterization of low to negligible risk.

Currently, compliance with NAAQS and state standards are the cornerstone of safety regulation of UNGD. These standards are designed to monitor compliance over a region, but not over individual sites. A review of the form of the application of the NAAQS illustrates the problem. The forms of the six criteria pollutant standards are similar to other air monitoring guidelines. Compliance with each is based on average findings typically collected

at 3-day intervals. Performance criteria are based on the number of times the standard is exceeded each year.

These standards have been developed to reliably determine when a source is repeatedly out of compliance with permitted emissions. The regulatory assumption is that the variations in ambient air levels are negligible. The findings in this report show that the variability of emissions in UNGD is extreme and assessing this variability is critical to understanding health responses. Of the six studies evaluated here, only McCawley (27) measured in "real time" and reported finding high levels of fluctuation in emissions. McKenzie et al. reported health risks to short, subchronic but high emissions. However, they found that there were no appropriate measurements for assessing effects from acute exposures. In contrast, the Pennsylvania DEP report found nothing above NAAQS or other levels of concern. It should be noted that even if realtime equipment is deployed, given the high variability of emissions based on the stage of UNGD, care must be taken to use the appropriate equipment at the appropriate time to ensure accurate and meaningful data collection.

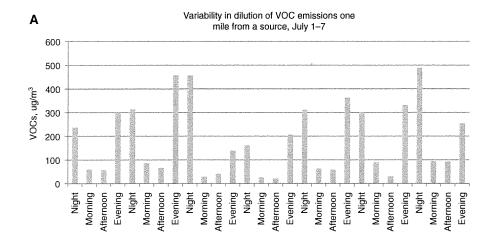
HI and PM - synergistic response

Underlying current standards is the assumption that each toxic agent in air emission mixtures acts independently when it is inhaled or ingested into the body. The ratios of the average ambient air level to the standards are summed in an HI (EPA.gov/airtoxics). At UNGD sites, this assumption is negated by the fact that PM is generally present at all sites; and it has been demonstrated that PM increases the amount of absorbed toxin by increasing transport into the deep lung. The surface area of the particle is what drives this synergistic response, producing greater than additive synergistic response (39).

EHP continuously measured particulate matter at 14 houses near UNGD in southwestern Pennsylvania. The monitoring periods ranged from 44 to 353 h. EHP found a range of 1 to 57 h (0.5% to 34.3%) with peak values over 150 cts/0.01 cubic feet. The findings in the literature and in EHP's PM monitoring indicated that episodes of high values were typical in gas fields. In the EHP data, peak values occurred at varying times of day and night. Figure 1 illustrates these results.

Meteorological impacts

Local weather conditions affect the dispersion of air pollutants from industrial sources (31). Figure 2 shows modeled



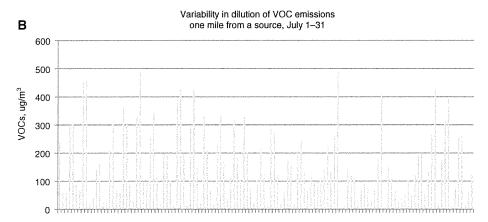


Figure 2 (A, B) Demonstration of the variability in dilution of 300 g/min VOC emissions from a source one mile away, in 6-h increments^a, modeled using Pittsburgh International Airport weather data.

^aCalculations are based on July 2012 weather data from the Pittsburgh International Airport. The 6-h increments for the graphs above are broken down as follows: night: 12 midnight to 6:00 am; morning: 6:00 am to 12 noon; afternoon: 12 noon to 6:00 pm; evening: 6:00 pm to 12 midnight.

estimated exposures from a source of VOCs at 6-h intervals for 30 days. The chart reflects only the effects of weather conditions and illustrates that weather conditions alone can cause extreme variation in exposures at ground level. The 6-h exposures vary from 25 to over 200 µg/m³. As expected, the monthly average 6-h exposure ranged from 43 to 89 μ g/m³, and the 90th percentile ranged from 123 to $206 \mu g/m^3$. Both Figures 1 and 2 help make the argument that continuous measures, in conjunction with weather data, are needed to identify periods of extreme exposure.

Mixtures

The variety of point source types and the combinations of chemical gases present at UNGD sites complicate the assessment of health risk. The Commonwealth of Pennsylvania requires that certain permitted facilities report yearly emissions of 13 compounds to their oil and gas inventories. In 2012, there were 214 reporting sites in Washington County, PA. These included 196 well pads, 14 compressor stations, two gas processing plants, a booster station, and an interconnecting station. These installations are connected by pipelines that are under pressure and are vented as necessary. Table 6 shows a portion of the PA DEP emissions inventory data from the 214 reporting sites in Washington County (40).

Examining the discrepancy between the median and maximum values, it is easy to see that sites vary significantly in their emissions. The data show concurrent releases of multiple compounds (Table 6). Several of these have known interactions in the body, for example VOCs and particulates. The interactions with inhalable particulates, found at 110 of the 214 sites, are of concern because the doses increase synergistically when PM combines with air toxins. Thus, the commonly used HI is insufficient to



Table 6 Seven most prevalent chemicals emitted in 2012 across all reported sites in Washington County, PA (total, median and maximum by weight/tons per year).^a

Chemical	Total tons/	Median	Maximum
	year		
Benzene	3.1	0.2	0.8
VOCs	501	0.8	30
PM _{2.5}	60	55	6
NO,	1838	9.4	95
Formaldehyde	53	0.0008	4.2
Trimethyl pentene	0.13	0.004	0.12
Ethyl benzene	0.34	0.00003	0.07

^aOther reported chemicals are carbon monoxide, sulfur dioxide, PM₁₀, n-hexane, toluene and xylene. Methane is not reported. Not every site reports every compound. As noted, these reports are for yearly emissions, but during well pad development, many stages occur for shorter time periods.

evaluate the health impact of the mixtures because it uses average exposures and reference doses based on a single exposure to an agent. In this case, HI is also insufficient because the duration of the typical averaging time used to evaluate exposure is longer than the duration of concern. These findings show that the current protocols used to evaluate safety are not sufficient and that a change is needed.

Conclusion

Several factors should be included in all measures. First, based on the analysis presented in this paper, it is clear that the use of current standards is not appropriate for good pathophysiological evaluation, and consequently for good public health protection. The currently used methods of data collection also cannot provide the necessary data for determining an exposure's composition, intensity, duration, or frequency.

In sum, our findings indicate the presence of peak emissions occurring near UNGD, which may lead to extreme exposures among people in close proximity to these sites. Furthermore these exposures can be exacerbated by local weather conditions and by the presence of particulate matter. Exposures are highly variable and can be difficult to monitor. Moreover, current monitoring efforts and health standards do not adequately track these events, though health reports from persons living near these sites are consistent with episodic exposure (EHP, Earthworks). The risk of developing chronic diseases due to exposures, especially by vulnerable populations, has yet to be determined. Revisions to health

Table 7 Assessment of sampling methods for determining pathophysiological impacts from air pollution.

Sampling method	Does it measure quantities of mixed compounds?	Does it measure frequency of peaks?	Does it measure intensity of peaks?	Does it measure duration of peaks?
Summa Canister	Yes	No	No	No
Ambient air monitors	No	Some yes, some no	No	No
DNPH-coated cartridges	No	No	No	No
OP-FTR open path sampler ^a	No	Yes	Yes	Yes

^aOP-FTR does have sensitivity and specificity limitations.

standards are necessary to protect public health in regions of UNGD. Toxicity values must be developed for shorter durations for residents in other than emergency situations. Research is also needed to evaluate the health effects of short, repeated, higher than background exposures (Table 7).

In order to overcome limitations of sampling methodologies commonly used to gauge risks, we suggest that a combination of strategies be adopted because no single sampling method can accurately capture all of the essential data. Finally, realistic reference values that focus on the potential pathophysiologic effects caused by exposures are needed. In the re-examination of reference values for water pollutants, Minnesota's Department of Health provides a good example to emulate.

In order to properly evaluate and respond to the public health problem posed by UNGD activities, we suggest a new strategy for collecting air data and interpreting findings. The following three components ought to be at the center of this new strategy:

- continuous measures of a surrogate compound to show periods of extreme exposure;
- a continuous screening model based on local weather conditions to warn of periodic high exposures; and
- comprehensive detection of chemical mixtures using canisters or other devices that capture the major components of the mixtures.

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Appendix A Glossary of abbreviations

AEGL	acute exposure guideline level	IUR	Inhalation unit risk
AERR	air emissions reporting requirement	LCL	lowest comparison level
AMCV	air monitoring comparison values	UNGD	unconventional natural gas development
ATSDR	Agency for Toxic Substances and Disease	MDH	Minnesota Department of Health
	Registry	MDL	method detection limit
BEETEX	benzene and other toxics exposure study	NAAQS	National Ambient Air Quality Standards
BTEX	benzene, toluene, ethylbenzene, and xylene	NATA values	National-Scale Air Toxics Assessment
DEP	Department of Environmental Protection	NEI	National Emissions Inventory
DNPH	2.4. dinitrophenylhydrazene	OC	organic carbon
DOH	Department of Health	OP-FTR	Fourier transform infrared spectrometer
EC	elemental carbon	PA	Pennsylvania
EHP	Environmental Health Project	PID	photo-ionsitization detector
EPA	U.S. Environmental Protection Agency	PNC	particle number concentration
ERPG	Emergency Response Planning Guidelines	PM	particulate matter
ESL	effects screening levels	REL	reference exposure level
FLIR	forward-looking infrared camera	RfC	reference concentrations
GC/MS	gas chromatography-mass spectrometry	SNMOC	speciated non-methane organic
HAP	hazardous air pollutant		compounds
HARC	Houston Area Research Center	TCEQ	Texas Commission on Environmental
HI	hazard index		Quality
HQ	hazard quotient	TEOM	tapered element oscillating micro-
HRL	health risk limits		balance, a particulate monitor
IRIS	EPA integrated risk information system	VOC	volatile organic compounds

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An Exploratory Study of Air Quality near Natural Gas Operations

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An Exploratory Study of Air Quality near Natural Gas Operations

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ABSTRACT

This exploratory study was designed to assess air quality in a rural western Colorado area where residences and gas wells co-exist. Sampling was conducted before, during, and after drilling and hydraulic fracturing of a new natural gas well pad. Weekly air sampling for 1 year revealed that the number of non-methane hydrocarbons (NMHCs) and their concentrations were highest during the initial drilling phase and did not increase during hydraulic fracturing in this closed-loop system. Methylene chloride, a toxic solvent not reported in products used in drilling or hydraulic fracturing, was detected 73% of the time; several times in high concentrations. A literature search of the health effects of the NMHCs revealed that many had multiple health effects, including 30 that affect the endocrine system, which is susceptible to chemical impacts at very low concentrations, far less than government safety standards. Selected polycyclic aromatic hydrocarbons (PAHs) were at concentrations greater than those at which prenatally exposed children in urban studies had lower developmental and IQ scores. The human and environmental health impacts of the NMHCs, which are ozone precursors, should be examined further given

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that the natural gas industry is now operating in close proximity to human residences and public lands.

Key Words: drilling, endocrine disruptors, hydraulic fracturing, natural gas, non-methane hydrocarbons, PAHs, VOCs.

INTRODUCTION

Over the past 25 years the U.S. Environmental Protection Agency (USEPA) has supported research on ozone, particulate matter, and VOCs derived from the combustion of gasoline and diesel fuel by mobile and stationary sources. Air quality monitoring has focused primarily on large urban and industrialized areas in and around heavily populated regions across the U.S. and along chemical factory fence lines. Quantitative results dating back several decades are available from studies designed to test detection methodologies and to detect the quantity of selected VOC compounds in large urban areas or specific cities (Baker *et al.* 2008; Mohamed *et al.* 2002; Seila *et al.* 1989). This kind of air sampling has typically been done in regions of ozone non-compliance to determine the source of the precursors to ozone, providing guidance for regulating the source. Studies of urban air have also documented the damage these compounds cause to human health (Brunekreef *et al.* 2009; Chahine *et al.* 2007; Crüts *et al.* 2008; Dejmek *et al.* 2000; Green *et al.* 2009; Koren *et al.* 1989; Perera *et al.* 1999).

In the past two decades, natural gas development and production in the U.S. has increased rapidly by tapping into domestic resources. Natural gas wells are now being drilled in close proximity to urban and rural communities, and across broad expanses of public lands. Potential sources of air pollution from natural gas operations include volatile chemicals introduced during drilling and hydraulic fracturing (in which fluids are injected under high

² ACCEPTED MANUSCRIPT



pressure to fracture the underlying formation that holds the gas), combustion byproducts from mobile and stationary equipment, chemicals used during maintenance of the well pad and equipment, and numerous NMHCs that surface with the raw natural gas. The USEPA estimates that on average the mass composition of unprocessed natural gas is 78.3% methane, 17.8% NMHCs, 1.8% nitrogen, 1.5% carbon dioxide, 0.5% hydrogen sulfide, and 0.1% water (Skone *et al.* 2011; USEPA 2011).

Two independent air sampling studies conducted near natural gas fields in Colorado have recently been published. McKenzie *et al.* (2012) measured air quality around the perimeter of natural gas wells from a stationary site among rural residences and ranches, assessing several NMHCs for the purpose of risk assessment. Petron *et al.* (2012) took a regional approach using data collected over 3 years by both fixed and mobile sampling equipment looking for sources and mixing ratios of methane and benzene and several other NMHCs. The authors identified an alkane signature as evidence of oil and gas activity. Both studies indicate a need for better air monitoring and research on air quality near natural gas operations.

The present study was designed to explore the presence of volatile chemicals, many of which are associated with the production of natural gas, in a rural natural gas production area for 1 year. The sampling period spanned the time before, during, and after development of a natural gas well pad. Development included drilling, hydraulic fracturing, and production operations. To our knowledge, no study of this kind has been published to date.

PROJECT DESIGN

Baseline and weekly air samples were collected between July, 2010, and October, 2011, from a fixed sampling station near a well pad on which 16 vertical (directional) gas wells had



been drilled, hydraulically fractured and put into production during the course of the study. Air sample data are presented along with a timeline of events on the well pad, including drilling, fracturing and production dates acquired from the website of the Colorado Oil and Gas Conservation Commission (COGCC). The COGCC serves as the primary government resource for the public regarding oil and gas development in Colorado and maintains a publicly available online information system as part of its oil and gas regulatory processes (COGCC 2012a).

Sampling Site

Site selection was dictated by our ability to set up a permanent sampling station with access to electricity near a well pad about to be developed. In July, 2010, a permanent air sampling location was selected in Garfield County, Colorado, at approximately 5,850 feet (1783 m) elevation and 0.7 miles (1.1 km) from the well pad of interest. The site was located at a rural residence in semi-arid terrain surrounded by pinyon, juniper, sagebrush, and native grasses. One major highway (I-70) runs through the area, approximately 1.1 miles (1.8 km) north of the sampling site. According to the COGCC (2012a), there were 130 wells producing natural gas within 1 mile (1.6 km) of the sampling site at the time of the study. In addition, two other well pads were developed using vertical drilling within 1 mile (1.6 km) of the sampling site after development of the well pad of interest, and within the timeframe of the study.

Natural Gas Well Pad

The vertical well pad of interest penetrated the Williams Fork Formation of the Mesa Verde Group at a total depth of approximately 8,300 feet (2530 km) in tight sands (FracFocus 2012). The land for the well pad was cleared of vegetation and leveled and service roads were constructed in the spring of 2010.

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According to the COGCC website, drilling of the first of 16 wells started on October 22, 2010, and the last well was started on March 16, 2011. Hydraulic fracturing of the first four wells began on January 4, 2011. Fracturing reportedly began on another five wells on February 15, 2011 (not including the seventh drilled well, which was not fractured until April 20th). Between April 14 and 16, 2011, six more wells were fractured. Volumes of hydraulic fracturing fluids ranged between 1.1 and 2.3 million gallons (4.2 and 8.7 million liters) per well (FracFocus 2012). Wells typically went into production within 5 days of being fractured.

According to the COGCC, the well pad was located in a sensitive area with regard to wildlife habitat and water resources, and was in close proximity to surface and domestic water wells (COGCC 2010). This required the operator to abide by a variety of requirements and best management practices designed to minimize impacts. For example, a closed loop drilling system was used that requires drilling fluids to be captured in tanks instead of separated from the cuttings and held in an open pit. A closed loop system was also used to pipe fracturing fluids to the pad and immediately capture the flow back fluids and pipe them to another facility for treatment.

METHODS

A baseline air sample for VOCs was collected July 17, 2010. A complete set of baseline samples was taken on October 19, 2010. Weekly sampling commenced beginning November 2, 2010 through October 11, 2011. Samples were collected on all dates except for December 28, 2010 because the lab was closed for Christmas. Samples were collected every 7 days and shipped by a trained technician according to standard operating procedure for each instrument (AAC 2012a; SKC Inc. 2001; Tisch Environmental, Inc.). The 24-hour samples were taken weekly



from noon Monday to noon Tuesday, and the 4-hour samples were taken from 10:00–2:00 on Tuesdays.

Samples were sent to two USEPA certified laboratories using chain of custody procedures to assure proper handling of the samples from the technician to the lab. VOCs were sampled over a 4-hour period using a Six-Liter Summa Canister. Lab analyses were conducted to test for the following VOCs: 56 speciated C2-C12 hydrocarbons using USEPA Method TO-12/USEPA PAMS Protocol (Photochemical Assessment Monitoring Stations, using gas chromatography/flame ionization detection); methane, using USEPA Method 18 (to detect fixed gases by gas chromatography/flame ionization detection/ thermal conductivity); and 68 target VOCs using USEPA Method TO-15 (to detect VOCs using gas chromatography/mass spectrometry).

PAHs were sampled over 24 hours using a Filter/PUF (Polyurethane) combination. Sixteen PAHs were tested using USEPA Method TO-13A (to detect a select group of PAHs with gas chromatography/mass spectrometry). Carbonyls were sampled over a 4-hour period using a DNPH (2-4 dinitrophenylhydrazine) coated Silica Gel Cartridge, and 12 carbonyls were tested using USEPA Method TO-11A (to detect aldehydes and ketones using high-pressure liquid chromatography with a UV detector).

The 4-hour sampling of VOCs and carbonyls was extended to 6 hours, generally from 9:00 am to 3:00 pm with a few samples taken from 10:00 am to 4:00 pm, beginning April 5, 2011. This change was made upon approval by the lab, in order to accommodate the schedule of the sampling technician. Additionally, due to the high cost of the PAH assay, and the findings of

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PAH concentrations three orders of magnitude lower than the other NMHCs, PAH sampling was discontinued when drilling on the well pad of interest ended (after March 29, 2011).

The samples from the Summa Canisters and the DNPH Cartridges were analyzed by Atmospheric Analysis & Consulting, Inc., Ventura, CA, a National Environmental Laboratory Accreditation Conference approved air quality analytical laboratory. The Filter/PUF analyses were conducted by American Environmental Testing Laboratory, Inc., Burbank, CA. Quality control data including duplicate and spike recoveries was provided in all laboratory reports. Chemicals analyzed in more than one assay are reported as follows: for hexane, toluene, heptane, benzene, and cyclohexane, TO-12 values were used instead of TO-15; and for acetone, TO-15 values were used instead of TO-11A.

All test values were reported by the laboratories without problems, with the exception of one Summa Canister sample with a pressure problem, and six DNPH Cartridge samples—two with equipment problems and four with visible water contamination. The results of all tests with reported problems were omitted from analysis, resulting in 48 samples reported for VOCs, 21 for PAHs, and 43 for carbonyls.

Analyses

Means, ranges, and standard deviations are presented for all chemicals detected at least once. Means were calculated by summing the values for each chemical and dividing by the number of detects for that chemical. Mean, standard deviation, and range values are reported in parts-per-billion (ppbv) or parts-per-trillion (pptv) volume. Conversions from parts-per-billion carbon and ng/m³ were conducted as necessary to arrive at this common reporting unit (AAC 2012b). Sample detection values greater than one standard deviation above the mean for each



chemical were defined as spikes. Because of the exploratory nature of the study and the relatively small data set, values for non-detects were not imputed, no data transformations were performed, and statistical tests of significance were not conducted.

RESULTS

Chemicals that were tested but never detected (non-detects) are presented in Table 1, along with the Method Reporting Limit (MRL). Shown in Table 2 are basic descriptive statistics for all the VOCs and carbonyls detected at least once during the sampling period, in order of the percent of detections. Among the VOCs, four chemicals were detected in every sample: methane, ethane, propane, and toluene. Chemicals with the highest mean values across the sampling period include (in order of mean value): methane, methylene chloride, ethane, methanol, ethanol, acetone, and propane. Regarding the carbonyls, formaldehyde and acetaldehyde were detected in every sample. The highest values were for crotonaldehyde and formaldehyde. Also shown in Table 2 are the numbers of times each chemical spiked during the sampling period.

Shown in Table 3 are the results for the PAHs, which were sampled from November 2, 2010, to March 29, 2011. Naphthalene was the only PAH detected in every sample and it was also found at the highest concentration among the PAHs detected.

Related Events on the Well Pad

Pertinent events on the pad (e.g., start dates for drilling and hydraulic fracturing) are shown in Figure 1. Dates are included for the well pad of interest (Pad #1) as well as for the two pads that were developed during the latter half of sampling (Pads #2 and #3). The percent and number of chemicals detected on each date of sampling is also shown in Figure 1. Percents were calculated by dividing the number of chemicals detected on a particular date by the total number



of chemicals analyzed on that day, not including chemicals that were never detected during the study. The number and percent of detections were generally higher during development of Pad #1 than Pads #2-3. The most chemical detections occurred during the first four months of drilling, at a time when only one fracturing event occurred, which did not change the pattern of detections.

The number of spikes on each date of sampling is shown in Figure 2, presented separately by type of compound (VOC, PAH, carbonyl). By far the most spikes occurred during drilling of Pad #1, particularly between mid-December and mid-January. The carbonyls spiked on and around March 15, 2011. There were also spikes beginning in July, 2011, when drilling of Pad #3 began.

DISCUSSION

The data in this study show that air sampling near natural gas operations reveals numerous chemicals in the air, many associated with natural gas operations. Some of the highest concentrations in the study were from methane, ethane, propane, and other alkanes that have been sourced to natural gas operations (Baker *et al.* 2008; Gilman *et al.* 2012). In contrast we found very low levels of chemicals such as ethene and other alkanes that are more likely to come from urban road-based pollution (Baker *et al.* 2008; Gilman *et al.* 2012). Acetylene, which is only formed from combustion, was found at low concentrations and in only four samples. Isoprene, which arises primarily from vegetation, was only detected in one sample throughout the study, attesting to the semi-arid landscape of the sampling site (Baker *et al.* 2008; Jobson *et al.* 1994). The chemicals reported in this exploratory study cannot, however, be causally connected to natural gas operations.



Air Resource Specialists, Inc. provides quarterly weather reports from Parachute, Colorado, which is 7.4 miles (11.9 km) southwest of the sampling site (Air Resource Specialists, Inc. 2011a, 2011b, 2011c, 2011d). Wind rose data show that the predominant wind directions throughout the year are from the NE and SW, which is aligned with the topography of the valley along the Colorado River Corridor. During all four quarters of the study year the wind blew from the ESE (from the well pad toward the sampling site) 2–3% of the time, independent of the time of year. There was no correlation between detected emissions (which varied by quarter and were highest in the winter) and wind direction.

Calm winds, however, (wind under 1 mph) were greatest during times when detections were highest. For example, in the fourth quarter of 2010, winds were calm 10.9% of the time, and in the first quarter of 2011 they were calm 8.1% of the time. During the second and third quarters of 2011, when air sampling detections were lower, calm winds were reported 3.5% and 1.8% of the time, respectively. Because of the rugged topography of the area under study it is subject to air inversions, particularly in winter, which trap air at ground level and tend to increase air pollution from local sources (Sexton and Westberg *et al.* 1984). The phenomena of air inversions may explain the higher readings during December and January than in other months.

There was a great deal of variability across sampling dates in the numbers and concentrations of chemicals detected. Notably, the highest percentage of detections occurred during the initial drilling phase, prior to hydraulic fracturing on the well pad. This is not surprising, considering the numerous opportunities for release of NMHCs during drilling. On a typical well pad, when the raw natural gas surfaces it is piped to a glycol dehydrator (heater treater) on the pad where it is heated to evaporate off the water, which then condenses and is

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NMHCs are vented while others are piped to a condensate tank on the pad. NMHCs also escape when the glycol in the dehydrator is being regenerated. Transferring of fluids from the produced water and condensate tanks to tanker trucks is another opportunity for the release of NMHCs. Next, the gas goes to a compressor station where is prepped and sent on to a processing plant where the BTEXs (benzene, toluene, ethylbenzene, and xylene), and other NMHCs, some of which are liquids at low temperatures are removed. A number of volatile chemicals, such as benzene, toluene, xylenes and others, have economic value and are captured and used to make diverse products such as plastics, glass, construction material, pesticides, detergents, cosmetics, and pharmaceuticals, and in the U.S. they are added to gasoline.

For well pad #1 in the present study, after all the wells were completed and hooked into the national supply line, according to the COGCC the well pad produced 487,652 Mcf (thousand cubic feet) of raw natural gas during June, 2011 (COGCC 2012b). Using the USEPA estimate of 17.8% NMHCs, that calculates to 2,893 Mcf per day of NMHCs potentially released into the air while the pad is producing, although not all the NMHCs are released on-site.

Methylene chloride stood out due to the extremely high concentrations in some of the samples, including one reading of 1730 ppbv, and three other readings more than 563 ppbv (the cutoff value for spikes) during the period of well development. In contrast, after activity on the pad came to an end and the wells went into production, the highest level of methylene chloride detected was 10.6 ppb. Methylene chloride is not a natural component in raw gas, and is predominantly used as a solvent (USEPA 2000). As far as we are aware, it is not a component in drilling or fracturing fluids. It does not appear on two extensive lists of more than 750 chemicals



that companies admit they use during either operation (Colborn *et al.* 2011; US House of Representatives Committee on Energy and Commerce Minority Staff 2011) and it does not appear on the voluntary fracturing chemical disclosure registry (FracFocus 2012) for the well pad of interest in this study. However, residents and gas field workers have reported that methylene chloride is stored on well pads for cleaning purposes. Raw gas in the region under study also contains commercially valuable levels of a mixture of alkanes referred to as paraffin wax that becomes solid at ambient temperatures. As the raw gas escapes on the pad, this slippery material could build up on equipment, requiring cleaning. Given that methylene chloride was found in such high concentrations in air samples in the present study, its source and potential exposure scenarios should be explored with respect to exposure of individuals working on the pads and living nearby.

Regarding the PAHs, although concentrations found in this study appear low, they may have clinical significance. Several studies have been published by the Columbia Center for Children's Environmental Health in which pregnant women in urban settings wore personal air monitors that measured their level of exposure to eight PAHs (benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(g,h,i)perylene, benzo(k)fluoranthene, chrysene, dibenzo(a,h)anthracene, indeno(1,2,3-cd)pyrene). In 2006, Perera *et al.* demonstrated that among children in New York City, those who were prenatally exposed to eight PAHs with a summed concentration greater than 4.16 ng/m³ had lower mental development scores at age three. In 2009, Perera *et al.* reported lower IQ scores among 5-year olds with prenatal exposure greater than 2.26 ng/m³. In a similar study in Krakow, Poland, Edwards *et al.* (2010) found decreased IQ scores among 5-year olds prenatally exposed to PAHs greater than 17.96 ng/m³. In the present



study, the summed composite of the same eight PAHs was 15.5 ng/m³. There are many sources of variability when comparing personal air monitoring and ambient air sampling results. For example, not all eight PAHs summed above were detected in every one of our samples.

Nonetheless, these findings suggest that the concentrations of PAHs in rural neighborhoods near natural gas operations deserve further investigation, regardless of the source.

The concentrations of the carbonyls were lowest during the time when the VOCs and PAHs were spiking, but spiked later when the other chemicals did not. Many carbonyls, such as formaldehyde and acetaldehyde, are formed from the reaction of VOCs with nitrogen oxide and sunlight, and thus have peak seasons, which may have accounted for the spikes (Ho *et al.* 2002; National Research Council 1981). Carbonyls are also used as solvents and are associated with diesel emissions (ATSDR 1999; Mitran *et al.* 1997). It is possible that solvents were needed following the accident that occurred when a drilling contractor was removing drill cuttings from the mud tanks (COGCC 2011), which coincided with the time the carbonyls spiked in March.

In order to identify potential hazards associated with the chemicals detected during development of the well pad of interest, a rigorous literature search was conducted. Thirty-five chemicals were found to affect the brain/nervous system, 33 the liver/metabolism, and 30 the endocrine system, which includes reproductive and developmental effects. The categories with the next highest numbers of effects were the immune system (28), cardiovascular/blood (27), and the sensory and respiratory systems (25 each). Eight chemicals had health effects in all 12 categories. There were also several chemicals for which no health effect data could be found. The categories of health effects for each chemical are presented in Table 4, which is supported by Supplemental Material available from the authors that contains a complete list of 400



references. It should be mentioned that laboratory studies typically measure exposure to one chemical at a time, while real-life conditions entail exposure to several volatile chemicals at once, with interactions that cannot be predicted.

The health effects found in the literature are relevant as indicators of potential hazards associated with the chemicals detected in the air samples. They do not address the issue of exposure. The concentrations at which these chemicals were detected in the air are far less than U.S. government safety standards such as NIOSH Recommended Exposure Limits and OSHA Permissible Exposure Limits (NIOSH 1992; OSHA 1993). However, government standards are typically based on the exposure of a grown man encountering relatively high concentrations of a chemical over a brief time period, for example, during occupational exposure. Consequently, such standards may not apply to exposure scenarios faced by individuals (including pregnant women, children, and the elderly) experiencing chronic, sporadic, low-level exposure, 24 hours a day 7 days a week in natural gas neighborhoods. Safety standards also do not account for the kinds of effects found from low-level exposure to endocrine disrupting chemicals (Vandenberg et al. 2012), which can be particularly harmful during prenatal development and childhood.

Lessons can be learned from the results of this simple exploratory investigation into air quality in a rural neighborhood interspersed with natural gas operations. In retrospect, we regret not having continued sampling PAHs throughout the entire year. It was not until we began searching the literature for health effects of the chemicals that we discovered the developmental effects of extremely low levels of PAHs. In addition, our study would have benefited from more baseline samples. Unfortunately, there was no way to know exactly when drilling would start and we were only alerted when the drill rig was being installed. If we were to sample again, we

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would rotate sampling every six days and at varied times around the clock. Most importantly, we would record meteorological data on-site throughout each sampling period. In rural mountainous areas, where local topography varies greatly, public sources of weather data may not be applicable for air quality research.

While natural gas development and production continues to spread across the land it is moving closer to homes, schools, and places of business. At the same time more and more raw gas will be released into the atmosphere on a steady, daily basis. In order to determine how to reduce human exposure for both those who work on the well pads and those living nearby, systematic air quality monitoring of natural gas operations must become a regular part of permitting requirements. It is apparent from what is presented in this paper that the NMHCs need far more attention not only because of their potential immediate and long term chronic health effects, but also for their secondary indirect health and environmental impacts as precursors to ozone.

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Nomenclature

COGCC Colorado Oil and Gas Conservation Commission

Mcf thousand cubic feet

ng/m3 nanograms per cubic meter

NMHCs non-methane hydrocarbons

PAHs polycyclic aromatic hydrocarbons



ppbc parts per billion carbon

ppbv parts per billion by volume

pptv parts per trillion by volume

μg/m3 micrograms per cubic meter

μg/ml micrograms per milliliter

VOCs volatile organic compounds

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Table 1. Chemicals not detected in air samples in western Colorado from July, 2010 to October, 2011.

Chemical	CAS#	Reporting limit ^a
1,1,1-trichloroethane	71-55-6	0.5 ppbv
1,1,2,2-tetrachloroethane	79-34-5	0.5 ppbv
1,1,2-trichloro-1,2,2-		
trifluoroethane	76-13-1	0.5 ppbv
1,1,2-trichloroethane	79-00-5	0.5 ppbv
1,1-dichloroethane	75-34-3	0.5 ppbv
1,1-dichloroethene	75-35-4	1 ppbv
1,2,3-trimethylbenzene	526-73-8	1 ppbv
1,2,4-trichlorobenzene	120-82-1	0.5 ppbv
1,2-dibromoethane	106-93-4	0.5 ppbv

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1,2-dichloro-1,1,2,2-		
tetrafluoroethane	76-14-2	0.5 ppbv
1,2-dichlorobenzene	95-50-1	0.5 ppbv
1,2-dichloroethane	107-06-2	0.5 ppbv
1,2-dichloropropane	78-87-5	0.5 ppbv
1,3,5-trimethylbenzene	108-67-8	1 ppbc
1,3-butadiene	106-99-0	0.5 ppbv
1,3-dichlorobenzene	541-73-1	0.5 ppbv
1,4-dichlorobenzene	106-46-7	0.5 ppbv
1,4-dioxane	123-91-1	0.5 ppbv
1-butene	106-98-9	1 ppbc
1-hexene	592-41-6	1 ppbc
1-pentene	109-67-1	1 ppbc
2,2,4-trimethylpentane	540-84-1	1 ppbc
2,2-dimethylbutane	75-83-2	1 ppbc
2,3,4-trimethylpentane	565-75-3	1 ppbc
2,3-dimethylpentane	565-59-3	1 ppbc
2,4-dimethylpentane	108-08-7	1 ppbc
2-hexanone	591-78-6	0.5 ppbv
4-ethyltoluene	622-96-8	0.5 ppbv
acenaphthene	83-32-9	2 ng/m³ (pql)
acrolein	107-02-8	0.025 μg/ml

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acrylonitrile	107-13-1	1 ppbv
allyl chloride	107-05-1	0.5 ppbv
anthracene	120-12-7	2 ng/m³ (pql)
benzyl chloride	100-44-7	0.5 ppbv
bromodichloromethane	75-27-4	0.5 ppbv
bromoform	75-25-2	0.5 ppbv
bromomethane	74-83-9	0.5 ppbv
carbon disulfide	75-15-0	0.5 ppbv
carbon tetrachloride	56-23-5	0.5 ppbv
chlorobenzene	108-90-7	0.5 ppbv
chlorodifluoromethane	75-45-6	0.5 ppbv
Table 1. (cont.)		

1	a	b	e	1.	. (CC	on	t.))
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Chemical	CAS#	Reporting limit ^a
chloroethane	75-00-3	0.5 ppbv
chloroform	67-66-3	0.5 ppbv
chloromethane	74-87-3	0.5 ppbv
cis-1,2-dichloroethylene	156-59-2	0.5 ppbv
cis-1,3-dichloropropene	10061-01-5	0.5 ppbv
cis-2-butene	590-18-1	1 ppbc
cis-2-pentene	627-20-3	1 ppbc
dibromochloromethane	124-48-1	0.5 ppbv
dichlorodifluoromethane	75-71-8	0.5 ppbv

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dichlorofluoromethane	75-43-4	0.5 ppbv
ethyl acetate	141-78-6	0.5 ppbv
fluoranthene	206-44-0	$2 \text{ ng/m}^3 \text{ (pql)}$
hexachlorobutadiene	87-68-3	0.5 ppbv
isooctane	540-84-1	0.5 ppbv
isopropyl alcohol	67-63-0	2 ppbv
m-diethylbenzene	141-93-5	1 ppbc
methyl isobutyl ketone (MIBK)	108-10-1	0.5 ppbv
methyl tert-butyl ether	1634-04-4	0.5 ppbv
m-ethyltoluene	620-14-4	1 ppbc
m-tolualdehyde	620-23-5	0.025 μg/ml
n-propylbenzene	103-65-1	l ppbc
n-undecane	1120-21-4	1 ppbc
o-ethyltoluene	611-14-3	1 ppbc
o-xylene	95-47-6	1 ppbc
p-diethylbenzene	105-05-5	1 ppbc
propylene oxide	75-56-9	1 ppbv
pyrene	129-00-0	2 ng/m³ (pql)
t-1,3-dichloropropene	10061-02-6	0.5 ppbv
tetrachloroethene	127-18-4	0.5 ppbv
trans-1,2-dichloroethylene	156-60-5	0.5 ppbv
trans-2-butene	624-64-6	1 ppbc

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trans-2-pentene	646-04-8	1 ppbc
trichloroethene	79-01-6	0.5 ppbv
trichlorofluoromethane	75-69-4	0.5 ppbv
valeraldehyde	110-62-3	0.025 μg/ml
vinyl acetate	108-05-4	1 ppbv
vinyl bromide	593-60-2	0.5 ppbv
vinyl chloride	75-01-4	0.5 ppbv

^aReporting limit is mrl (method reporting limit) unless pql (practical quantification limit) is specified.

Table 2. Volatile chemicals detected in air samples in western Colorado from July, 2010 to October, 2011.

						Std	
		n	%	Mean	Range	Dev	n
Chemical name	CAS#	Detects	Detects	ppbv	ppbv	ppbv	Spikes
VOCs							
					1600.0-		
methane	74-82-8	48	100	2472.9	5500.0	867.3	6
ethane	74-84-0	48	100	24.4	3.6-118.0	23.7	5
propane	74-98-6	48	100	9.3	1.1-46.7	9.0	7
toluene	108-88-3	48	100	1.2	0.4-4.3	0.9	4

isopentane	78-78-4	43	90	1.8	0.4-7.3	1.3	6
n-butane	106-97-8	42	88	3.2	0.8-14.0	2.6	4
isobutane	75-28-5	42	88	2.9	0.6-13.5	2.5	4
acetone	67-64-1	41	85	9.5	3.4-28.3	6.2	6
n-pentane	109-66-0	40	83	1.5	0.4-5.6	1.0	5
n-hexane	110-54-3	38	79	0.9	0.3-3.0	0.6	4
methylcyclohexane	108-87-2	36	75	0.9	0.3-3.1	0.6	4
methylene chloride	75-09-2	35	73	206.2	2.7-1730.0	357.4	4
	108-38-3/						
m/p-xylenes	106-42-3	29	60	0.4	0.2-0.7	0.2	6
2-methylpentane	107-83-5	27	56	0.8	0.3-2.2	0.4	3
n-heptane	142-82-5	22	46	0.6	0.3-1.4	0.3	3
3-methylpentane	96-14-0	21	44	0.8	0.3-2.0	0.4	3
benzene	71-43-2	21	44	0.5	0.3-1.1	0.2	3
methanol	67-56-1	19	40	18.3	12.1-30.6	5.6	4
methylcyclopentane	96-37-7	18	38	0.6	0.3-1.3	0.3	3
cyclohexane	110-82-7	17	35	0.6	0.3-1.6	0.4	2
n-octane	509-84-7	15	31	0.4	0.2-0.8	0.2	3
3-methylhexane	589-34-4	12	25	0.5	0.3-1.1	0.3	1
2-butanone (mek)	78-93-3	10	21	3.4	2.3-5.1	1.0	2
2-methylhexane	591-76-4	9	19	0.4	0.2-0.7	0.2	2
ethylene	74-85-1	8	17	1.2	0.8-1.8	0.4	1

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acetylene	2122-48-7	4	8	1.4	0.9-2.4	0.7	1
isoprene	78-79-5	4	8	0.6	0.4-0.7	0.2	0
n-nonane	111-84-2	4	8	0.2	0.2-0.3	0.0	1
2,3-dimethylbutane	79-29-8	3	6	0.4	0.4-0.5	0.1	1
ethanol	64-17-5	3	6	11.4	3.2-19.4	8.1	0
2-methylheptane	592-27-8	3	6	0.3	0.3	0.0	0
1,2,4-							
trimethylbenzene	95-63-6	2	4	na	0.2-0.3	na	0
tetrahydrofuran	109-99-9	1	2	na	2.1	na	0
styrene	100-42-5	1	2	na	0.9	na	0
ethylbenzene	100-41-4	1	2	na	0.7	na	0
cyclopentane	287-92-3	1	2	na	0.4	na	0
3-methylheptane	589-81-1	1	2	na	0.3	na	0

Table 2. (cont.)

Auto-						Std	
		n	%	Mean	Range	Dev	n
Chemical name	CAS#	Detects	Detects	ppbv	ppbv	ppbv	Spikes
isopropylbenzene	98-82-8	1	2	na	0.3	na	0
n-dodecane	112-40-3	1	2	na	0.3	na	0

Carbonyls



formaldehyde	50-00-0	43	100	1.0	0.3-2.4	0.5	6
acetaldehyde	75-07-0	43	100	0.6	0.3-1.8	0.3	4
crotonaldehyde	123-73-9	42	98	1.3	0.1-3.0	0.8	8
mek &	78-93-3/						
butyraldehyde	123-72-8	37	86	0.2	0.0-0.4	0.1	7
hexaldehyde	66-25-1	9	21	0.1	0.1-0.2	0	2
propionaldehyde	123-38-6	6	14	0.1	0.1-0.2	0	1
benzaldehyde	100-52-7	5	12	0.1	0.1	0	1
methacrolein	78-85-3	5	12	0.1	0.1	0	1

na = not applicable. Statistics were not calculated for chemicals in which there were fewer than three detections.

Table 3. PAHs detected in air samples in western Colorado from October, 2010 to March, 2011.

						Std	
		n	%	Mean	Range	Dev	n
Chemical name	CAS#	Detects	Detects	pptv	pptv	pptv	Spikes
naphthalene	91-20-3	21	100	3.01	0.81-6.08	1.44	4
phenanthrene	85-01-8	16	76	0.36	0.21-0.61	0.14	4
fluorene	86-73-7	11	52	0.20	0.15-0.32	0.06	2
indeno(1,2,3-cd)pyrene	193-39-5	8	38	0.18	0.09-0.49	0.13	1
benzo(g,h,i)perylene	191-24-2	7	33	0.22	0.09-0.45	0.13	1





dibenzo(a,h)anthracene	53-70-3	7	33	0.20	0.11-0.51	0.15	1
benzo(a)pyrene	50-32-8	5	24	0.21	0.13-0.36	0.09	1
benzo(b)fluoranthene	205-99-2	5	24	0.20	0.13-0.26	0.05	1
benzo(k)fluoranthene	207-08-9	5	24	0.18	0.13-0.25	0.05	1
benzo(a)anthracene	56-55-3	2	10	na	0.13-0.16	na	0
chrysene	218-01-9	2	10	na	0.12-0.16	na	0
acenaphthylene	208-96-8	1	5	na	0.20	na	0

na = not applicable. Statistics were not calculated for chemicals in which there were fewer than three detections.

Table 4. Health effects^a of chemicals detected in air samples collected in western Colorado.

Charita I Name	C	n	Castu	Brain/	Imm-	Kidn	Card/	Canc/	Geno-	Endo	Liver/	Othr
Chemical Name	Sens	Resp	Gastr	Nerv	une	Kidii	Bld	Tum	toxic	Endo	Met	Othr
1,2,4-	Х	X	X	X	X	X	X	X	X	X	X	X
trimethylbenzene	Λ	Λ	Λ	Λ	Λ	28	71	Λ	Λ	Λ	Λ	Λ
2,3-dimethylbutane												
2-butanone (mek)				X		X				X	X	
2-methylheptane												
2-methylhexane												
2-methylpentane				X								
3-methylheptane												
3-methylhexane												
3-methylpentane				X								
acenaphthylene										X	X	X





acetaldehyde	X	X	X	X	X	X	X	X	X	X	X	X
acetone	X	X	X	X	X	X	X			X	X	Х
acetylene												
benzaldehyde	X	X	X	X	X	X	X		X	X	X	Х
benzene	X	X		X	X		X	X	X	X	X	X
benzo(a)anthracene	X	X						X	X		X	X
benzo(a)pyrene	X	X	X	X	X	X	X	X	X	X	X	X
benzo(b)fluoranthen		X			X	X		X	X	X	X	X
e		Λ			Λ	Λ		Λ	Λ	Λ	Λ	Λ
benzo(g,h,i)perylene									X			
benzo(k)fluoranthen					X		X	X	X	X	X	
e					Λ		Λ	Λ	Λ	Λ	Λ	
butyraldehyde				X								
chrysene		X			X	X	X	X	X	X	X	X
crotonaldehyde		X	X	X	X	X	X	X	X	X	X	X
cyclohexane				X		X		X			X	
cyclopentane				X								
dibenzo(a,h)anthrac	X	X	X	X	v	X	X	v	v	v	v	v
ene	Λ	Λ	Λ	Λ	X	Λ	Λ	X	X	X	X	X
ethane												
ethanol	X	X	X	X			X	X		X	X	X
ethylene											X	X
fluorene	X			X	X	X	X				X	X
formaldehyde	X	X	X	X	X	X	X	X	X	X	X	X
hexaldehyde	X			X	X		X		X	X		X
indeno(1,2,3-		X		X	X			X	X	X	X	

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cd)pyrene												
isobutane												
isopentane												
isoprene	X	X	X	X	X	X	X	X	X	X	X	X
methacrolein	X	X										
methane												
methylcyclohexane												
methylcyclopentane				X								
methylene chloride	X	X	X	X	X	X	X	X	X	X	X	X
m-xylene	X	X		X	X	X	X			X	X	
naphthalene	X	X	X	X	X	X	X	X	X	X	X	X
n-butane				X			X					X

Table 4. (cont.)

Chemical Name	Sens	Resp	Gastr	Brain/	Imm-	Kidn	Card/	Canc/	Geno-	Endo	Liver/	Othr
	waw.wa.			Nerv	une		Bld	Tum	toxic		Met	
n-decane	X	X		X	X							X
n-heptane	X			X			X		X	X	X	
n-hexane				X	X		X			X	X	
n-nonane	X			X	X	X	X			X	X	X
n-octane	X	X		X	X	X	X			X	X	X
n-pentane												
phenanthrene	X	X		X	X		X			X	X	X
propane												
propionaldehyde					X				X			X





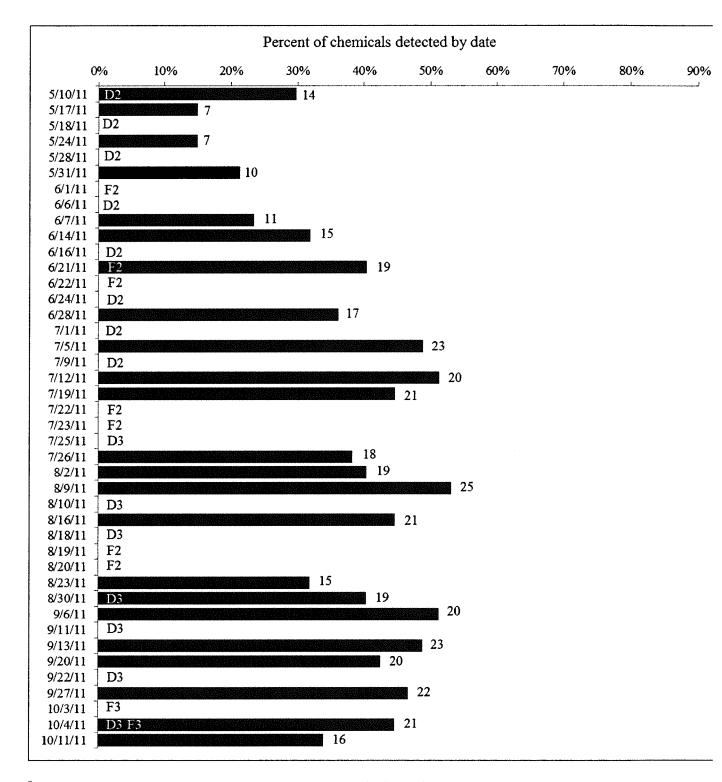
propylene	X	X		X	X	X				X	X	
p-xylene	X	X		X		X	X		X	X	X	X
tetrahydrofuran			X	X	X	X	X	X	X	X	X	X
toluene	X	X	X	X	X	X	X		X	X	X	Х
Total	25	25	14	35	28	23	27	18	23	30	33	29

^aSens = skin/eye/sensory organ; Resp = respiratory; Gastr = gastrointestinal; Brain/Nerv = brain/nervous system; Immune = immune system; Kidn = kidney; Card/Bld = cardiovascular/blood; Canc /Tum = cancer/ tumorigen; Genotoxic = genotoxic; Endo = endocrine system; Liver/Met = liver/metabolic; Othr = other.

Figure 1. Percent and number^a of chemicals detected in air samples collected in western Colorado from July, 2010 to October, 2011, and drilling/fracturing events, by date.







^a The number of chemicals detected is shown at the end of each bar.



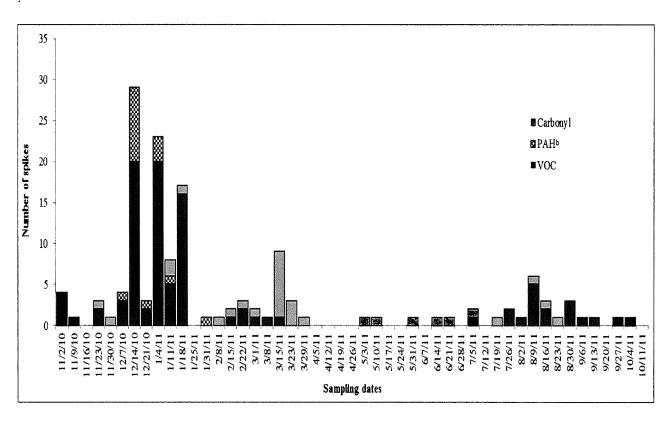
D1 FI: Drilling and fracturing events during development of Pad #1.

D2 F2: Drilling and fracturing events during development of Pad #2.

D3 F3: Drilling and fracturing events during development of Pad #3.

Figure 2. Number of chemical spikes^a from air samples collected in western Colorado from

November, 2010 to October, 2011, by compound type and date of sampling event.



^a A spike is a detected chemical level that is at least one standard deviation above the mean.



^b PAHs were sampled from 11/2/10 to 3/29/11.



RESEARCH Open Access

Air concentrations of volatile compounds near oil and gas production: a community-based exploratory study

Gregg P Macey¹, Ruth Breech², Mark Chernaik³, Caroline Cox⁴, Denny Larson², Deb Thomas⁵ and David O Carpenter^{6*}

Abstract

Background: Horizontal drilling, hydraulic fracturing, and other drilling and well stimulation technologies are now used widely in the United States and increasingly in other countries. They enable increases in oil and gas production, but there has been inadequate attention to human health impacts. Air quality near oil and gas operations is an underexplored human health concern for five reasons: (1) prior focus on threats to water quality; (2) an evolving understanding of contributions of certain oil and gas production processes to air quality; (3) limited state air quality monitoring networks; (4) significant variability in air emissions and concentrations; and (5) air quality research that misses impacts important to residents. Preliminary research suggests that volatile compounds, including hazardous air pollutants, are of potential concern. This study differs from prior research in its use of a community-based process to identify sampling locations. Through this approach, we determine concentrations of volatile compounds in air near operations that reflect community concerns and point to the need for more fine-grained and frequent monitoring at points along the production life cycle.

Methods: Grab and passive air samples were collected by trained volunteers at locations identified through systematic observation of industrial operations and air impacts over the course of resident daily routines. A total of 75 volatile organics were measured using EPA Method TO-15 or TO-3 by gas chromatography/mass spectrometry. Formaldehyde levels were determined using UMEx 100 Passive Samplers.

Results: Levels of eight volatile chemicals exceeded federal guidelines under several operational circumstances. Benzene, formaldehyde, and hydrogen sulfide were the most common compounds to exceed acute and other health-based risk levels.

Conclusions: Air concentrations of potentially dangerous compounds and chemical mixtures are frequently present near oil and gas production sites. Community-based research can provide an important supplement to state air quality monitoring programs.

Keywords: Benzene, Community monitoring, Formaldehyde, Grab and passive samples, Hydraulic fracturing, Hydrogen sulfide, Oil and gas

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Background

New drilling and well stimulation technologies have led to dramatic shifts in the energy market. The Energy Information Administration forecasts that by the 2030s, the United States will become a net exporter of petroleum liquids such as shale oil [1]. Already an exporter of natural gas, the U.S. will retrieve nearly half of its gas from shale formations by that time [2]. Reserves such as shale oil and gas are referred to as "unconventional" because fuels within them do not readily flow to the surface [3]. Instead, they are distributed among tight sandstone, shale, and other geologic strata. Intensive practices are used to retrieve them, such as directional drilling (many kilometres underground and one or more kilometres horizontally through a formation) and hydraulic fracturing to break up the formation and ensure movement through source rock (using millions of gallons of water mixed with chemicals and sand, or "proppants") [4]. These technologies present public health challenges, including threats to air quality [5-7].

Unconventional oil and gas (hereinafter "UOG") development and production involve multiple sources of physical stressors (e.g., noise, light, and vibrations) [6], toxicants (e.g., benzene, constituents in drilling and hydraulic fracturing fluids) [8], and radiological materials (e.g., technologically-enhanced, naturally-occurring radioactive material) [9], including air emissions [10,11]. Air quality near UOG sites is an underexplored human health concern for several reasons. For a time, environmental scientists and regulators were primarily interested in potential impacts to surface and groundwater quality. Highprofile impacts and the subsurface nature of technologies (e.g., hydraulic fracturing) encouraged this research trajectory [12]. This was true despite the fact that UOG development brings to the surface, in the case of natural gas, methane (78.3%), non-methane hydrocarbons (17.8%), nitrogen (1.8%), carbon dioxide (1.5%), and hydrogen sulfide (0.5%) [13]. These constituents, as well as emissions from combustion processes at the surface, are released to the air throughout the life cycle of a productive well [14].

Air emissions from UOG operations have been generally understood for some time – volatile organic compounds (VOCs), polycyclic aromatic hydrocarbons (PAHs), and criteria air pollutants such as NOx and PM_{2.5} can be released at the wellhead, in controlled burns (flaring), from produced water storage pits and tanks, and by diesel-powered equipment and trucks, among other sources [15]. Yet the full range of emissions from drilling, well completion, and other activities remains elusive. New source categories are discovered, emissions from life cycle stages such as transmission and well abandonment have yet to be determined, and even stages such as drilling continue to present uncertainty [16]. We do not understand the extent of drilling-related

air emissions as pockets of methane, propane, and other constituents in the subsurface are disturbed and released to the atmosphere [17]. Emissions measurements during flowback vary by orders of magnitude [18]. These and other data gaps limit the accuracy of state and federal emissions inventories, which compile and track known emissions sources. Inventories are also limited by self-reporting and data collection, and rely in some cases on outmoded emissions factors [15]. Flawed inventories constrain human health risk assessment and other research [7] and slow the identification of phenomena such as photochemical ozone production during winter months [19].

State pollution monitoring networks also constrain research on the air impacts of UOG development. Historically, air quality monitoring targeted urban areas, and criteria air pollutants such as particulate matter and ozone precursors were the primary chemicals of concern [10]. Monitoring stations were designed to ensure compliance with National Ambient Air Quality Standards (NAAQS) for a half-dozen pollutants. Even networks that focus on oil and gas emissions, such as one operated by public health officials in Garfield County, Colorado, do not target individual well pads. The Garfield County network encompasses five sites to monitor a suite of VOCs and (at three sites) particulate matter, in a jurisdiction that covers nearly 3,000 square miles of complex terrain [20]. The Texas Commission on Environmental Quality has arguably the most extensive monitoring network for UOG air emissions in oil and gas regions. Its monitors were sited to minimize urban source impacts and target locations where the public might be exposed to air emissions [21]. Still, its networks can be sparse; there are five permanent monitoring stations in the Eagle Ford Shale region, where 7,000 oil and gas wells have been drilled since 2008 [22]. These and other limited networks potentially mask local hot spots, the effects of unique topography, and fugitive emissions at certain well pads.

Even a denser monitoring network taking continuous samples may be unable to capture the full range of air impacts of UOG operations. Sources of variability of air emissions and concentrations of VOCs and other pollutants near UOG sites include: (1) the spatial variability of UOG operations; (2) the discontinuous use of equipment such as diesel trucks, glycol dehydrators, separators, and compressors during preparation, drilling, hydraulic fracturing, well completion, and other stages; (3) the composition of shale and other formations and the specific constituents of the drilling and hydraulic fracturing fluids used on-site (which can influence the makeup of produced or flowback water stored in pits and tanks); (4) intermittent emissions from venting, flaring, and leaks; (5) the shifting location, spacing, and intensity of well pads in response to market conditions,



improvements in technology, and regulatory changes; (6) the effects of wind, complex terrain, and microclimates; and (7) considerable differences among states in permitting, leak detection and repair, and other requirements [10,16,23-25]. Wind, for example, can influence outdoor and indoor concentrations of air pollutants. Brown et al. found that local air movement and mixing depth contribute to peak exposure to VOCs one mile from a compressor station [25]. Colborn et al. noted the role of wind and topography in higher VOC concentrations during winter months, when inversions trap air near ground level [10]. Fuller et al. identified wind speed and wind direction as significant predictors of indoor particulate matter levels near highways [26]. Similar variation can be found within and across geologic formations. Unconventional wells in the Barnett Shale play, for example, differ considerably in terms of reservoir quality, production rates, and recoverable gas [27]. Domestic shale gas plays exhibit even greater diversity, including depth and thickness of recoverable resources, the amount and range of chemicals present in produced water, and the presence of constituents such as bromide, naturally occurring radioactive material, hydrogen sulfide, and other toxic elements [23,28].

These and other sources of variability, and the adaptive drilling and well completion techniques they encourage, complicate the design of setback and well spacing rules that are protective of the public. They also explain why air quality studies carried out in UOG regions yield conflicting results. For example, McKenzie et al. [11] found greater cumulative cancer risks and higher non-cancer hazard indices for residents living less than 0.5 miles from certain well pads in Colorado, while Bunch et al. [21] analyzed data from monitors focused on regional atmospheric concentrations in the Barnett Shale region and found no exceedance of health-based comparison values. Colborn et al. [10] gathered weekly, 24-hour samples 0.7 miles from a well pad in Garfield County, and noted a "great deal of variability across sampling dates in the numbers and concentrations of chemicals detected." Eapi et al. [29] found substantial variation in fenceline concentrations of methane and hydrogen sulfide, which could not be explained by production volume, number of wells, or condensate volume at natural gas development sites.

Institutional factors also influence research on ambient air quality near UOG sites. Congressional exemption of oil and gas operations from provisions of the Clean Air Act, Clean Water Act, Safe Drinking Water Act, Emergency Planning and Community Right-to-Know Act, and other statutes limits data collection on the impacts of oil and gas development [30,31]. In addition, the peer-reviewed literature is divided between "top-down" and "bottom-up" treatments of air quality. The first set of studies explores the impact of UOG operations on regional air quality, with a

concern for methane emissions and ozone precursors in regions such as the Green River Basin in Wyoming [32], the Uintah Basin in northeastern Utah [33], and the Denver-Julesburg Basin, home of the Wattenberg Field in northeastern Colorado [34]. These studies rely on airborne and tower measurements, and are at times supplemented by ground measurements such as mobile monitoring.

For example, Petron et al. [35] found a strong alkane signature downwind from the Denver-Julesburg Basin, based on samples taken at a 300-m tall tower (the National Oceanic and Atmospheric Administration Boulder Atmospheric Observatory) and a mobile monitoring unit. In the Uintah Basin, where winter ozone levels exceeded the NAAQS 68 times in 2010, Helmig et al. [36] carried out vertical profiling of ozone precursors at a tower at the northern edge of a gas field. They found levels of atmospheric alkanes during temperature inversion events in 2013 that were 200-300 times greater than regional background. These and other "top-down" studies are also used to estimate methane leakage, which is helpful in comparing the climate-forcing impact of UOG to the use of coal-fired power plants. Loss rate estimates for methane and other hydrocarbons vary considerably by study, from 17% [37] (Los Angeles Basin) to 8.9% [38] (Uintah Basin) (6.2-11.7%, 95% C.I.) to 4% [35] (Denver-Julesburg Basin) (2.3-7.7%, 95% C.I.). A number of studies share the finding that EPA underestimates methane leakage rates across the life cycle (their estimate was 1.65% in 2013) [16], but others, extrapolating from emissions factors and/or direct measurement, produce estimates as low as 0.42% [18]. None of these studies attempts to characterize air concentrations within residential or publicly-accessible areas near UOG operations.

Other studies follow a "bottom-up" approach to air quality, which is limited by access to well pads and other infrastructure, the availability of a power source for monitoring equipment, the stage of operation underway, scheduled or unscheduled flashing, flaring, and fugitive releases, or movement of truck traffic and equipment at or near a well pad during a given sampling period. Thus, bottom-up studies vary in terms of distance to site, sample frequency, and chemicals targeted. This helps explain the range of findings in the published literature. Nevertheless, existing research gives support to resident reports of acute and long-term health symptoms and other reductions in quality of life. Even as they offer conflicting evidence of the relative importance of one stage of production or another to air emissions [10,11], or differ in their ultimate conclusion regarding the existence [10,11,14,35,36,39] or lack [21,40,41] of human health threats from air emissions, they find VOC concentrations in ambient air considerable distances from well pads, including in residential areas and public spaces.



The research questions that guide existing studies create a final barrier to our ability to characterize air emissions in UOG regions. Top-down studies are motivated by questions such as identifying sources of regional nonattainment of ozone standards, or estimating methane and other hydrocarbon leakage rates from UOG operations. Bottom-up research gathers data from one or a limited number of well pads, chosen for reasons such as access or cooperation by owners and operators. The data are used to discuss general exposure conditions for an oftenhypothetical community, or used to derive a risk factor. In either mode of study, resident exposure does not directly motivate the sampling protocol. Rather, it is considered obliquely in a study's choice of sample location (e.g., a one that is "near a small community"), assumed in measurements of concentrations within a certain distance of UOG activity, or ignored. What are missing from these studies are protocols grounded in a community's experience of air quality impacts of UOG operations.

Our multi-state air quality monitoring study uses a community-based, participatory research (CBPR) design to explore conditions near UOG operations [42]. Its sampling protocol is based not on access to a well pad, data needs conditioned by an existing averaging standard, or regional policy concerns. Rather, we partnered with residents in UOG regions to measure air quality under circumstances that, given local knowledge of operations (e.g., emissions from particular equipment or intermittent practices) gained through daily routines (e.g., regular observation of well pads) and use of public and private spaces nearby (e.g., livestock movement, farming) were viewed by community members as potential threats to human health. Existing studies often lack a data set suitable for statistical analysis. When such analyses are occasionally imposed on bottom-up data sets, they explain only a fraction of the variance in air quality outcomes. For example, the highest R² values in a study of 66 sites, which, due to the study's broad spatial range was limited to measurements of methane and hydrogen sulfide, were 0.26 (H₂S concentration vs. condensate volume nearby) and 0.17 (H₂S and number of wells nearby) [29]. CBPR studies, by comparison, are place-based they begin with the experience of a population in order to identify environmental stressors and explore the heterogeneity of circumstances under which they arise [43,44]. Rather than discount these circumstances for lack of statistical power, they can be used to define the scope of confirmatory studies, tailor air quality monitoring networks and studies, or suggest novel pollution control measures and best management practices.

Methods

We explore air quality at a previously neglected scale: near a range of UOG development and production sites

that are the focus of community concern. Residents conducted sampling in response to operational conditions, odor events, and a history of the onset of acute symptoms. Residents selected sampling sites after they completed a training program run by Global Community Monitor (GCM), an organization that has developed and modified community-based sampling protocols for more than twenty years. Sampling is designed to obtain accurate readings of public exposure near UOG development in the part-per-billion range [45]. Training sessions followed a written manual on proper sampling protocol and included instruction by experienced members of GCM in a classroom setting for five hours. In addition, samplers were trained in the field to properly demonstrate Quality Assurance/Quality Control (QA/QC) methods, such as use of data sheets and chain of custody records, sampling procedures including not taking samples in the presence of vehicle traffic or other sources of VOCs, and protocols for storage and delivery to an analytic laboratory [45]. Chain of Custody forms provided by the laboratory were explained and filled out in exercises in which each sampler participated. The trainings for community-based air sampling and related QA/QC measures were developed in conjunction with the Environmental Protection Agency under the federal Environmental Monitoring for Public Access and Community Tracking (EMPACT) program, and refined in cooperation with agencies including the Health Services Department of Contra Costa County, California and the Delaware Department of Natural Resources [46,47]. Any sample that did not meet QA/QC criteria was not included in the final data set.

Community monitors gauged industrial activity using field log sheets ("pollution logs") that allow each resident to record what they see, hear, feel, smell, and taste in areas downwind of industrial activity as they go about their daily routines. Each community monitor participated voluntarily in data collection for this study. They provided consent to use data gathered with questionnaires that they co-designed as well as grab and passive samplers. Residents documented activity including: (a) visible emissions drifting off-site; (b) odors that appear to derive from a site; (c) acute health symptoms that occur while in proximity to a site or during a specific industrial activity; (d) audible sounds of particular equipment in use within the boundaries of an operating well pad or related infrastructure; and (e) visible activity onsite, including the number and types of heavy trucks and tanks, vehicle traffic, workers present and job categories, and physical changes such as noise and vibrations near certain equipment. Similar to a neighborhood police watch, each resident determined locations that they would continue to observe and potentially return to for sampling.

Sampling for volatile compounds other than formaldehyde was carried out using methods described in



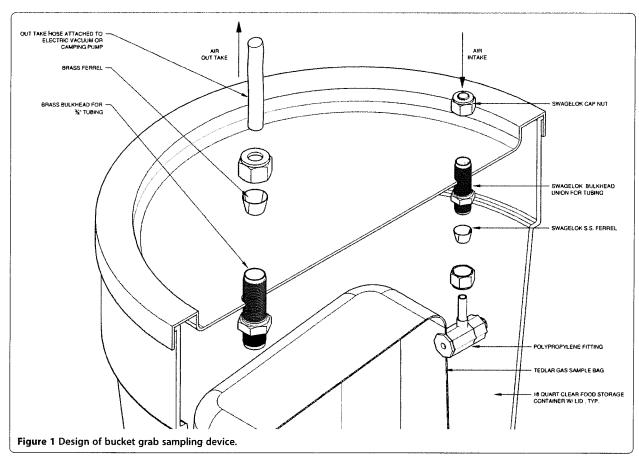
O'Rourke and Macey [48] and Larson et al. [49] using an evacuated sampling ("bucket") vessel modelled after the Summa canister [50]. The bucket is inexpensive, portable, and consists of a 10-liter Tedlar bag and vacuum to take a grab sample of air for two to three minutes (Figure 1). Air is collected using a batteryoperated pump that forces air out of the bucket. Negative pressure created inside the sealed bucket by the external vacuum pump opens the bag when a stainless steel bulkhead is opened. After taking the sample, the Tedlar bag is sealed and sent to an analytical laboratory. The bucket sampler operates on the same principle that Summa canisters employ. Rather than collect a sample in a stainless steel can, the bucket contains a special bag made of Tedlar to hold the sample. Bags are obtained from the laboratory that processes the sample and purged three times with pure nitrogen by the laboratory prior to use. GCM's founder developed the sampling program under a project for Communities for a Better Environment, a non-profit organization founded in 1978 that provides legal, scientific, and technical assistance to heavily polluted communities. The device has been subjected to numerous validation tests organized by government agencies and independent laboratories [51-54].

Refinements include the use of field duplicates, which demonstrate no significant variation in results across comparison studies [45].

Residents collected 35 grab samples at locations of community concern, under conditions that would lead them to register a complaint with relevant authorities such as a county public health department or state oil and gas commission. Health symptoms contributed to the decision to take a grab sample on 29 occasions. The most common symptoms reported by samplers were headaches (17 reports), dizziness or light-headedness (13 reports), irritated, burning, or running nose (12 reports), nausea (11 reports), and sore or irritated throat (11 reports). Further details regarding each sample are provided in Additional file 1 (Tables S1 through S5).

In addition to grab samples, 41 formaldehyde badges were deployed in the five states targeting production facilities and compressor stations based on the results of pollution patrols. UMEx100 Passive Samplers for Formaldehyde are manufactured by SKC Inc. Samplers were placed near operating compressor stations and production facilities for a minimum of eight hours.

Samples were ultimately collected near production pads, compressor stations, condensate tank farms, gas





processing stations, and wastewater and produced water impoundments in five states (Arkansas, Colorado, Ohio, Pennsylvania, and Wyoming). The states were chosen to reflect a diverse range of urban and rural communities, operations (e.g., number of wells permitted and developed), history of development, and stages of production (see Table 1).

Air samples were analyzed for 75 volatile organic compounds (VOCs), including benzene, ethylbenzene, acrylonitrile, methylene chloride, toluene, hexane, heptane, and xylene by ALS Laboratories (Simi Valley, CA 93065) using EPA Method TO-15 or TO-3 (methane) by gas chromatograph/mass spectrometer interface to a whole air preconcentrator. Formaldehyde samples were analyzed using EPA Method TO-11A, modified for the sampling device by high performance liquid chromatography with UV detection. Samples were also analyzed for 20 sulfur compounds by ASTM D 5504-08 using a gas chromatograph equipped with a sulfur chemiluminescence detector. All compounds with the exception of hydrogen sulfide and carbonyl sulfide were quantitated against the initial calibration curve for methyl mercaptan. Chemicals of concern were compared to U.S. Agency for Toxic Substances and Disease Registry (ATSDR) minimal risk levels (MRLs) and EPA Integrated Risk Information System (IRIS) cancer risk levels. MRLs are estimates of daily human exposure that can occur without appreciable risk of human health effects. They are derived for acute (1-14 days), intermediate (15-364 days), or chronic (365 days or longer) periods of exposure. The laboratory is certified by ten state departments of health or environment, the American Industrial Hygiene Association, and the U.S. Department of Defense.

Results

Table 1 shows the diverse range of operation, including number of wells permitted and developed and setbacks from housing and other occupied structures, in UOG regions where grab and passive air samples were collected through partnership with community-based organizations.

Air contaminants

We identified unique chemical mixtures at each sample location (see Tables S1 through S5 in Additional file 1). In addition, we identified eight volatile compounds at concentrations that exceeded ATSDR minimal risk levels (MRLs) or EPA Integrated Risk Information System (IRIS) cancer risk levels (see Table 2). Although our samples represent a single point in time, we compared concentrations to acute as well as chronic risk levels as many of the activities that generate volatile compounds near UOG operations are long-duration (the life cycle of an unconventional natural gas well can span several decades) [16]. Residents chose sample locations where

odors and symptoms were the "norm" for the area, not a one-time event. In addition, a growing body of research suggests that peak (e.g., 1-hr. maximum), rather than average exposure to air emissions may better capture certain risks to human health [55-57].

Sixteen of the 35 grab samples, and 14 of the 41 passive samples, had concentrations of volatiles that exceeded ATSDR and/or EPA IRIS levels. ATSDR MRLs and EPA IRIS levels for chemicals of concern are provided in Table 2. The chemicals that most commonly exceeded these levels were hydrogen sulfide, formaldehyde, and benzene. Background levels for these chemicals are $0.15~\mu g/m^3$ for hydrogen sulfide, $0.25~\mu g/m^3$ for formaldehyde, and $0.15 \mu g/m^3$ for benzene [58-60]. Our samples that exceeded health-based risk levels were 90-66,000× background levels for hydrogen sulfide, 30-240× background levels for formaldehyde, and 35-770,000× background levels for benzene. Details of our results are presented in Tables 3, 4, and 5 and in Figures 2, 3, and 4 (greater detail is provided in Additional file 1). A stateby-state summary follows.

Wyoming (Park County)

Nine of the ten grab samples contained volatiles above ATSDR MRLs or EPA IRIS risk levels. Seven contained high concentrations of hydrogen sulfide (one was over 600× the ATSDR acute MRL) and three contained high levels of benzene, including one over $12,000\times$ the ATSDR acute MRL. The sample with the highest benzene concentrations also contained 480,000 micrograms per cubic meter of heptane, 3,100,000 micrograms per cubic meter of pentane, and 4,100,000 micrograms per cubic meter of butane, all hydrocarbons that are frequently associated with methane. These hydrocarbon concentrations exceeded occupational health standards (NIOSH recommended exposure limits). Four of the seven samples with high levels of hydrogen sulfide were taken in northeast Park County (near Deaver), and three of the four samples with high benzene levels were taken in northwest Park County (near Clark). One of the five passive samples contained formaldehyde at levels that exceeded ATSDR MRLs and the 1/10,000 cancer risk level (Table 3, Figure 2).

Wyoming (Fremont County)

Four of the five grab samples contained volatiles at concentrations that exceeded ATSDR MRLs or EPA IRIS risk levels. One sample contained six volatiles exceeding these levels, including benzene at 75× the ATSDR acute MRL and 22× the EPA IRIS 1/10,000 cancer risk level. A second sample contained three volatiles exceeding ATSDR or EPA IRIS levels and also contained 4,167,000 micrograms per cubic meter of methane, an amount that exceeds its occupational health standard (Threshold Limit Value). None of the passive samples contained



Table 1 Oil and gas operations by state

5	Drilling permits	אם אם אם אם אם אויי	Wolle	Prod			AMAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAA
,		THE STATE OF THE S	Wells	ם	rroduction	Setback requirements	Ambient air quality
State	issueu (year)	Drilled (year)	Producing (year)	Gas (Tcf) (year)	Gas (Tcf) Oil (MMbbl) (year) (year)	(dwellings and occupied structures)	standards
AR	~ 890 (2012) ^a		8,538 (gas) (2012) ^b 1.15 (2012) ^b	1.15 (2012) ^b	6.59 (2012) ^a	200 ft. (from produced fluids storage tanks to habitable dwelling) 20 ppm (5 min.); 80 ppb (8-hr.) (H ₂ S) ^c	20 ppm (5 min.); 80 ppb (8-hr.) (H ₂ S) ^c
	~ 1,090 (2011) ^a					300 ft. (from produced fluids storage tanks to school, hospital, or other public use building)	
8	4,025 (2013) ^a	ı	46,697 (2014) ^d 1.71 (2012) ^b 64.88 (2013) ^a	1,71 (2012) ^b	64.88 (2013) ^a	500 ft. (from well to home or building, absent waiver)	سُّرْن ن
	3,775 (2012) ^a					1,000 ft. (from well to high occupancy building, absent hearing and approval)	
Ö	903 (2012)³	553 (2012) ^a	51,739 (2012)ª	.084 (2012) ^b	4.97 (2012) ^a	150 ft. (occupied dwelling in urbanized area, absent consent)	ى ن ا
	690 (2011) ^a					150 ft. (occupied or public dwelling, non-urban área)	
						200 ft. (occupied dwelling w/in drilling unit due to mandatory pooling)	
PA	4,617 (2013) ^a 4,090 (2012) ^a	2,174 (2013) ^a	55,812 (2011) ^f	2.26 (2012) ^b	2.7 (2011) ^a	500 ft. (from well bore to building or water well)	0.1 ppm (1-hr.); 0.005 ppm (24-hr.) (H ₂ S) ^{c. e}
$\stackrel{\textstyle \searrow}{\otimes}$	3,230 (Sept. 2013-Aug. 2014) ^a	I	37,301 (2012) ^a	2.23 (2012) ^b	57.5 (2012) ^a	350 ft. (from wellhead, pumping unit, pit, production tank, and/or production equipment to residence, school, or hospital)	40 μg/m³ (half-hr. ave., 2x w/in 5 days) (H ₂ S) ^{c. e}

*State agency data.

**Bul.S. Energy Information Administration data.

**In addition to National Ambient Air Quality Standards for criteria air pollutants and federal emissions standards – new source performance standards (40 C.F.R. §§ 60.5360 - 60.5430) and national emission standards for hazardous air pollutants (40 C.F.R. §§ 63.760 - 63.777) – applicable to the oil and gas industry.

**In addition to nation with state agency.

**In addition to state emissions standards (e.g., VOC emissions from glycol dehydrators; green completions; valve requirements for pneumatic devices). See, for example, Colorado Department of Public Health and Environment's revised Air Quality Control Commission Regulation Numbers 3, 6, and 7 (adopted 23 February 2014).

**Farthworks data.

Table 2 ATSDR minimal risk levels and EPA IRIS cancer risk levels for chemicals of concern (all data in $\mu g/m^3$)

Chemical		ATSDR MRLs		IF	RIS cancer risk levels	
	Acute	Intermediate	Chronic	1/1,000,000	1/100,000	1/10,000
Benzene	29	20	10	.45	4.5	45
1,3 butadiene				0.03	0.3	3
Ethylbenzene	21,700	8,680	260			
Formaldehyde	49	37	10	0.08	0.8	8
N-hexane			2,115			
Hydrogen sulfide	98	28				
Toluene	3,750		300			
Xylenes	8,680	2,604	217			

Table 3 Concentrations of volatile compounds exceeding health-based risk levels in samples collected in Wyoming

State/ID	County	Nearest infrastructure	Chemical	Concentration (µg/m³)	ATSDR MRLs exceeded	EPA IRIS cancer risk exceeded
WY-4586	Fremont	5 m from separator	Hydrogen sulfide	590	I, A	n/a
WY-4586	Fremont	5 m from separator	Benzene	2,200	C, I, A	1/10,000
WY-4586	Fremont	5 m from separator	Toluene	1,400	\in	n/a
WY-4586	Fremont	5 m from separator	Ethylbenzene	1,200	C	n/a
WY-4586	Fremont	5 m from separator	Mixed xylenes	4,100	C, I	n/a
WY-4586	Fremont	5 m from separator	n-hexane	22,000	C	n/a
WY-1103	Fremont	20 m from separator	benzene	31	C, I, A	1/100,000
WY-2069	Fremont	110 m from work-over rig ^a	Hydrogen sulfide	30	·venera	n/a
WY-4861	Fremont	5 m from separator	Benzene	230	C, I, A	1/10,000
WY-4861	Fremont	5 m from separator	Mixed xylenes	317	C	n/a
WY-4861	Fremont	5 m from separator	n-hexane	2,500 -	C	n/a
WY-4478	Park	25 m from separator	Hydrogen sulfide	91	440	n/a
WY-4478	Park	25 m from separator	Benzene	110,000	C, I, A	1/10,000
WY-4478	Park	25 m from separator	Toluene	270,000	C, A	n/a
WY-4478	Park	25 m from separator	Mixed xylenes	135,000	C, I, A	n/a
WY-4478	Park	25 m from separator	n-hexane	1,200,000	C	n/a
WY-129	Park	55 m from separator	benzene	100	C, I, A	1/10,000
WY-3321	Park	5 m from compressor	benzene	35	C, I, A	1/100,000
WY-4883-005	Park	5 m from compressor	Formaldehyde	46	C, I	1/10,000
WY-4864	Park	5 m from discharge canal	Hydrogen sulfide	210	1, A	n/a
WY-4865	Park	10 m from discharge canal	Hydrogen sulfide	1,200	i, A	n/a
WY-4496	Park	20 m from well pad	Hydrogen sulfide	6,100	I, A	n/a
WY-106	Park	Adjacent to discharge canal	Hydrogen sulfide	5,600	I, A	n/a
WY-184	Park	15 m from discharge canal	Hydrogen sulfide	240	I, A	n/a
WY-187	Park	15 m from discharge canal	Hydrogen sulfide	66,000	I, A	n/a
WY-187	Park	15 m from discharge canal	Benzene	23	C, I	1/100,000



C = chronic; A = acute; I = intermediate.

all and replace a well completion.

Table 4 Concentrations of volatile compounds exceeding health-based risk levels in samples collected in Arkansas

State/ID	County	Nearest infrastructure	Chemical	Concentration (µg/m³)	ATSDR MRLs exceeded	EPA IRIS cancer risk exceeded
AR-3136-003	Faulkner	355 m from compressor	Formaldehyde	36	C	1/10,000
AR-3136-001	Cleburne	42 m from compressor	Formaldehyde	34	C	1/10,000
AR-3561	Cleburne	30 m from compressor	Formaldehyde	27	C	1/10,000
AR-3562	Faulkner	355 m from compressor	Formaldehyde	28	C	1/10,000
AR-4331	Faulkner	42 m from compressor	Formaldehyde	23	C	1/10,000
AR-4333	Faulkner	237 m from compressor	Formaldehyde	44	C, I	1/10,000
AR-4724	Van Buren	42 m from compressor	1,3-butadiene	8.5	n/a	1/10,000
AR-4924	Faulkner	254 m from compressor	Formaldehyde	48	С, І	1/10,000

C = chronic; I = intermediate.

volatiles at concentrations that exceeded ATSDR MRLs or EPA IRIS cancer risk levels (Table 3, Figure 2).

Arkansas (Cleburne, Faulkner, and Van Buren Counties)

One of the 8 grab samples, and 7 of the 13 passive samples, contained volatiles above ATSDR MRLs or EPA IRIS risk levels. One of the passive samples (taken at a residence) had formaldehyde levels that were close to the ATSDR MRL and exceeded EPA's 1/10,000 cancer risk level (Table 4, Figure 3).

Pennsylvania (Susquehanna County)

One of the four grab samples contained benzene at concentrations that exceeded the EPA 1/100,000 cancer risk level. Six of the ten passive samples contained formal-dehyde at levels that exceeded ATSDR MRLs or EPA IRIS risk levels. Two of the samples exceeded both the acute MRL and the 1/10,000 cancer risk level (Table 5, Figure 4).

Colorado (Boulder and Weld Counties)

One of the five grab samples contained 41 micrograms per cubic meter of hydrogen sulfide and exceeded the

ATSDR intermediate MRL. None of the passive samples had volatiles exceeding the ATSDR MRLs or EPA IRIS risk levels.

Ohio (Athens, Carroll, and Trumbull Counties)

None of the four grab samples or five passive samples contained volatiles at concentrations that exceeded the ATSDR MRLs or EPA IRIS risk levels.

State air quality monitoring survey

We reviewed air quality monitoring by state agencies in the five states covered by our sampling. We reviewed one study in Arkansas, seven in Colorado, one in Ohio, four in Pennsylvania, and one in Wyoming. Most of the studies measured VOC levels, two included hydrogen sulfide, and seven included methane and/or other hydrocarbons. Sampling durations ranged from four hours to 24 months; five of the studies lasted more than four weeks. Target compounds were detected in all studies that have been completed, including mixtures of 42 nonmethane VOCs. None of the studies concluded that detected compounds posed significant human health risk (Table 6).

Table 5 Concentrations of volatile compounds exceeding health-based risk levels in samples collected in Pennsylvania

		•	-		•	
State/ID	County	Nearest infrastructure	Chemical	Concentration (µg/m³)	ATSDR MRLs exceeded	EPA IRIS cancer risk exceeded
PA-4083-003	Susquehanna	420 m from compressor	Formaldehyde	8.3		1/10,000
PA-4083-004	Susquehanna	370 m from compressor	Formaldehyde	7.6		1/100,000
PA-4136	Washington	270 m from PIG launch ^a	Benzene	5.7		1/100,000
PA-4259-002	Susquehanna	790 m from compressor	Formaldehyde	61	C, I, A	1/10,000
PA-4259-003	Susquehanna	420 m from compressor	Formaldehyde	59	C, I, A	1/10,000
PA-4259-004	Susquehanna	230 m from compressor	Formaldehyde	32	C	1/10,000
PA-4259-005	Susquehanna	460 m from compressor	Formaldehyde	34	C	1/10,000

C = chronic; A = acute; I = intermediate.



^aLaunching station for pipeline cleaning or inspection tool.

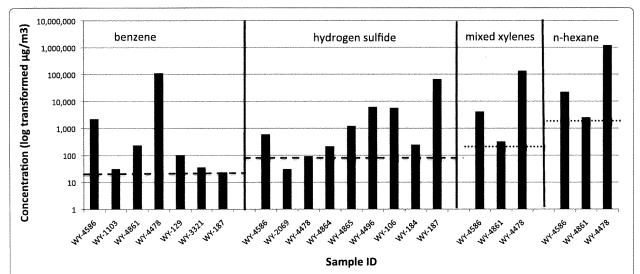


Figure 2 Concentrations of volatile compounds exceeding health-based risk levels in samples collected in Wyoming. Note log scale on y-axis. Dashed lines represent ATSDR intermediate-term MRLs. Dotted lines represent ATSDR chronic MRLs (not displayed: toluene, ethylbenzene, and formaldehyde).

Discussion

We identified significant concentrations of four well-characterized chemicals: benzene, formaldehyde, hexane, and hydrogen sulfide. Benzene was detected at sample locations in Pennsylvania and Wyoming. Concentrations exceeded health-based risk levels by as many as several orders of magnitude. Previous studies similarly found benzene concentrations near oil and gas development [10,11]. Our monitors detected benzene at higher concentrations

 $(5.7-110,000~\mu g/m^3)$ than those found in the published literature. The results are of concern given their proximity to subdivisions, homes, and farms. In Wyoming, multiple samples with high benzene concentrations were taken on residential property 30–350 yards from the nearest well, or on farmland along the perimeter of a well pad. Equipment included separators, compressor stations, discharge canals, and pipeline cleaning operations. The results suggest that existing regulatory setback distances from wells to

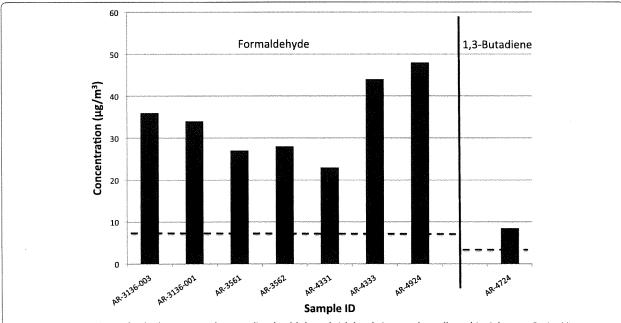


Figure 3 Concentrations of volatile compounds exceeding health-based risk levels in samples collected in Arkansas. Dashed lines represent EPA IRIS 1/10,000 cancer risk for formaldehyde and 1,3 butadiene.

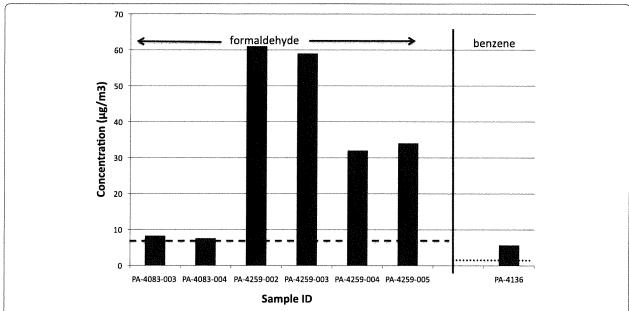


Figure 4 Concentrations of volatile compounds exceeding health-based risk levels in samples collected in Pennsylvania. Dashed line represents EPA IRIS 1/10,000 cancer risk for formaldehyde. Dotted line represents EPA IRIS 1/100,000 cancer risk for benzene.

residences may not be adequate to reduce human health risks [61]. Setbacks from wellheads to homes and other occupied structures cluster around the 150 to 500 feet range in the five states (see Table 1). We found high concentrations of volatile compounds at greater distances, including formaldehyde (up to 2,591 feet) and benzene (up to 885 feet). High levels of benzene near oil production wells indicate that EPA should revisit the extent to which oil wells are addressed in its new source performance standards [62].

Benzene is a known human carcinogen. Chronic exposure to benzene increases the risk of leukemia [63]. The increased risk occurs at low levels of exposure with no evidence of threshold level [64]. Benzene exposure increases risk of birth defects [65], including neural tube and other defects found near natural gas development [24]. Respiratory effects include pulmonary edema, acute granular tracheitis, laryngitis, and bronchitis [60].

UOG fields present multiple sources and exposure routes for benzene. Benzene occurs naturally in shale and other hydrocarbon deposits, and is vented, flared, or released as fugitive emissions along numerous points of production, such as wells, production tanks, compressors, and pipelines [6]. It can volatize and disperse from flowback and produced water at drilling sites and remain in the air for several days [66]. It was among the first pollutants found in air samples near shale gas operations [67]. Previous studies found benzene to be the largest contributor to excess lifetime cancer risk near gas fields [12]. Residents exposed to VOCs including benzene experience immediate health symptoms and illness. Within days after a flaring event at a

Texas City refinery, children exhibited altered blood profiles, liver enzymes, and somatic symptoms [68]. Future research is needed to determine whether the concentrations of benzene we measured are due to continuous releases or flaring, fugitive emissions, or facility upsets.

Formaldehyde is another volatile compound that exceeded health-based risk levels near compressor stations in Arkansas, Pennsylvania, and Wyoming. As with benzene, there are known sources of formaldehyde emissions along the production chain. Formaldehyde is a product of incomplete combustion emitted by natural gas-fired reciprocating engines at compressor stations [69]. Formaldehyde is also formed from methane in the presence of sunlight, which may be an important source given significant amounts of methane that are known to escape from UOG sites [70]. But air monitoring studies, particularly in shale gas regions, either do not measure for formaldehyde [12,14] or find it at lower concentrations. For example, the Barnett Shale Energy Education Council [71] found levels that did not pose a risk to human health. Colborn et al. [10] found formaldehyde and acetaldehyde in each of 46 samples with a mean of 1.0 part per billion by volume. In contrast, our CBPR framework resulted in the targeting of compressor stations for passive sampling, where diesel emissions likely account for the higher levels that we found. Our results are similar to the Fort Worth Natural Gas Air Quality Study, which found formaldehyde concentrations in areas with multiple large compressor engines [72]. We found high concentrations of formaldehyde near fourteen compressor stations in three states.

Agency (year)	Target compound	Sampling equipment	Sample sites	Duration	Representative findings
ADEQ (2011)	VOCs (total) NO NO ₂	PID (fixed) PID (handheld)	4 compressor stations 6 drilling sites 3 well sites (fracking) 1 upwind	1 d (4–6 hrs.)	VOCs at drilling sites elevated (ave. 38–678 ppb; max. 350–5,321 ppb) NO/NO ₂ rarely exceed detection limits
CDPHE (2012)	NMOCs (78) Methane	Canister	1 well pad (Erie)	3 wks.	Detects = 42 of 78 compounds in >75% of samples Benzene "well within EPA's acceptable cancer risk range" Acute and chronic HQs "well below" 1
CDPHE (2009)	NMOCs (78) VOCs PM ₂ S	Canister PID (handheld) Filter (handheld)	8 wells (4 drilling, 4 completion)	1 9	Total NMOC ave. 273 – 8,761 ppb at 8 sites Total VOC ave. 6–3,023 ppb at 8 sites $PM_{2.5}$ ave. 7.3 - 16.7 $\mu g/m^3$ at 8 sites
CDPHE, GCPHD (2007)	>	Canister Filter	14 sites 7 sites	24 mos.	Detects = 15 of 43 compounds Benzene ave. 28.2 µg/m³, max 180 µg/m³ (grab) Toluene ave. 91.4 µg/m³, max 540 µg/m³ (grab)
CDPHE (2003–2012)	NMOCs Carbonyls	Canister	5 sites (2003) 6 sites (2006) 3+ sites (2012)	2 mos.	Methane ave. 2,535 ppb (Platteville) vs. (1,780 ppb Denver) Top NMOCs in Platteville = ethane, propane, butane Benzene, toluene higher in Platteville
CDPHE (2002)	VOCs (42) SO ₂ NO, NO ₂	Continuous	2 well sites 1 residential 1 active flare 2 up., down-valley 1 background	1 mo.	Detects = 6 of 42 VOCs Benzene in 6 of 20 (2.2-6.5 μg/m³) Toluene in 18 of 20 (1.5-17 μg/m³)
OEPA (2014)	VOCS (69) VOCS PM ₁₀ /PM ₂₅ H ₂ S CO	Ganister GC/MS Filter	1 well site 1 remote site	12 mos.	Ongoing; data update provided in February 2014 Detects include BTEX, alkanes (e.g., ethane, hexane), H ₂ S Second site planned near processing plant
PA DEP (2010)	VOCs (48) Alkanes Leak detection	Ganister OP-FTIR GC/MS FLIR	2 compressor stations 1 condensate tank 1 wastewater impoundment 1 background	5 wks.	Detects include methane, ethane, propane, benzene (max. 758 ppb) No conc.'s "that would likely trigger air-related health issues" Fugitive gas stream emissions
PA DEP (2011)	VOCs (48) Alkanes Leak detection	Ganister OP-FTIR GC/MS FLIR	2 compressor stations 1 completed well 1 well site (fracking) 1 well (tanks, separator) 1 background	4 wks.	Detects include BTEX (benzene max, 400 ppb), methylbenzenes No conc.'s "that would likely trigger air-related health issues" Fugitive emissions from condensate tanks, piping
PA DEP (2011)	VOCs (48) Alkanes	Canister OP-FTIR GC/MS	2 compressor stations 1 well site (flaring) 1 well site (drilling) 1 background	4 wks.	Detects include benzene (max. 400 ppb), toluene, ethylbenzene Natural gas constituent detects near compressor stations Conc.'s "do not indicate a potential for major air-related health issues"
PA DEP (2012)	Criteria VOCs/HAPs Methane H ₂ S	"Full suite"	1 gas processing 2 large compressor stations 1 background	12 mos.	Ongoing; report due in 2014



	evelopment t station s samples s sources)
inued)	7 permanent stations (e.g., Boulder, Juel Spring, Moxa) Ongoing WDEQ mobile monitors placed at locations w/ oil & gas development and a mesonet stations (Mesa, Paradise Warbonnet) Mini-SODAR also placed adjacent to Boulder permanent station a mesonet stations (Mesa, Paradise Warbonnet) Mini-SODAR also placed adjacent to Boulder permanent station and mentalism (Mesa, Paradise Signalism (Mesa, Paradise Paradise Signalism (Mesa, Paradise Paradise Signalism (Mesa, Paradise
t ions (Con	Ongoing
Table 6 Five-state survey of air quality monitoring studies, unconventional oil and gas operations (Continued)	7 permanent stations (e.g., Boulder, Juel Spring, Moxa) 3 mesonet stations (Mesa, Paradise Warbonnet) 2 mobile trailer locations (Big Piney, Jonah Field)
	Canister UV Photometric FID Chemiluminescence Beta Attenuation
	VOCs/NMHCs Ozone Methane NO, NO ₂ PM ₁₀ /PM ₂₅
Table 6 Five-	WDEQ (2013)

BTEX = benzene, toluene, ethylbenzene, and xylenes; FID = flame ionization detector; FLIR = forward looking infrared; GC/MS = gas chromatography/mass spectrometry, HAP = hazardous air pollutant; NAAQS = National Ambient Air Quality Standard; NMHC = non-methane infrared pollutant; NMOC = non-methane organic compound; OP-FTIR = open-path Fourier transform infrared; PID = photoionization detector; VOC = volatile organic compound.



Formaldehyde is a suspected human carcinogen [73]. It can affect nearly every tissue in the human body, leading to acute (dermal allergies, asthma) and chronic (neuro-, reproductive, hematopoietic, genetic and pulmonary toxicity and cellular damage) health effects [74]. The science of childhood exposure to formaldehyde is progressing rapidly [75]. State agencies and international organizations continue to lower exposure limit values and guidelines for formaldehyde [76]. Our results exceed those guidelines. Symptoms reported by community members mirror the effects of acute formaldehyde exposure, which causes irritation of the eyes, nose, throat, and skin.

Other volatiles of concern included hexane and hydrogen sulfide. Hexane detects were most prevalent near oil and gas operations in Wyoming near well pads, compressor stations, separators, and produced water discharges. Other studies in oil and gas regions found hexane, but at low concentrations [10,12]. The circumstances under which high concentrations of hexane were found in Wyoming suggest a combination of leaks, spills, and fugitive emissions as potential causes. Acute exposure to hexane affects the central nervous system, causing dizziness, nausea, and headache. Chronic effects include neurotoxicity [77].

We also found elevated levels of hydrogen sulfide in Wyoming along the chain of production (pump jacks, produced water discharge impoundments, discharge canals) and near a well pad in Colorado. Hydrogen sulfide is a broad-spectrum toxicant that can impact most organ systems [78]. As such, it contributes to a range of short-and long-term neurological, upper respiratory, and blood-related symptoms, including those that were prevalent among community samplers in Wyoming (headaches, dizziness, eye irritation, fatigue) [79]. Hydrogen sulfide is a natural component of crude oil and natural gas [5] and is released during many industrial processes. In addition, five samples from Wyoming exceeded ATSDR health-based risk levels for toluene and xylenes.

Health-based risk levels provide only a limited sense of potential human health impacts from air emissions. They do not fully account for vulnerable subpopulations, and toxicity values are available for a comparatively small number of compounds. The levels that we found for the above chemicals of concern suggest that state monitoring studies are incomplete. Recent state-funded projects found air volatiles at UOG sites that were either near detection limits or within acceptable limits to protect the public [80-82]. One area of agreement between our community-based and state monitoring studies concerns the presence of complex chemical mixtures. These mixtures demonstrate the contingent nature of ambient air quality near UOG infrastructure.

For example, one sample, taken midday in early winter near a well pad in Wyoming with clicking pneumatic pumps, found high concentrations of hydrogen sulfide,

hexane, benzene, and xylenes. It also captured cyclohexane, heptane, octane, ethylbenzene, nonane, 1,2,4-trimethylbenzene, and 15 tentatively identified compounds (TICs). TICs are compounds that a device or analytic process is not designed to measure. Total VOC concentrations in the sample exceeded 1.6 million µg/m³, excluding methane. While toxicity values are not available for every TIC in our samples, they exceeded reference concentrations available for related compounds such as hexane [77]. Another sample taken in Arkansas, during autumn in the afternoon near a compressor station, captured 17 volatile compounds and five TICs. A third sample, near a separator shed in Wyoming in late autumn at midday, showed spikes in hydrogen sulfide, benzene, and hexane, 19 additional VOCs, and 15 TICs, with total VOC concentrations exceeding 25 million µg/m³, excluding methane. These and other complex mixtures are provided in Additional file 1.

The mixtures that we identified are related to sources commonly used in well pad preparation, drilling, well completion, and production, such as produced water tanks, glycol dehydrators, phase separators, compressors, pipelines, and diesel trucks [14]. They can be released during normal operating conditions and persist near ground level, especially in regions where topography encourages air inversions [83]. The toxicity of some constituents is well known, while others have little or no toxicity information available. Our findings of chemical mixtures are of clinical significance, even absent spikes in chemicals of concern. The chemical mixtures that we identified should be further investigated for their primary emissions sources as well as their potential cumulative and synergistic effects [84]. Clinical and subclinical effects of hydrocarbons such as benzene are increasingly found at low doses [85]. Chronic and subchronic exposure to chemical mixtures is of particular concern to vulnerable subpopulations, including children, pregnant women, and senior citizens [86].

Apart from chemicals of concern (including known and suspected human carcinogens) and chronic exposure to complex mixtures, our findings point to the value of community-based research to inform state testing protocols. Air quality near the diverse range of equipment and stages of UOG development is inherently complex. While states sometimes rely on state-of-the-art technologies such as wireless sensors to characterize local air quality, they continue to collect only a "snapshot" of near-field conditions. For example, Arkansas carried out a technologically ambitious program, placing multi-sensor gas monitors on five-foot tripods along each perimeter of a well pad at several sites. AreaRAEs (the trade name for a wireless monitor produced by RAE Systems) use electrochemical sensors to measure nitrous oxides and a photoionization detector to determine VOC concentration.

The continuous monitors wirelessly transmitted data at five-second intervals over a four- to six-hour period (see Table 6). In addition, Arkansas Department of Environmental Quality (ADEQ) personnel carried handheld versions of the AreaRAE along the perimeter of the sites every one or two hours. While the study did not identify individual VOCs, it found that total VOC emissions at the edge of a well pad fluctuate wildly over a five-hour period. The agency concluded, "The spatial and temporal distribution of VOC concentrations at most drilling sites was significantly affected by monitor location, wind, and the interaction between location and wind direction" [81]. Other studies noted similar variation, although the extent to which short-term spikes and unique chemical mixtures might pose a risk to human health was not considered.

Community-based research can improve the spatial and temporal resolution of air quality data [87] while adhering to established methods. Our findings can inform and calibrate state monitoring and research programs. Additional file 1: Table S6 gives a more in-depth overview of community monitoring in action, including sample site selection factors, sources of public health concern at each site, and the range of infrastructure present and life cycle stage when samples were taken. For example, grab samples in Wyoming with some of the highest VOC concentrations were collected during production, as opposed to well completion (see Table S6, Additional file 1). The timing and location of our samples were driven by two primary factors: local knowledge gleaned from daily routines, and a history of chronic or subchronic symptoms reported by nearby residents. For example, a separator shed was targeted because of subchronic symptoms (dizziness, nausea, tight chest, nose and throat problems, metallic taste, and sweet smell) and loud sounds nearby ("hissing, clicking, and whooshing"). Well pads were selected based on impacts to livestock, pasture degradation from produced water, and observations of residents and farmers. Other samples were driven by observations of fugitive emissions, including vapor clouds, deposition, discoloration, and sounds (see Table S6 in Additional file 1).

Community-based research can identify mixtures, and their potential emissions sources, to prioritize for study of their additive, cumulative, and synergistic effects [88]. The mixtures can be used to determine source signatures [14] and isolate well pads for more intensive monitoring. Symptom-driven samples can define the proper length of a sampling period, which is often limited to days or weeks. They can inform equipment placement for continuous monitoring and facilitate a transition from exploratory to more purposive sampling. Testing informed by human health impacts, and more precise knowledge of the mix and spacing of sources that may

contribute to them, contrasts with state efforts, which are limited by access to property, sources of electrical power, fixed monitoring sites, and the cooperation of well pad owners and operators. In these ways, community-based monitoring can extend the reach of limited public resources.

Conclusions

Community-based monitoring near unconventional oil and gas operations demonstrates elevations in concentrations of hazardous air pollutants under a range of circumstances. Of special concern are high concentrations of benzene, hydrogen sulfide, and formaldehyde, as well as chemical mixtures linked to operations with observed impacts to resident quality of life.

Additional file

Additional file 1: Contains six tables, including complete results from grab and passive sampling (Tables S1 through S5) and data on sample location selection in Wyoming (Table S6).

Abbreviations

ADEQ: Arkansas Department of Environmental Quality; ATSDR: Agency for Toxic Substances and Disease Registry: BTEX: benzene, toluene, ethylbenzene, and xylenes; CBPR: community-based participatory research; CDPHE: Colorado Department of Public Health and Environment; EMPACT: Environmental Monitoring for Public Access and Community Tracking; EPA: Environmental Protection Agency; FID: flame ionization detector; FLIR: forward looking infrared; GCM: Global Community Monitor; GC/MS: gas chromatography/mass spectrometry; GCPHD: Garfield County Public Health Department; HAP: hazardous air pollutant; IRIS: Integrated Risk Information System: MRL: minimal risk level: NAAOS: National Ambient Air Quality Standard: NIOSH: National Institute for Occupational Safety and Health; NMHC: non-methane hydrocarbon; NMOC: non-methane organic compound; OEPA: Ohio Environmental Protection Agency; OP-FTIR: open path Fourier transform infrared; PA DEP: Pennsylvania Department of Environmental Protection; PAH: polycyclic aromatic hydrocarbon; PID: photoionization detector; QA/QC: Quality Assurance/Quality Control; TIC: tentatively identified compound; UOG: unconventional oil and gas; VOC: volatile organic compound; WDEQ: Wyoming Department of Environmental Quality

Competing interests

The authors declare they have no competing financial interest. Ruth Breech, Mark Chernaik, Caroline Cox, Denny Larson, and Deb Thomas are employed by non-profit organizations whose mission is to reduce exposure to toxic chemicals.

Authors' contributions

GPM provided study design and project management, a survey of state-sponsored air quality monitoring studies, data analysis, and initial drafts of the Background, Methods, Discussion, and Tables 1 and 6, and Additional file 1: Tables S1 through S6. RB managed air quality monitoring teams and provided an initial draft of the Methods. MC provided data analysis and interpretation of grab and passive samples. CC provided data analysis and interpretation of grab and passive samples and initial drafts of the Results, Tables 2, 3, 4, 5 and Figures 2, 3 and 4. DL developed the protocol for community-based air sampling and provided an initial draft of the Methods. DT managed air quality monitoring teams in Wyoming and provided an initial draft of Additional file 1: Table S6. DOC provided study design and guidance, data analysis, and initial drafts of the Background and Discussion. All authors participated in the study design, data analysis and interpretation, and drafting of the manuscript. All authors read and approved the final manuscript.



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