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An Exploratory Study of Air Quality Near Natural Gas Operations

Theo Colborn, Kim Schultz, Lucille Herrick, and Carol Kwiatkowski
The Endocrine Disruption Exchange, Paonia, CO, USA

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 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 volatile organic compounds (VOCs) derived from the combustion of gasoline and diesel fuel by mobile and

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Address correspondence to Carol Kwiatkowski, The Endocrine Disruption Exchange (TEDX), P.O. Box 1407, Paonia, CO 81428, USA. E-mail: carolkw@tds.net

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stationary sources. Air quality monitoring has focused primarily on large urban and industrialized areas in and around heavily populated regions across the United States 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 United States 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 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 non-methane hydrocarbons (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 5850 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 8300 feet (2530 m) 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.

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 20). 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.

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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. 1998). The 24-h samples were taken weekly from noon Monday to noon Tuesday, and the 4-h 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-h 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 h 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-h 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-h sampling of VOCs and carbonyls was extended to 6 h, generally from 9:00 a.m. to 3:00 p.m. with a few samples taken from 10:00 a.m. to 4:00 p.m., 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 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 were 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 and 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.

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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
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/m ³ (pql)
acrolein	107-02-8	0.025 µg/ml
acrylonitrile	107-13-1	1 ppbv
allyl chloride	107-05-1	0.5 ppbv
anthracene	120-12-7	2 ng/m ³ (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
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

(Continued on next page)

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

Chemical	CAS#	Reporting limit ^a
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
dichlorofluoromethane	75-43-4	0.5 ppbv
ethyl acetate	141-78-6	0.5 ppbv
fluoranthene	206-44-0	2 ng/m ³ (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	1 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/m ³ (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
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.

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 alkenes 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

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

Chemical name	CAS #	n detects	% detects	Mean ppbv	Range ppbv	Std dev ppbv	n spikes
VOCs							
methane	74-82-8	48	100	2472.9	1600.0-5500.0	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
m/p-xylenes	108-38-3/ 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
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
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

(Continued on next page)

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

Chemical name	CAS #	n detects	% detects	Mean ppbv	Range ppbv	Std dev ppbv	n spikes
mek & butyraldehyde	78-93-3/ 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.

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,b,c,d). 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

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

Chemical name	CAS #	n detects	% detects	Mean pptv	Range pptv	Std dev pptv	n spikes
naphthalene	91-20-3	21	100	4.19	1.13-8.45	2.00	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.

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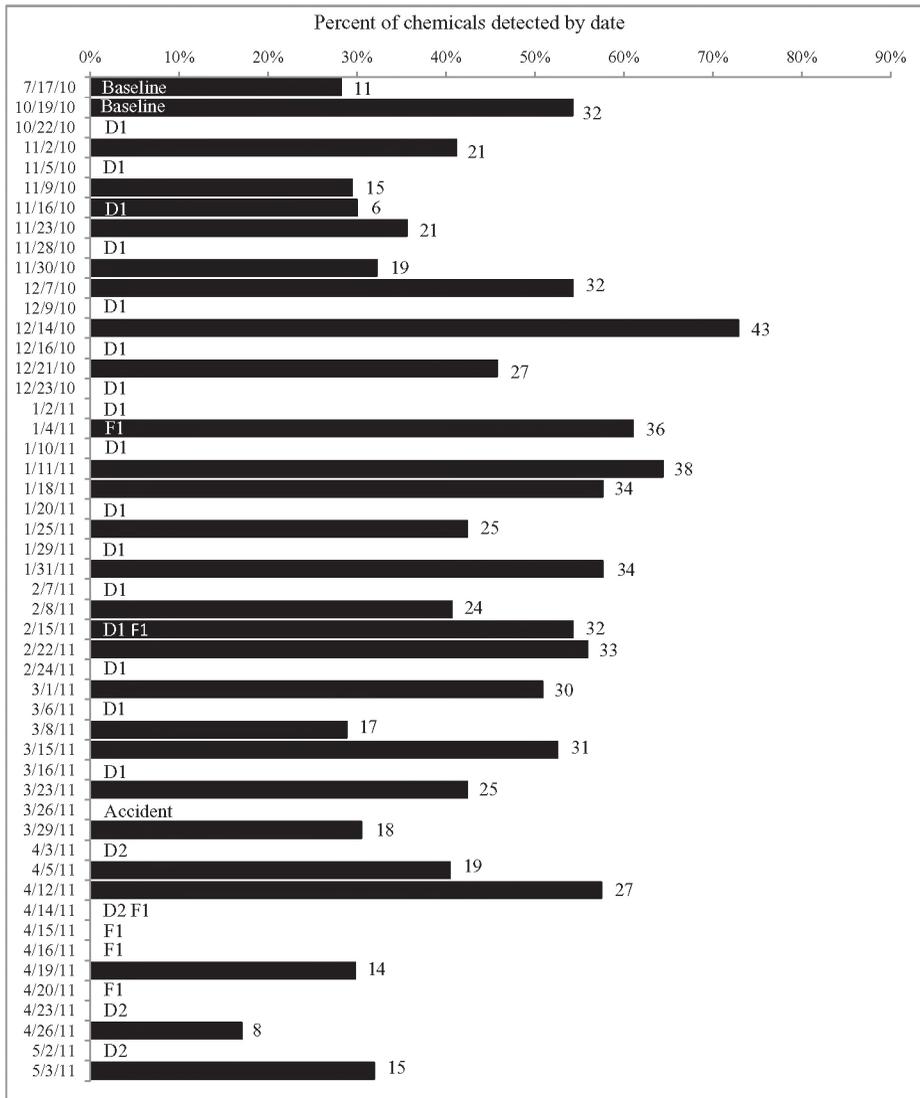


Figure 1. Percent and number of chemicals detected in air samples collected in western Colorado from July 2010 to October 2011, and drilling/fracturing events, by date. The number of chemicals detected is shown at the end of each bar. D1 F1: Drilling and fracturing events during development of Pad #1. D2 F2: Drilling and fracturing events during development of Pad #2. D3 F3: Drilling and fracturing events during development of Pad #3.

correlation between detected emissions (which varied by quarter and were highest in the winter) and wind direction.

Calm winds (wind under 1 mph), however, were greatest during times when detections were highest. For example, in the fourth quarter of 2010, winds were calm

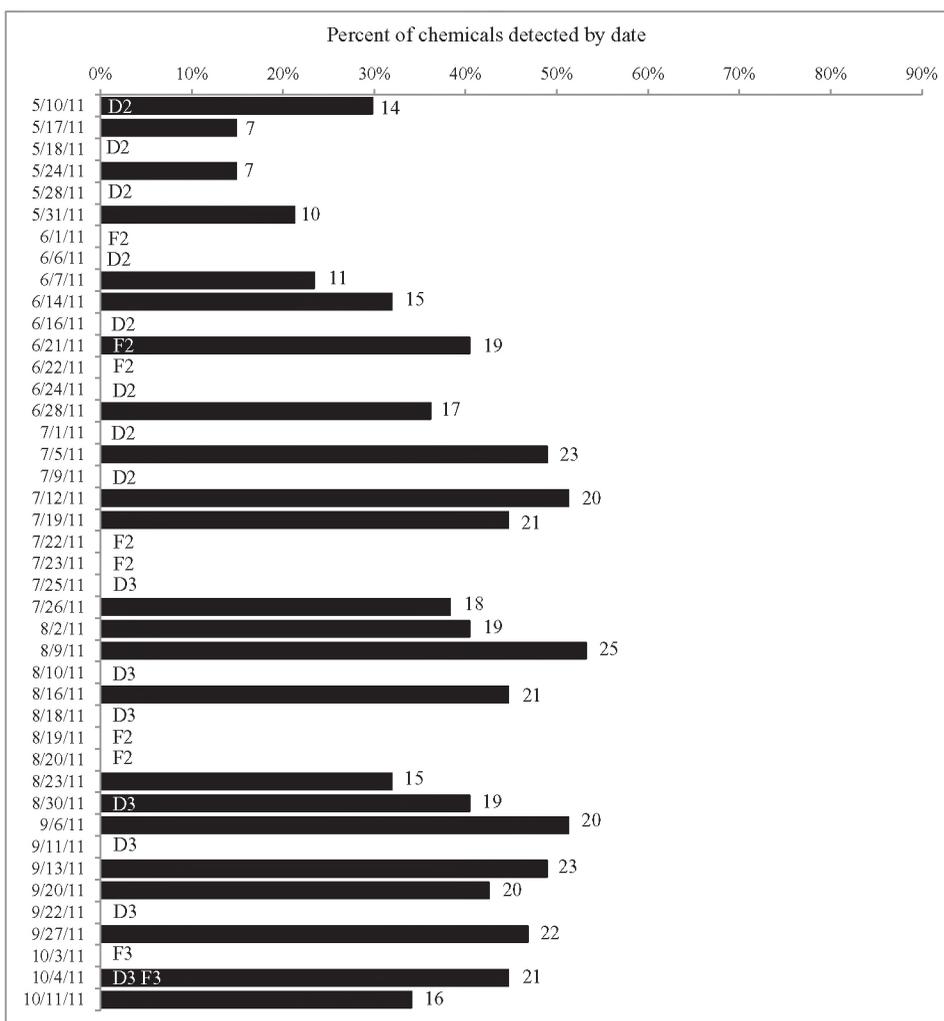


Figure 1. (Continued)

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 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

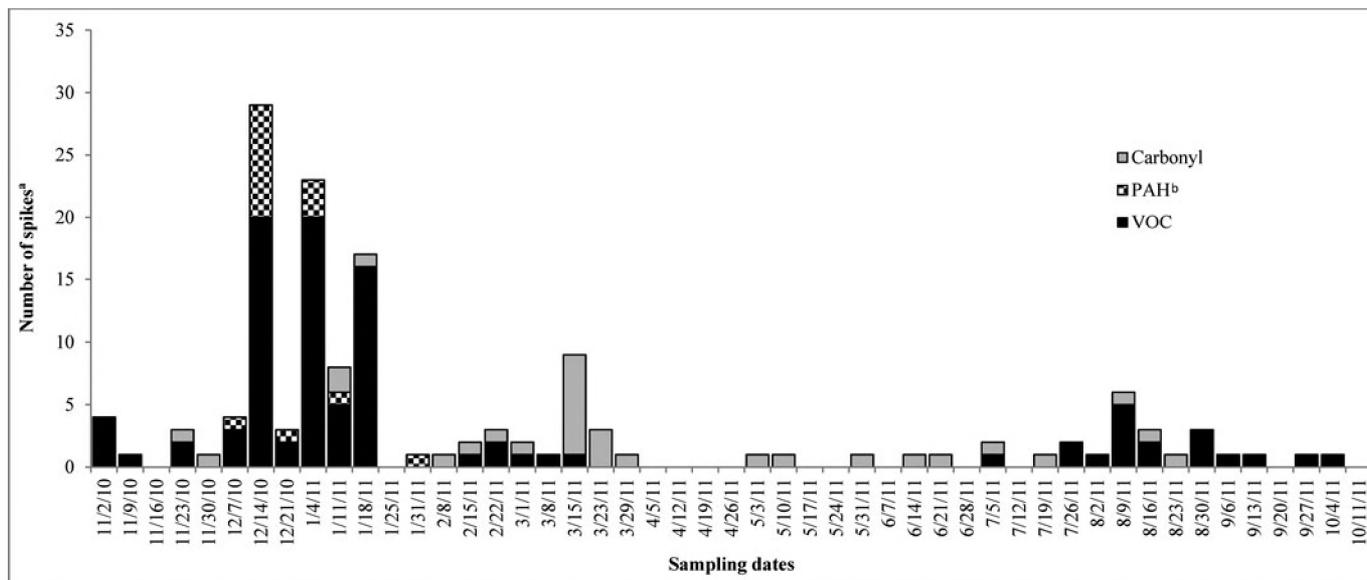


Figure 2. Number of chemical spikes^a from air samples collected in western Colorado from November, 2010 to October, 2011, by compound type and date of sampling event. ^aA spike is a detected chemical level that is at least one standard deviation above the mean. ^bPAHs were sampled from November 2, 2010 to March 29, 2011.

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 stored on the pad in tanks marked "produced water." During the heating process numerous 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 it 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 United States 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 1186 Mcf (propane equivalent) 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

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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

hexaldehyde	X			X	X		X		X	X		X
indeno(1,2,3-cd)pyrene		X		X	X			X	X	X	X	
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
n-decane	X	X		X	X							X
n-heptane	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	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	X
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.

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 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 article 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.

NOMENCLATURE

COGCC	Colorado Oil and Gas Conservation Commission
Mcf	thousand cubic feet
ng/m ³	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/m ³	micrograms per cubic meter
μg/ml	micrograms per milliliter
VOCs	volatile organic compounds

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