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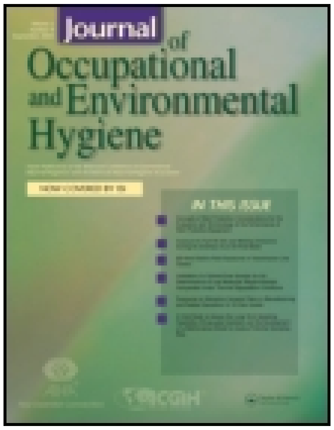

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Evaluation of Some Potential Chemical Exposure Risks During Flowback Operations in Unconventional Oil and Gas Extraction: Preliminary Results

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Case Study

Evaluation of Some Potential Chemical Exposure Risks During Flowback Operations in Unconventional Oil and Gas Extraction: Preliminary Results

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INTRODUCTION

Approximately 562,000 workers were employed in the U.S. oil and gas extraction industry in 2012; nearly half of those workers were employed by well servicing companies, which include companies that conduct hydraulic fracturing and flowback operations.(1) To understand possible risks for chemical exposures in modern oil and gas extraction operations, the National Institute for Occupational Safety and Health (NIOSH) initiated the *Field Effort to Assess Chemical Exposures in Oil and Gas Workers*.(2) Initial research identified exposure risks for respirable crystalline silica during hydraulic fracturing as an occupational health hazard.(3–5) This report describes industrial hygiene sampling during flowback operations at six unconventional oil and gas extraction sites in Colorado and Wyoming during spring and summer 2013. The results are considered preliminary; additional exposure assessments are needed to better understand the range of possible exposures, risk factors, and controls during flowback operations.

BACKGROUND

Hydrocarbon extraction is the primary objective of oil and gas exploration and production (E&P). Notwithstanding flammability hazards, the potential for chemical exposures may be encountered during many stages of E&P, including drilling, completions (which includes hydraulic fracturing), and well servicing. Chemicals used in the oil and gas industry, as well as the petroleum produced, can present exposure risks to volatile organic compounds (VOCs), including naphthalene, benzene, toluene, ethylbenzene and xylene (NBTEX). Additionally, other aliphatic and aromatic compounds (e.g., gasoline and diesel-range organics and mixtures), alcohols, aldehydes, and combustion products (e.g., oxides of nitrogen, ozone, and diesel particulate) can pose concomitant exposure risks for workers during E&P operations. Benzene is a VOC of major concern because of its carcinogenic potential and because it can be acutely toxic to the nervous system, liver, and kidneys at high concentrations.(6–9) Other VOCs associated with hydraulic fracturing and flowback

TABLE I. Occupational Exposure Limits

Benzene	Criteria
Occupational Safety and Health Administration (OSHA)	1 ppm TWA
Permissible Exposure Limit (PEL) - General Industry[A]	5 ppm STEL
OSHA PEL - Sectors Excluded from General Industry	10 ppm TWA
(includes oil and gas extraction)[B]	25 ppm Ceiling
	50 ppm maximum peak above ceiling (10 minutes)
National Institute for Occupational Safety and Health (NIOSH)	0.1 ppm TWA
Recommended Exposure Limit (REL)[C]	1 ppm STEL Ca/Skin
American Conference of Governmental Industrial Hygienists (ACGIH®)	0.5 ppm TWA
Threshold Limit Value (TLV®) (2013)[D]	2.5 ppm STEL A1; Skin; BEI
California OSHA PEL[E]	1 ppm TWA 5 ppm STEL Skin

Notes: California Dept. Industrial Relations, Table AC-1
Ca: denotes NIOSH criteria, potential occupational carcinogen.
A1: denotes an ACGIH confirmed human carcinogen.
BEI: An ACGIH Biological Exposure Index exists for the substance.
[A] OSHA *CFR* 1910.1028 Table Z-1
[B] OSHA *CFR* 1910.1028 Table Z-2
[C] *NIOSH Pocket Guide.*
[D] ACGIH *Threshold Limit Values, Benzene.*
[E] Skin: denotes a skin notation referring to a potential significant contribution to the overall exposure by the cutaneous route.

(e.g., propargyl alcohol, methanol, and dimethylformamide) have the potential to injure multiple organ systems when exposures in excess of occupational exposure limits (OELs) are repeated and not well controlled. Inhalation is the primary route of exposure to VOCs; however, dermal exposures are also possible. Table I lists relevant OELs for benzene.

Contemporary "unconventional" oil and gas extraction has grown dramatically in the past 10–15 years. Technological advances (e.g., horizontal drilling) and highly effective reservoir completions techniques (e.g., high-volume hydraulic fracturing) enable access and extraction of petroleum reserves previously not considered economically or technologically feasible to extract from low porosity "tight shale" reservoirs. Along with technological innovation in drilling and hydraulic fracturing, the work site and work practices of contemporary oil and gas extraction have evolved, including consistent increases in the safety of oil and gas extraction activities. Examples include improved drill rig designs and engineering, enhanced mechanization of drill pipe and casing handling, and improved protection from well blowouts, fires, and explosions. Despite these advances, the oil and gas extraction industry has a high fatality rate and while the main causes of worker fatalities have been described by NIOSH, (10–12) few systematic studies describing occupational health risks during contemporary land-based, unconventional oil and gas extraction have been published in the peer-reviewed literature.

Hydraulic fracturing operations are typically conducted to enhance hydrocarbon recovery following well drilling and casing operations. To begin recovery of the hydrocarbons, treatment fluids injected into the well during hydraulic fracturing flow back up the wellbore where they are recovered. Returned fluids, referred to as "flowback," are considered process fluids and handled accordingly. During flowback, the pressurized fluid includes dissolved hydrocarbon gases, water, liquid hydrocarbons, sand, and debris from plugs used in the well during hydraulic fracturing. After the initial return of fluids, three- or four-phase separators are used to separate the returning flowback fluid into gas, water, sand, and concentrated hydrocarbons. Products from the separators are routed to portable flowback tanks for temporary storage of water with diluted hydrocarbons and other chemicals, to production tanks (for concentrated oil/condensate), or to final gas processing prior to sale.

In addition to the treatment slurry injected during hydraulic fracturing, returned process fluids may contain endogenous chemicals, including hydrocarbons, and other chemicals from the reservoir formation, including salts (also called well brines), clays, dissolved metal ions, total dissolved solids (TDS), and naturally occurring radioactive materials (NORM), including uranium, thorium, and radium isotopes.(13,14) The composition of flowback fluids varies considerably and appears to be influenced by the reservoir formation, the phase of the flowback process, and how flowback tanks are engineered and configured. A majority of flowback fluids are recovered seven to ten days after flowback begins; the remainder flows back over three to four weeks. Process fluid recovery has been reported to range between 20% and 40% of the volume initially pumped during hydraulic fracturing.(15) Composition of flowback fluids also varies considerably over a typical 30-day period when most fluid is recovered.

Flowback tanks are typically arranged to accept separated process fluids sequentially, often flowing through six or more tanks. In addition to flowback tanks, fixed-vessel production tanks are typically located on the well pad to store recovered liquid hydrocarbons (oil/condensate).

To determine the volume of liquids in flowback and production tanks, workers must periodically gauge fluid levels using hand-held gauging sticks for flowback tanks or hand-cranked gauging tapes for the deeper production tanks. Workers access the tanks through hatches located on the tops of tanks. Periodically, recovered liquid hydrocarbons/condensate is pumped to production tanks or to trucks, which collect and transport process fluids off the well pad; natural gas is typically piped to gas gathering operations.

FIGURE 1. Well site with flowback tanks. (color figure available online)

FIGURE 2. Flowback technician gauging a flowback tank. (color figure available online)

Figure 1 shows a series of tanks in the background of a well pad. From left to right, numerous water tanks sit next to six flowback tanks followed by two separator buildings in a typical side-by-side configuration along the periphery of the well pad.

Tank gauging and other tasks required during flowback can present exposure risks for workers from alkane and aromatic hydrocarbons produced by the well and diluted treatment chemicals used during hydraulic fracturing (typically a combination of acid, pH adjusters, surfactant, biocides, scale and corrosion inhibitors, and, in some cases, gels, gel demulsifiers, and cross-linking agents). Task-based activities during flowback include tank gauging, setting, and changing chokes to manage fluid flows; checking valves and determining volume, flow rate, and accumulation of process liquids; maintenance of piping; and monitoring and maintaining oil/gas/water separators.

Figure 2 shows a flowback technician gauging a flowback tank.

METHODS

NIOSH partnered with oil and gas operators and service companies to evaluate worker exposures to VOCs at six completions sites in Colorado and Wyoming. Sites and equipment used were typical of contemporary flowback operations. Samples were collected from volunteer workers who participated by wearing sampling equipment designed to collect full-shift (typically 12-hr) and task-based personal breathing zone (PBZ) samples. Because the flowback technicians' work shift was 12- hr, a reduction factor of 0.5 was calculated to modify the American Conference of Governmental Industrial Hygienists (ACGIH®), Threshold Limit Value (TLV®) TWA for benzene from 0.5 ppm to 0.25 ppm. (16) No adjustments were made to the NIOSH REL-TWA (0.1 ppm) as the value was developed by NIOSH as a lowest feasible limit considering the fact that benzene is an occupational carcinogen.

To assess internal uptake (i.e., dose) from potential benzene exposures, workers were asked to provide urine samples to analyze for benzene metabolites. A biological monitoring study protocol was developed, reviewed, and approved by the NIOSH Human Subjects Review Board. Each study participant provided informed consent before participating and could withdraw from the study at any time.

Typical flowback operations have two to four flowback personnel performing flowback tasks; these were the typical number of workers at each of the sites visited. Air sampling, typically collected over two days, included workers with the following job titles and descriptions:

- Flowback lead: recorded well pressures and temperature, monitored separators and other equipment
- Flowback tech: gauged flowback tanks 1–4 times per hr, recorded volumes, assisted in tank pumping and fluid transfers to trucks
- Production watch lead: monitored rate and volume of natural gas and liquid hydrocarbons
- Production watch technician: gauged production tanks
- Water management operator: gauged water tanks, ran pumps

Full-shift and short-term PBZ sampling, and full-shift area sampling, was performed using methods and analyses listed in the *NIOSH Manual of Analytical Methods (NMAM)*.(17) Samples were analyzed at an American Industrial Hygiene Association (AIHA)-accredited laboratory.

Integrated samples for benzene and other hydrocarbons were collected using SKC Pocket Pumps or Gilian low-flow personal sampling pumps (Gilian Instruments, St. Petersburg, Fla.) and Anasorb CSC activated coconut shell charcoal sorbent tubes (100/50 mg) (Lot 2000, SKC Inc., Eighty Four, Pa.). Sampling trains were calibrated at a nominal flow rate of approximately 100 cubic centimeters per min (cc/min). Samples were analyzed according to NIOSH Methods 1500, 1501 and 1550 for aromatic (e.g., NBTEX) hydrocarbons. Full-shift PBZ and area sampling was also conducted for polycyclic aromatic hydrocarbons (PAHs), glutaraldehyde, propargyl alcohol, and methanol using NIOSH or the Occupational Health and Safety Administration (OSHA) sampling and analytical methods.

Real-time, direct-reading instruments were used to characterize peak concentrations at various workplace areas for VOCs, benzene, and flammable/explosive atmospheres in relation to the lower explosive limit (LEL). Direct reading instruments, including ToxiRae, MiniRae 2000 and MultiRae Plus instruments (RAE Systems, San Jose, Calif.) with photoionization detectors (PIDs) (configured with a 10.6 electron volts (eV) lamp and data logging capability) were used to measure VOC concentrations. A MultiRae Plus (real-time PID equipped with four gas sensors; RAE Systems, San Jose, Calif.) was used to measure oxygen, LEL, carbon monoxide (CO,) and hydrogen sulfide (H_2S). An UltraRAE 3000 PID (configured with a 9.8 eV lamp and benzene separator tube, RAE Systems, San Jose, Calif.), and a Dräger Chip Measurement System (CMS; Draeger, Pittsburg, Pa.) were used to measure airborne concentrations of benzene using benzene-specific CMS chips with measuring ranges of 0.2–10 and 10–250 ppm. The UltraRAE3000 and the CMS were used to take quantitative spot measurements of benzene in the headspace of tanks, atop the flowback and production tanks (outside of thief hatches), at the tops of ladders, and under shade tents used as the workers' break or rest area.

Sampling trains (pumps, tubing, and sample media) were calibrated on site, before and after sampling, using a BIOS Dry-Cal Defender 520 and 530 airflow calibrators (BIOS International, Butler, NJ). Workers reported that, during the site visits, activities were representative of typical flowback operations.

Biological monitoring (urine) was conducted pre-and post-shift each day using a study design consistent with previous NIOSH research using urine for exposure assessments.(18) Twelve worker volunteers provided urine specimens along with wearing PBZ samplers on one or more days of sampling. Samples were stored on ice until transport to the laboratory.

TABLE II. Full-Shift, Personal Breathing Zone Benzene Samples, TWA

Site #s, Basin	n	Benzene (ppm)[A]	Job Titles[B]
1–2 Piceance, Colorado	13	0.007–0.59	LFT, FT, PT, WT
3 DJ/Niobrara Colorado	4	0.11–0.17	FT
4–5 Piceance,Colorado	14	0.02–0.50	LFT, FT, PT, PW
6 Jonah, Wyoming	4	0.004–0.02	FT

[A] Limit of detection = 0.4 μg, limit of quantification = 1.5 μg, minimum detectable concentration = 0.002 ppm, minimum quantifiable concentration = 0.007 ppm.
[B] LFT = Lead Flowback Tech, FT = Flowback Tech, PT = Production Tech, PW = Production Watch, WT = Water Tech.

A benzene metabolite in urine, S-phenyl mercapturic acid (s-PMA) normalized to creatinine (to account for kidney function and worker hydration), was used as a marker for benzene uptake or "dose." Urinary s-PMA is a sensitive and specific biomarker for benzene exposures utilized in petrochemical operations.(19) Urinary s-PMA was measured using high-performance liquid chromatography-mass spectrometry/mass spectrometry (HPLC-MS/MS). The results were compared against the ACGIH Biological Exposure Index (BEI) of 25 μg s-PMA/g creatinine.(20) The analytical laboratory used 5 μg s-PMA/mL as the lowest calibrator in the assay, which results in a reporting limit of approximately 3 μg s-PMA/g creatinine when samples are corrected for creatinine. Biological monitoring provides information regarding the total dose received from all routes of exposure, including dermal exposure.

Because some quantity of quartz-containing sand from the proppant injected during hydraulic fracturing flows back with the water and hydrocarbons, respirable particulates and crystalline silica were simultaneously collected using BGI GK 2.69 cyclones (BGI, Waltham, Mass.) and SKC XR-5000 personal sampling pumps (SKC Inc. Eighty Four, Pa.). Sampling trains were calibrated to a flow rate of 4.2 liters per min (LPM). Samples were analyzed gravimetrically, according to NIOSH Method 0600 (respirable particulates, not otherwise regulated), and by X-ray diffraction, according to NIOSH Method 7500 for the presence of crystalline silica.

Glutaraldehyde can be used as a biocide during hydraulic fracturing. PBZ samples for glutaraldehyde were collected using Chem Express TraceAir (high sampling rate) passive aldehyde badges. Samples were analyzed using HPLC (Assay Technologies, Livermore, Calif.) with ultraviolet detection using a modified NIOSH Method 2532. Area samples were located at approximately breathing zone height under worker sun shade tents adjacent to flowback tanks.

Alcohols (methanol and propargyl) are sometimes used as scale and corrosion inhibitors in hydraulic fracturing fluids. Methanol samples were collected using SKC Pocket Pumps (SKC Inc. Eighty Four, Pa.) or Gilian low-flow personal sampling pumps (Gilian Instruments, St. Petersburg, Fla.) and SKC silica gel sorbent tubes (100/50 mg; SKC Inc. Eighty Four, Pa.) with sampling trains calibrated at a nominal flow rate of approximately 20 cc/min. Samples were analyzed according to NIOSH Method 2000 for methanol. Samples for propargyl alcohol were collected using similar low-flow personal sampling pumps (Sigma-Aldrich, St. Louis, Mo.), but Anasorb 747 sorbent tubes treated with hydrobromic acid were used as the collection media. Sampling trains were calibrated to a nominal flow rate of 50 cc/min. Chemical analysis was conducted according to the OSHA Method 97 using gas chromatography/electron capture detection.

TABLE III. Benzene PBZ Arithmetic Means (TWAs) for Workers Gauging and Not-Gauging Tanks Compared to a 12-hr adjusted TLV®[A]

Date	Basin	Gauging Tanks Benzene TWA (ppm) mean, [sd] (n)	Exceeded 12hr TLV[A]	Not-Gauging Tanks Benzene TWA (ppm) mean, [sd] (n)	Exceeded 12hr TLV[A]
6/12/2013	Piceance, Colorado	0.30,[0.07] (2)	Yes	0.05,[0.03] (3)	No
6/13/2013	Piceance, Colorado	0.32, [0.17] (3)	Yes	0.05,[0.04] (5)	No
6/26/2013	DJ/Niobrara Colorado	0.11,[0.005] (2)[B]	No	Only 2 workers on location	
6/27/2013	DJ/Niobrara Colorado	0.15,[0.015] (2)[B]	No	Only 2 workers on location	
8/7/2013	Piceance, Colorado	0.37,[0.11] (3)	Yes	0.05,[0.01] (4)	No
8/8/2013	Piceance, Colorado	0.31,[0.11](3)	Yes	0.04,[0.02] (4)	No
8/25/2013	Jonah, Wyoming	0.02 (1)	No	0.006 (1)	No
8/26/2013	Jonah, Wyoming	0.01 (1)	No	0.004 (1)	No

[A] Correction factor of 0.5 was used to adjust benzene TLV-TWA using the formula: 0.5 ppm × [8/12 × (24 − 12)/16] = 0.25 ppm for samples greater than 8 hr.
[B] Workers shared periodic tank gauging tasks.

TABLE IV. Task-based Personal Breathing Zone (PBZ) Benzene Airborne Concentrations

Type, Location, Time (if available) (ppm)	Concentration
6/12/2013. Site 1. PBZ, short-term (24 min): flowback tech during pump down. Worker atop tanks, all hatches were open.	1.7[A]
6/13/2013 Site 1. PBZ, short-term (3 min): production tech gauging 500 barrel production tank.	2.0[B]
6/13/2013 Site 1. PBZ, short-term (30 min): water management tech on water tank	2.0[A]
6/13/2013 Site 2. PBZ, short-term (7 min): tech gauging.	1.95[B,D]
6/13/2013 Site 2. PBZ, short-term (15 min): tech gauging.	1.79[B]
6/13/2013 Site 2. PBZ, short-term (17 min): tech not gauging.	ND[B]
6/26/2013, PBZ, short-term (7 min): flowback tech changing out a choke.	7.45[c]
8/7/2013 PBZ, short-term (5 min): water tank worker on ladder next to open hatch	0.53[c]
8/27/2013 PBZ, Short-term (30 min): water hauler	0.05[B]
8/27/2013 PBZ, Short-term (2.5 min): treatment operator changing filter media, water treatment	3(*peak*); 0.2[c]

[A] Dräger Chip Measurement System.
[B] Charcoal tube, NMAM 1501.
[C] RAE systems Ultra RAE 3000 w/ benzene separator tube.
[D] When adjusted to a 15-min TWA benzene concentration was 0.91 ppm.

TABLE V. Airborne Area Benzene Measurements Using Direct-reading Instruments[A] Sites 1 and 2

Type, Location, Time (if available) (ppm)	Concentration
Area, headspace, front hatch of flowback tank, 1300 hr	209
Area, ladder of flowback tank, 18" from front hatch, worker gauged tank from this location, 1305 hr	149
Area, headspace, hatch of 500 barrel production tank 1056 hr	172
Area, front hatch of closed flowback tank,	2.56
Area, underneath workers' break tent	1.58
Area, workers' break tent	0.46
Area, next to area air samples east of NIOSH vehicle	0.2
Area, front hatch of a closed flowback tank, 0922 hr	52
Area, front hatch of same closed flowback tank, 0927 hr	1
Area, front hatch of same closed flowback tank, 0932 hr	2.5
Area, front hatch of same closed flowback tank, 1345 hr	12.5
Area, front hatch of same closed flowback tank, 1425 hr	5.3
Area, on top of flowback tank, 0831 hr	9.5
Area, workers' break tent, 0826 hr	< 0.2

[A] RAE systems Ultra RAE 3000 w/ benzene separator tube, Dräger Chip Measurement System.

TABLE VI. Airborne Area Benzene, Direct-reading Instruments[A] Site 3

Type, Location, and Time of Collection (ppm)	Concentration
Area, directly downwind of flowbank tanks, 1200 hr	4.9
Area, workers' break tent, 1214 hr	5.75 and 4.10 (two consecutive samples)
Area, workers' break tent, 1554 hr	1.25 and 0.55 (two consecutive samples)
Area, corner of flowback tank, 1345 hr	10
Area, near wellhead on XK90 equipment, 1552 hr	0.45 and 0.40 (two consecutive samples)
Area, near sand separator and worker station, 0740hr	0.4 and 0.45 (two consecutive samples)
Area, headspace flowback tank, 0750 hr	40.5

[A] RAE systems Ultra RAE 3000 w/ benzene separator tube, Dräger Chip Measurement System.

TABLE VII. Airborne Area Benzene, Direct-reading Instruments ^{A} Sites 4–5

Type, Location, and Time of Collection (ppm)	Concentration
Area, directly downwind of production tank, on catwalk 1100 hr	5.2
Area, headspace of production tank, 1105 hr	>250
Area, workers' break tent, 1313 hr	< 0.2
Area, entrance to separator, 1320 hr	< 0.2
Area, flowback tank headspace, with controls 1202 hr	3.3
Area, water tank headspace 1210 hr	36
Area, worker tent, 1053 hr	2.5
Area, near separator, workers working on manifold 1054 hr	2.2
Area, headspace of production tank, 1605 hr	>250
Area, production tank catwalk, upwind of open hatch, 1608 hr	5
Area, production tank catwalk, downwind of open hatch, 1612 hr	40

^{A}RAE systems Ultra RAE 3000 w/ benzene separator tube and Dräger Chip Measurement System.

Samples for the vapor and particulate phases of PAHs were collected using SKC XR-5000 personal sampling pumps and XAD-2 sorbent tubes and polytetrafluoroethylene (PTFE) filters (SKC Inc. Eighty Four, Pa.). Sampling trains were calibrated to a flow rate of 2 LPM. Samples were desorbed and analyzed according to NIOSH Method 5506.

RESULTS

Full-shift (typically 12-hr) exposure assessments were conducted during normal operations at six flowback sites in two states identified benzene as the primary VOC exposure hazard for workers. Table II lists the sites visited, numbers of samples collected, range of benzene TWA measurements, and worker job titles. Inhalation risks for benzene exposures appear to be associated with time spent working in close proximity to hydrocarbon sources (i.e., around hatches on flowback and production tanks).

TABLE VIII. Airborne Benzene, Direct-reading Instruments ^{A} Site 6

Type and Location of Sample (ppm)	Concentration
Area: inlet end of open-top flowbank tank, 10:00 hr	2
Area: Separator shed, pneumatic control box venting inside, 10:50 hr	5
Area: Separator shed, pneumatic control box venting outside, 13:00 hr	<0.2
Area: Top of production tanks, 08:00 hr	30
Area: Near vacuum pump exhaust, water truck, 14:00 hr	2.5

^{A}RAE systems Ultra RAE 3000 w/ benzene separator tube and Dräger Chip Measurement System.

TABLE IX. Task-based, Personal Breathing Zone (PBZ) Airborne Benzene Measurements

Type, Location, Time (if available) (ppm)	Concentration
6/12/2013. Site 1. PBZ, short-term (24 min.): flowback tech during pump down. Worker atop tanks, all hatches were open 1200 hr	1.7_a
6/13/2013 Site 1. PBZ, short-term (3 min.): production tech gauging 500 barrel production tank, 1100 hr	2.0_a
6/13/2013 Site 1. PBZ, short-term (30 min): water management tech on water tank	2.0_a
6/13/2013 Site 2. PBZ, short-term (7 min): tech gauging	1.07_b
6/13/2013 Site 2. PBZ, short-term (15 min.): tech gauging	1.99_b
6/13/2013 Site 2. PBZ, short-term (17 min.):tech not gauging	ND_b
6/26/2013, PBZ, short term (7 min.): flowback tech, changing out a choke	7.45_c
8/7/2013 PBZ, short-term (5 min.): water tank worker on ladder next to open hatch, 1210 hr	0.53_c
8/27/2013 PBZ, Short-term (30 min.): water hauler	0.05_b
8/27/2013 PBZ, Short-term (2.5 min.): treatment operator changing filter media, water treatment, 09:00 hr	3 (peak); 0.2_c

^{A}Dräger Chip Measurement System.
^{B}Charcoal tube NMAM 1501.
^{C}RAE systems Ultra RAE 3000 w/ benzene separator tube.

Arithmetic mean PBZ benzene TWA exposures for workers gauging flowback or production tanks was 0.25 ppm, standard deviation, 0.16 ppm, n = 17. (Table III). Fifteen of the 17 samples met or exceeded the NIOSH REL of 0.1 ppm as a full-shift TWA.(7) Two of the 17 PBZ samples met or exceeded the ACGIH benzene TLV of 0.5 ppm as a full-shift TWA.(16)

Arithmetic mean benzene TWA exposures for flowback, production watch and water management workers who were *not* gauging tanks was 0.04 ppm, standard deviation, 0.03 ppm, n = 18. One of 18 PBZ TWA samples for workers not gauging tanks met the REL as a full-shift TWA. Differences between the arithmetic means of workers who gauged tanks compared to those who did not gauge tanks were statistically significant by Student's t test ($p < 0.01$).

Task-based PBZ samples for benzene collected on flowback technicians who gauged flowback tanks approached and in some cases exceeded the NIOSH STEL for benzene of 1 ppm as a 15-min TWA (Tables IV and IX). In several cases, peak

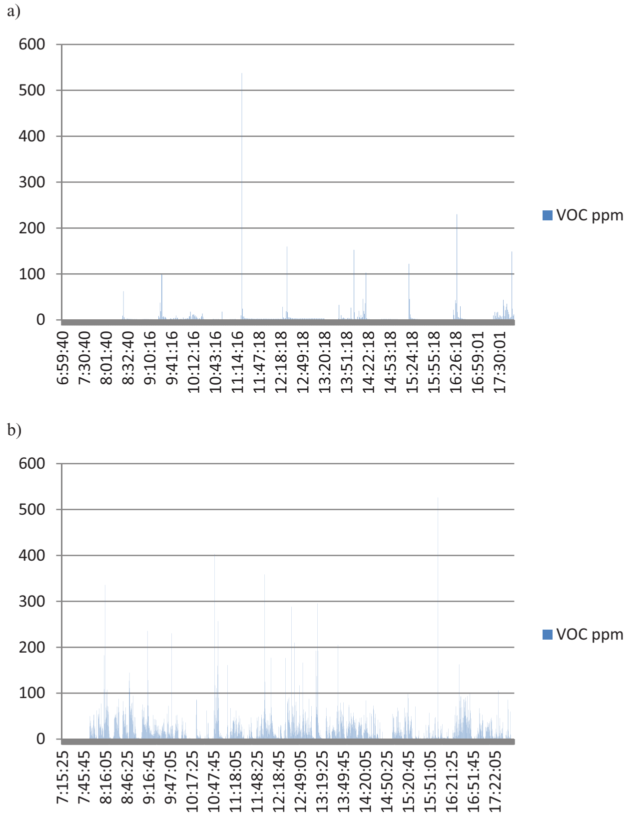

FIGURE 3. a) ToxiRae plot of VOC concentration vs. time for a flowback worker gauging tanks roughly every hour over a full shift. Peak VOC concentration was 538 ppm, minimum concentration was 0 ppm, and the time-weighted average (TWA) for total VOCs (as isobutylene equivalents) was 5.9 ppm. b) ToxiRae plot of VOC concentration vs. time for a flowback worker gauging tanks roughly every half hour over a full shift. Peak VOC concentration was 526 ppm, TWA for total VOCs (as isobutylene equivalents) was 20.2 ppm (minimum instrument resolution, 0.1 ppm). (color figure available online)

benzene concentrations (collected using direct reading instruments) near open tank hatches exceeded 200 ppm (Tables V, and VII). None of the 35 PBZ samples exceeded the OSHA permissible exposure limit (PEL) of 1.0 ppm as a TWA for general industry. (21,22)

Figures 3 and 4 are graphical plots of VOC concentration versus time for workers gauging flowback tanks and working immediately downwind of flowback tanks while plug drilling was occurring. The plots depict the variability of hydrocarbon emissions (and exposure potential) during these activities.

Respirable crystalline silica (alpha quartz) was detected on four of five PBZ samples. Four samples were below all OELs. A fifth sample was determined invalid because of contamination with quartz-containing soil. The worker wearing the sample reported he stumbled and fell on the ground and quartz-containing soil is presumed to have been aspirated into the cyclone and onto the filter. The presence of quartz is believed to be from soil, not quartz from proppant in flowback fluids.

Seventeen samples for glutaraldehyde (5 PBZ and 12 area) were collected. All results were below the limit of detection with the exception of one PBZ sample, which was calculated to have a trace concentration (between the minimum detectable concentration and minimum quantifiable concentration) of 0.010 milligrams per cubic meter (mg/m^3) of air sampled. The NIOSH REL for glutaraldehyde is 0.8 mg/m^3 as a ceiling limit.(7)

Thirteen area air samples for methanol were collected under worker sun shades and around flowback tanks where workers were commonly present. All sample results were below the LOD. The NIOSH REL for methanol is 200 ppm as a full-shift TWA.(7) Sixteen area air samples for propargyl alcohol were collected under worker sun shade tents and around flowback tanks. All but one (0.01 mg/m^3 or 0.0043 ppm) sample were reported as non-detected. The ACGIH references a TLV of 1 ppm as a TWA for propargyl alcohol.(16)

Four PBZ air samples for PAHs were collected on flowback technicians. Sixteen area air samples were collected in and around flowback tanks where workers were commonly present or working. Naphthalene was the most commonly detected PAH, frequently detected at part per billion concentrations, well below the NIOSH REL of 10 ppm as a TWA.

The arithmetic mean of s-PMA in urine from workers performing tank gauging was 6.5 micrograms per gram (μg/g) creatinine; the standard deviation was 5.5 μg/g. The arithmetic mean of s-PMA in urine from those workers *not* gauging tanks was 3.1 μg/g creatinine; the standard deviation was 3.7 μg/g. Despite limited sample numbers and no correction for smoking, worker urine s-PMA was moderately correlated ($r = 0.56$) with full-shift PBZ benzene TWA concentrations. While detectable concentrations of s-PMA were measurable in the urine of workers, none of the samples exceeded the ACGIH BEI of s-PMA of 25 μg/g creatinine. The BEI represents the concentration of a measurable metabolite most likely to be observed in specimens collected from healthy workers exposed to benzene at the ACGIH TLV. The method is sufficiently sensitive to detect s-PMA for benzene inhalation exposures that fall between the NIOSH REL and the ACGIH TLV in a range of 0.1–0.5 ppm as TWAs. However, confounders (smoking and other non-workplace benzene exposures) limit using urinary s-PMA to evaluate individual worker PBZ benzene exposures below 0.3 ppm.

Hydrocarbon vapors generated from dissolved gases in flowback fluids can be extremely flammable, depending on concentration, temperature, and pressure. Direct reading instruments identified instances of short term concentrations of total hydrocarbon vapor as high as 40% of the LEL. These measurements were made adjacent to separators and flowback tanks; typically, concentrations of 10–20% of the LEL are considered a risk for fires or explosions and are typical settings for direct reading personal and fixed flammable gas monitors.

On all locations, workers were observed wearing PPE, including flame-resistant clothing, steel toe boots, safety glasses and hard hat and, occasionally, fall protection, riggers gloves,

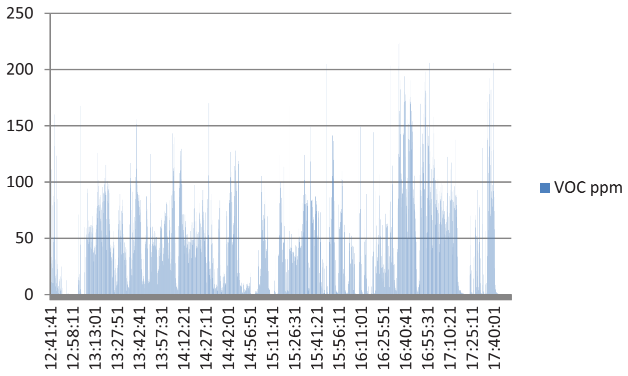

FIGURE 4. ToxiRae plot of VOC concentration vs. time for a flowback worker over a 5-hr period while plugs were drilled. Peak concentration was 281 ppm, minimum concentration was 0 ppm, and the TWA from 12:40 a.m.–5:36 p.m. was 37.9 ppm. (color figure available online)

and hearing protection, depending on work tasks. None of the flowback technicians, production watch technicians, or water management technicians was observed wearing respirators, nor were they clean-shaven (necessary if respirators had been used). At one site, a clean shaven lease operator wore a full-face respirator with organic cartridges while gauging production tanks and performing other activities having potential for VOC exposures.

CONCLUSION

The study was designed and conducted to determine whether risks for chemical exposures are present during flowback operations, specifically, work around flowback and production tanks and gauging fluid levels in tanks. In some cases, airborne concentrations of benzene were determined to exceed the NIOSH REL and STEL concentrations and, in a few instances, the ACGIH TLV when workers performed work tasks near a point source for benzene emissions. Benzene is naturally present in flowback fluids and the time spent working around flowback and production tanks (particularly when gauging tanks) appears to be the primary risk factor for inhalation exposures.

Real-time measurements of airborne benzene at a variety of point sources (e.g., headspace or immediately outside of tank hatches) and at locations where workers were commonly present on the well sites reached concentrations that, depending on the length of exposure, potentially pose health risks for workers considering the NIOSH and ACGIH criteria. Some TWA PBZ concentrations of benzene were an order of magnitude greater for flowback technicians who gauged tanks, compared to samples collected on workers who were not gauging tanks. Some flowback technicians who were not actively gauging (but in the near vicinity of sources such as flowback tanks) had full-shift PBZ benzene exposures that met or exceeded the NIOSH REL. Based on these initial studies, opening thief hatches and gauging tanks is the primary task-based activity that increases inhalation exposure risks; additional exposures may occur due to fugitive emissions from equipment in other areas in the flowback process (e.g., chokes, separators, piping, and valves), particularly when performing maintenance on these items.

These studies found that, during flowback, airborne concentrations of hydrocarbons, in general, and benzene, specifically, fluctuate greatly. Factors believed to influence the concentrations of VOCs include temperature and pressure of the process liquids and reservoir hydrocarbon conditions. There are likely to be other influencing factors yet to be determined. Because hydrocarbons and benzene concentrations have such dynamic spatial and temporal variability (as described in Figures 3 and 4 and listed in Tables IV–IX , the unpredictability of exposure risks warrants conservative approaches to protecting workers.

Worker exposures to other chemicals evaluated during this limited evaluation (glutaraldehyde, PAHs, methanol, propargyl alcohol, and respirable quartz) did not exceed any applicable OELs.

Combustible gas measurements indicate that hydrocarbon emissions during flowback operations have the potential to generate flammable and explosive concentrations, and this appears to be a temporal and spatial function of the volume of hydrocarbon emissions and locations when gases are measured.

Based on this preliminary field research, development and use of effective engineering and administrative controls are warranted to limit worker exposures to benzene and control flammable hydrocarbon emissions during flowback operations. Health and safety professionals at flowback sites should evaluate operations to determine the potential for worker exposures (especially to benzene) and implement controls as necessary to minimize exposures and protect workers. A combination of engineering, administrative, worker training, and PPE controls is recommended to minimize workplace exposures to flowback and production tank chemicals. Companies that conduct flowback operations should investigate control options that include:

- Developing alternative tank gauging procedures to limit exposures to hydrocarbon vapors emitted from hatches on the tops of tanks, and adapting flowback and production tank sampling ports with vents that exhaust away from the worker, or eliminating the use of hatches as the primary access point.
- Providing worker training to ensure flowback technicians understand the hazards of exposure to benzene and other hydrocarbons, the importance of monitoring atmospheric conditions for LEL concentrations and how to apply work practices that limit their exposures to chemicals and the potential for fires and explosions. Training should include the use, inspection, and maintenance of PPE.
- Limiting the time personnel spend in proximity to hydrocarbon sources and establish a controlled perimeter around flowback tanks. Require that any portable tents or sunshades remain out of, and upwind of, the controlled area. Use of

wind socks or vanes can help visually identify prevailing wind direction.

- Using calibrated personal flammable gas monitors with alarms in areas near flowback tanks and tank batteries during well control activities, drilling plugs, and snubbing. It is important to verify that workers understand how to use such monitors, respond to alarms, and use appropriate correction factors for mixed gas atmospheres.
- Using appropriate respiratory protection as an interim measure until engineering and administrative controls are implemented. Employers should consult with an occupational safety and health professional and/or certified industrial hygienist to determine the appropriate respirator best suited for the application and establish a comprehensive respiratory protection program that adheres to OSHA regulations 29 *CFR* 1910.134.
- Using appropriate hand protection to prevent skin exposure to liquid hydrocarbons. Skin protection from sources of benzene (and some other aromatic hydrocarbons) typically requires glove materials such as Teflon or Viton for protection against benzene permeation. Companies should consult an occupational safety and health professional or certified industrial hygienist to determine the most appropriate glove material suitable for specific work activities.
- Monitoring workers to determine risks for benzene exposures through PBZ and real-time air sampling for activities involving exposure to flowback fluids, including gauging of flowback and production tanks. Documenting exposures can verify the need for controls, determine the efficacy of controls that have been implemented, and ensure that the appropriate respiratory protection is used as an interim control until engineering controls can be implemented. Monitoring is also important to identify additional areas where exposures could occur and for informing workers about their exposures.
- Consulting with a physician trained in occupational medicine to ensure medical monitoring programs are implemented where appropriate.

Companies should consult with an occupational safety and health professional trained in industrial hygiene to ensure proper selection of respiratory protection and other PPE, and to develop/implement appropriate sampling strategies to assess worker exposures during flowback operations.

LIMITATIONS AND CONSIDERATIONS

While these study results are believed to be representative of typical flowback operations and working conditions during contemporary land-based oil and gas extraction, the sample size is relatively small and only six sites in two states were visited. Because of the dynamic nature of flowback operations, these results may not be broadly generalizable to all sites or operations. A larger study incorporating more samples and multiple sites across numerous oil and gas basins could provide greater understanding of exposure risks for benzene and other chemicals during flowback operations, and the relative efficacy of implemented controls.

While various OELs exist for benzene (Table I), the REL is the most conservative and therefore most protective value. Given the considerable variability in benzene exposures seen in this study, we recommend using the NIOSH REL for determining the need to limit worker exposures. A conservative approach is warranted because benzene is a confirmed human carcinogen, there is a potential for flowback workers to experience concomitant exposures to complex, highly variable hydrocarbons mixtures and risks for other exposures (e.g., NORM, diesel particulate, oxides of nitrogen and ozone) which, at the present time, are incompletely documented. Additional, compounding risk factors include extended work shifts (typically 12 hr) and tours of duty involving multiple weeks. Pre-existing health conditions, smoking or use of drugs or alcohol by workers may complicate considerations of health risks and reinforces a conservative approach in controlling worker exposure to flowback emissions.

There are few (if any) systematically conducted and peer-reviewed exposure assessment studies describing the scope and magnitude of chemical risks in modern, unconventional oil and gas extraction workers. As such, occupational health and safety professionals need to anticipate, recognize, evaluate, control and confirm the magnitude of risks (such as benzene) and also newly identified risks (i.e., silica exposures during hydraulic fracturing). Doing this, requires a deliberate, measured and determined approach in application of the art and science of industrial hygiene toward protecting a dynamic and growing global workforce.

DISCLAIMER

The findings and conclusions in this report are those of the author(s) and do not necessarily represent the views of the National Institute for Occupational Safety and Health. Mention of company names and/or products does not constitute endorsement by NIOSH. This article not subject to U.S. Copyright law.

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