



WHEN THE WIND BLOWS

TRACKING TOXIC CHEMICALS IN GAS FIELDS
AND IMPACTED COMMUNITIES



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Cover Photos

TOP: Gas well pads, farms and homes in Pavillion.

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BOTTOM LEFT: Study participant samples the air for VOC emissions at a produced water tank “thief hatch.”

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BOTTOM RIGHT: Study participant using a summa canister to grab an air sample at a gas separator in Pavillion.

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This report is a collaborative effort of Coming Clean and the partner organizations and individuals listed on page 5. Coming Clean is a national collaborative of diverse organizations and experts working to achieve safe chemical and clean energy solutions that protect public health and the environment, allow sustainable economies to flourish, and secure justice for all.

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EXECUTIVE SUMMARY



John Fenton points to Pavillion farms and gas development sites.

In 2014 a team of residents from the area of Pavillion, Wyoming, science and health experts, and environmental health groups, collaborated on a project to test the air and residents' bodies for chemicals known to be linked to oil and gas production. This is the first study which combines environmental sampling with the monitoring of body tissues or fluids (biomonitoring¹) of community members in very close proximity to gas production equipment and activities.

We began this research because the people living and working in the Pavillion area reported health conditions they fear are related to toxic chemicals from the gas wells they live with. Raw, unprocessed natural gas, such as that

extracted in the Pavillion area, is primarily methane,² a potent greenhouse gas that is linked to climate change.

“IF YOUR DRINKING WATER IS CONTAMINATED with chemicals, you might be able to make do with another source. But if your air is toxic, you can't choose to breathe somewhere else....”

— *Deb Thomas, ShaleTest*

1 Biomonitoring is the identification of levels of chemical substances or their breakdown product (metabolites) in body tissues or fluids.

2 Gilman, J B, Lerner, B M, Kuster, W C, de Gouw, J A (2013). Source: Signature of Volatile Organic Compounds from Oil and Natural Gas Operations in Northeastern Colorado; Environ Sci Technol. 2013 Feb 5;47(3):1297-305. doi: 10.1021/es304119a. Epub 2013 Jan 25. <http://www.ncbi.nlm.nih.gov/pubmed/23316938>.

But gas is also comprised of other volatile organic compounds (VOCs). The purpose of the project was to evaluate the extent to which VOCs are present in the air next to and downwind from gas production sites; that people living and working nearby these sites are therefore exposed to air containing VOCs and that we would find evidence of those VOCs in their bodies.

VOCs are oil and gas by-products, which evaporate easily and are commonly released into the air near oil and gas sites as well as found in many consumer products; they are associated with a range of different immediate and long-term health problems, including damage to the liver, kidney and central nervous system, with some VOCs considered to be carcinogens.

The project had three distinct elements: 1) develop methods for combined air monitoring and biomonitoring for toxic chemical emissions at oil and gas development sites, 2) assess the health and environmental hazards of the chemicals found in air and biomonitoring and 3) provide research and policy recommendations based on the monitoring and hazard assessment data, for the protection of communities and workers from the inherent hazards of oil and gas development.

This study is a follow up to research conducted in 2013–14, in which the group Pavillion Area Concerned Citizens and nineteen other organizations in six states participated in a community air monitoring program, led by the national environmental health organization Coming Clean, to determine which harmful chemicals might be emitted from oil and gas sites. The results were alarming: highly toxic chemicals were present at many sites and levels of some chemicals in the Wyoming air were up to 7,000

times the health based exposure standards set by the United States Environmental Protection Agency (EPA) and the Agency for Toxic Substances and Disease Registry (ATSDR).³ These levels were higher than those found in other states. Data from that air monitoring research was published in the peer reviewed journal *Environmental Health*⁴ and in a report called *Warning Signs: Toxic Pollution Identified at Oil and Gas Sites*.⁵

Through this research project, we designed and tested methods for environmental monitoring and exposure assessment in people living near oil and gas fields. We did this by using a variety of air monitoring tools with the capacity to test for VOCs, which are a large group of carbon-based chemicals that easily evaporate at room temperature. VOCs can be both naturally occurring and man-made. For example, many chemicals manufactured by the petrochemical industry are VOCs; they are also associated with oil and gas production sites. VOCs are found in numerous household products, so for our study participants were given a list of products and activities (including exposure to cigarette smoke) that might be alternative sources of VOCs to avoid during the sampling, so that any VOCs found in their personal air samples, urine or blood samples, might be more directly attributable to their proximity to gas well pads than to household products and activities.

Among the VOCs we tested, we looked for a set of VOCs called the BTEX (Benzene, Toluene, Ethylbenzene, and Xylene) chemicals, which are present in the mixture of hydrocarbon liquids in raw natural gas produced from many natural gas fields, known as condensate.⁶ BTEX chemicals are frequently identified and measured at oil and gas production sites.⁷ During the week that we col-

3 Pollutant levels were compared to exposure standards set by the federal Agency for Toxic Substances and Disease Registry (ATSDR), for health effects other than cancer, and the EPA's Integrated Risk Information System (IRIS) for cancer. See endnote 16 in Coming Clean and Global Community Monitor (2014).

4 Macey, G P, Breech, R, Charnaik, M, Cox, C, Larson, D, Thomas, D, Carpenter, D O (2014). Air Concentrations of Volatile Compounds Near Oil and Gas Production: A Community-based Exploratory Study. *Environmental Health* 201413:82, DOI: 10.1186/1476-069X-13-82. © Macey et al.; licensee BioMed Central Ltd. 2014, Published: 30 October 2014. <http://ebjournal.biomedcentral.com/articles/10.1186/1476-069X-13-82>.

5 Coming Clean and Global Community Monitor (2014). Warning Signs: Toxic Pollution Identified at Oil and Gas Sites. Results from Community Air Monitoring Reveal Chemicals Linked to Health Hazards, October 2014. <http://comingcleaninc.org/whats-new/warning-signs>.

6 Natural-gas condensate is a low-density mixture of hydrocarbon liquids that are present as gaseous components in raw natural gas. Some gas species within the raw natural gas will condense to a liquid state if the temperature is reduced to below the hydrocarbon dew point temperature at a set pressure. For further information see: CONCAWE, Environmental science for the refining industry: https://www.concawe.eu/uploads/files/Additives_in_imported_Natural_Gas_Condensates-2008-04062-01-E.pdf. Impurities such as BTEX chemicals are present in the condensate portion of natural gas; it is not refined out and remains in the natural gas distributed to gas fired facilities and for home use. BTEX chemicals are also contained in oil condensate and continue to be present in crude oil refined materials.

7 Moore, C W, Zielinska, B, Jackson, R B, (2013). Air Impacts of Shale Gas Extraction and Distribution, Desert Research Institute Division of Atmospheric Science, Reno, NV; Duke University, Nicholas School of the Environment and Center on Global Change, Durham, NC 27708. http://sites.nationalacademies.org/cs/groups/dbassesite/documents/webpage/dbasse_083226.pdf and presentation by Chris Moore May 30, 2013. http://sites.nationalacademies.org/cs/groups/dbassesite/documents/webpage/dbasse_083402.pdf.

VOCs ARE OIL AND GAS BY-PRODUCTS which are associated with a range of different immediate and long-term health problems, including damage to the liver, kidney and central nervous system, with some VOCs considered to be carcinogens.

lected air samples, we also took urine samples from people who live and work in close proximity to the gas well pads where air samples were taken.

We then used the GreenScreen® for Safer Chemicals (GreenScreen)⁸ method to identify the inherent hazards of the chemicals found in the air emissions and in the bodies of study participants. GreenScreen is a globally recognized chemical hazard assessment tool that companies, governments, scientists and health advocates use to identify the potential environmental and human health impacts of chemicals.

The results are a new data set which combines air monitoring, biomonitoring and hazard assessment findings. The new data set provides a more comprehensive understanding of what Pavillion area residents are breathing and what health outcomes might result from these chemical exposures. Specific results from multiple air monitoring tools, the biomonitoring data collected from eleven community residents, and GreenScreen chemical hazard assessments show:

- Toxic chemicals present in the air near Pavillion, WY, including BTEX chemicals, are consistent with those associated with oil and gas production and its associated infrastructure. This finding is consistent with other air monitoring findings from the Pavillion area as well as additional oil and gas production sites in Wyoming and in the US.⁹
- Hazardous breakdown products of BTEX chemicals and other VOCs associated oil and gas production are

also present in the bodies of the Pavillion area residents who participated in this study.

- Eight chemicals that were detected both in the air near Pavillion and in the bodies of project participants are linked to chronic diseases such as cancer or other illnesses including reproductive or developmental disorders and to health problems such as respiratory difficulties, headaches, nosebleeds, skin rashes, and depression.
- The results from both human and air monitoring indicate that study participants during the week of monitoring were intermittently exposed to complex mixtures of chemical substances associated with oil and gas production.
- Levels of some hazardous VOCs in air both near the gas production sites and that study participants were breathing exceeded one or more Environmental Screening Level (ESLs), which are the levels of toxic substances that public health agencies and environmental regulators have determined as warning signs for risk to human health.¹⁰
- Hazardous breakdown products of VOCs were present in the urine of study participants at much higher levels than those found in the general population, with one example up to ten times higher.

Our aim is that the data and protocols established in this study be used to:

- inform and engage Pavillion area residents and community members who live near oil and gas development throughout the US and internationally in decisions that affect their health;
- encourage legislators and government regulatory agencies to make precautionary decisions that protect the public from exposure to toxic oil and gas-related chemicals and from inherently hazardous oil and gas production;
- inspire further research by other community scientists and researchers, who could use, adapt and improve the study protocol to continue to monitor exposure to chemicals associated with oil and gas production and better understand their impact on worker and public health;

8 GreenScreen® for Safer Chemicals website: <http://www.greenscreenchemicals.org>.

9 Macey et.al. (2014). op.cit. and Coming Clean and Global Community Monitor (2014). op.cit.

10 ESLs are based on data concerning health effects, the potential for odors to be a nuisance, and effects on vegetation.... If predicted ambient levels of constituents in air exceed the screening levels, it does not necessarily indicate a problem but rather triggers a review in more depth. Both short- and long-term ESLs are listed on the ESL List. "Short-term" generally indicates a one-hour averaging period.... "Long-term" indicates an annual averaging period. <http://www.tceq.state.tx.us/toxicology/esl/ESLMain.html>.

“**BASED ON THESE RESULTS** and those from the increasing number of studies in areas under development, gas production is proven to be an inherently hazardous process. Residents are exposed to hazardous chemicals throughout exploration and development. Gas production is not a safe or clean source of energy.” — *Deb Thomas*

- reinforce our long term goal of transitioning our economy to energy sources that will not harm local communities and the environment.

Based on the monitoring research findings and the GreenScreen hazard assessment results, we recommend the following:

- Encourage further biomonitoring research and use results to effectively prevent exposure.
- Investigate the harmful impacts of cumulative exposure to multiple chemicals and how their toxicity may increase when they interact in mixtures, especially chemicals with endocrine disrupting effects, which may act at low levels.
- Implement precautionary regulations, ensure disclosure and transparency.
- Promote clean renewable energy sources and stop promoting natural gas as “clean” and “safe.”
- Provide ongoing monitoring, health evaluation and site remediation to protect people already affected by oil and gas production.

CHAPTER ONE INTRODUCTION

WELCOME TO PAVILLION

Pavillion is a small, rural ranching community situated in north central Wyoming. The town is home to around 240 residents, with approximately 200 more people living in the area east of Pavillion, in a community of small family farms and ranches that primarily produce alfalfa, hay and cattle. Although gas exploration began here in the 1950s, the Pavillion area has seen substantial increases in development over the last 10–20 years. As the industry increased the number of gas wells in the Pavillion/Muddy Ridge field, this development has expanded onto farms and encroached closer to homes. The field currently consists of approximately 169 active vertical gas production wells and their associated infrastructure (see Figure 1, Pavillion area map of gas wells and residences).

Although the Pavillion/Muddy Ridge field is comprised of conventional vertical wells, other unconventional processes including hydraulic fracturing have been used to stimulate gas production.^{11,12} Hydraulic fracturing entails the use of a large number of chemicals in the drilling process, many of which have been identified as substances of high hazard to both human health and the environment (see Box 4). However, the predominant methods of gas production used in the Pavillion gas field are conventional which also involves the release of hazardous chemicals inherent to gas production.

Pavillion area residents have lived with gas development for decades. Many residents experience health problems,

which they believe are linked to toxic chemical emissions associated with the fossil fuel extraction, processing and waste. These health symptoms include headaches, asthma and other respiratory illnesses, bloody noses, kidney problems, loss of smell and taste, cancer and cognitive disorders.¹³ After more than ten years of asking the State of Wyoming and the operating companies to investigate troubling changes in their water wells and receiving inadequate answers, area residents turned to the Environmental Protection Agency (EPA) for help.

In early 2008, the EPA conducted site visits in the Pavillion area and began an official investigation into residents' concerns in September.¹⁴ Their draft report, "Investigation of Groundwater Contamination near Pavillion, Wyoming,"¹⁵ released in 2011, linked the contamination of groundwater with benzene, methane and other hydrocarbons to oil and gas development in the Pavillion area. Also in 2011, the Wyoming Department of Environmental Quality (WDEQ) placed a mobile air monitor to determine ambient air quality near the Pavillion gas field. The monitor measured ozone, nitrogen oxides (NO_x), methane and particulate matter. Non-methane volatile organic compounds (VOCs) were included in the WDEQ's data, and although the cumulative amounts were measured, the monitor did not identify the air concentrations of specific VOCs being emitted in the densely developed gas field, which is in the farm fields where people work and close to homes. Even though residents requested that the State conduct additional monitoring in these vulnerable areas, they were refused, despite the fact

11 Conventional gas drilling technique: reserves of gas are easily accessible using vertical drilling. Unconventional drilling technique: the gas is trapped in layers accessible only by horizontal drilling. For more information see: UK Houses of Parliament. Unconventional gas, Number 374 April 2011. www.parliament.uk/documents/post/postpn374-unconventional-gas.pdf. "Both conventional and unconventional oil and gas operations involve heavy industrial processes, which by definition release a variety of health-harming pollutants." https://www.earthworksaction.org/library/detail/community_air_monitoring_of_oil_and_gas_pollution_a_survey_of_issues_and_te#.V09L8uT5OIV.

12 The *LA Times* reports that vertical fracking occurred around 2001. See SourceWatch (2016), Wyoming and Fracking, last modified on 15 February 2016, at 04:21. http://www.sourcewatch.org/index.php/Wyoming_and_fracking.

13 Macey et.al. (2014), op.cit. and Coming Clean and Global Community Monitor (2014), op.cit. and Agency for Toxic Substances and Disease Registry (ATSDR); Toxicological profile. <http://www.atsdr.cdc.gov/toxprofiles>.

14 September 2008, under authority of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA).

JOHN FENTON, WHO FARMS IN THE PAVILLION AREA, EXPLAINS:

“My wife’s family has been here for over 40 years. When I first came to the farm there were two gas wells on it. Over the next 15 years, 22 more were drilled. In 2006, we began to recognize that much of the water in our area is contaminated and that toxic air emissions are affecting our health. Our family has experienced phantom odors, rashes, hair loss, respiratory conditions, neurological problems, epileptic seizures, cancer, and huge hits to how we think and reason—our cognitive skills. The biomonitoring project was an opportunity to find out if the chemicals we know are in the air, are also in our bodies.”

that local people were increasingly concerned that their health symptoms were due to the toxic chemicals in the air.

In 2012, Pavillion Area Concerned Citizens was one of 20 organizations in six states that participated in a community air monitoring program with other local and national partners, led by the national environmental health organization Coming Clean, to determine which harmful chemicals, including VOCs, might be emitted from the oil and gas sites. The results¹⁶ were alarming: highly toxic chemicals, including BTEX chemicals, were present in the Wyoming air, some at levels up to 7,000 times the health based exposure standards set by the EPA and ATSDR.¹⁷

It is because of this previous air monitoring by the community in Pavillion, along with the groundwater contamination investigation by the EPA and health issues experienced by residents, that in 2014 Coming Clean began coordinating an air and biomonitoring study in the Pavillion area. In light of the failure by both the State and Federal authorities to perform more comprehensive monitoring, community members wanted to participate in this study in order to get answers to their questions about which chemicals they are breathing and to explore current technologies that could measure the levels of those chemicals in their bodies.

PURPOSE OF THE PROJECT

The purpose of the project was to evaluate the extent to which VOCs are present in the air next to gas wells and downwind; that people living and working nearby are therefore breathing air which contains VOCs; and that VOCs are also found in their bodies. VOCs are associated with a range of different immediate and long-term health problems, including damage to the liver, kidney and central nervous system, with some VOCs considered to be carcinogens.

The project had three distinct elements: 1) develop methods for combined air monitoring and biomonitoring for toxic chemical emissions at oil and gas development sites, 2) assess the health and environmental hazards of the chemicals found in air and biomonitoring and 3) provide research and policy recommendations based on the monitoring and hazard assessment data, for the protection of communities and workers from the inherent hazards of oil and gas development.

This project is the first study that attempts to combine environmental monitoring samples with biomonitoring samples from community members in very close proximity to gas production equipment and activities. We began

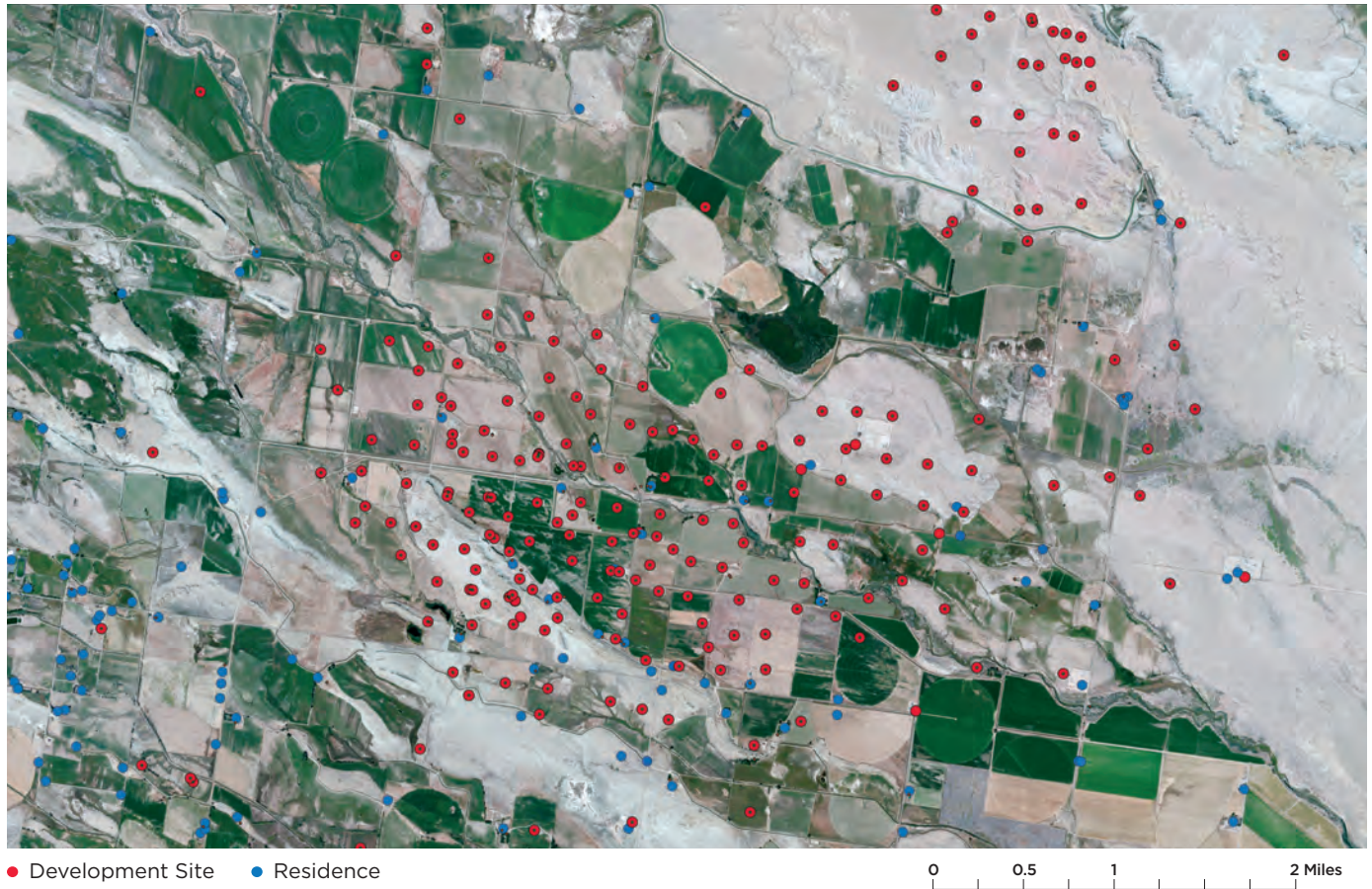
15 DiGiulio, D G, Wilkin R T, Miller C, Oberley G, (2011). Investigation of Groundwater Contamination near Pavillion, Wyoming; US Environmental Protection Agency, National Risk Management Laboratory & Region 8; EPA 600/R-00/000 December 2011. www.epa.gov/ord and https://www.epa.gov/sites/production/files/documents/EPA_ReportOnPavillion_Dec-8-2011.pdf.

16 Macey et.al. (2014) op.cit. and Coming Clean and Global Community Monitor (2014), op.cit.

17 Coming Clean and Global Community Monitor (2014), op.cit.

FIGURE 1

Pavillion Area Map with Residences and Oil and Gas Development Sites



Author: Caitlin Kennedy, Source: Garmin eTrex Venture, Source: National Atlas, Source, Fremont County Assessors Office, Source: EPA Pavillion Area Working Group, Data Frame: NA Equidistant and Equal Area Conic, Geographic Projection: NAD 1983, Date created: Fall 2012 and Winter 2013.

this research because the people living and working in the Pavillion area reported health conditions they fear are related to toxic chemicals from the gas development they live with.

Pavillion area community members hope to use the monitoring results to encourage legislators and regulatory agencies to protect residents' health and to help other communities facing existing or new oil and gas development avoid the health challenges that Pavillion area residents are facing. A precautionary approach to decision making is critical if we are to truly protect public health and the environment. For communities impacted by existing oil and gas development this needs to happen now and it is not too late to prevent future damage in communities which are threatened with new development.

Our aim is that the data and protocols be used to:

- inform and engage Pavillion area residents and community members who live near oil and gas development throughout the U.S. and internationally;
- encourage legislators and government regulatory agencies to make precautionary decisions that protect the public from exposure to toxic oil and gas-related chemicals, and from inherently hazardous oil and gas production;
- inspire further research by other community scientists and researchers, who could use, adapt and improve the study protocol to continue to monitor exposure to chemicals associated with oil and gas production and better understand their impact on worker and public health;

- reinforce our long term goal of transitioning our economy to energy sources that will not harm local communities and the environment.

PROJECT PARTNERS

Coming Clean is an environmental health and justice campaigning collaborative focused on protecting public health and the environment from toxic chemicals and pollution, and promoting clean energy and safe chemical solutions. Coming Clean provided the coordination leadership for this project, with the organizational and individual partners listed below. This report was written by the project leaders at the request of the Pavillion Area Concerned Citizens. Project partners were:

- **Clean Production Action**, a non-profit organization that designs and delivers strategic solutions for green chemicals, sustainable materials and environmentally preferable products, including the GreenScreen® for Safer Chemicals hazard assessment method;
- **Commonweal**, a non-profit environmental health research organization with expertise in biomonitoring as a tool for understanding how individuals and communities are exposed to chemicals;
- Pavillion Area Concerned Citizens, a non-profit organization of people interested in issues including oil and gas development which impact Pavillion, Wyoming area residents;

- **ShaleTest**, a non-profit organization which collects environmental data and provides testing for families and communities that are negatively impacted by oil and gas development;
- Wilma Subra of Subra Company, an award-winning chemist and microbiologist who for more than 30 years has researched the impacts of toxic chemicals on the environment and on public health.

The science team that designed and implemented the study in collaboration with the Pavillion area community included:

- Dr Robert Harrison, Director of Occupational Health Services at the University of California, San Francisco (UCSF);
- Zachary Wettstein, University of California San Francisco Medical Student. Study Assistant Science Advisor;
- Caitlin Kennedy, Master of Science in Public Health in Epidemiology and Environmental Health, Rollins School of Public Health of Emory University;
- Deb Thomas, Director, Shale Test;
- Wilma Subra, Subra Company.

Additional scientific expertise provided by:

- Dr David Brown, Public Health Toxicologist, Southwest Pennsylvania Environmental Health Project;
- Dr Detlev Helmig, INSTAAR Laboratories;
- Mark Chernaik, Science Advisor, Staff Scientist, Environmental Law Alliance Worldwide.

CHAPTER TWO

WHY STUDY VOC EMISSIONS AND HAZARDS?

Raw, unprocessed natural gas, such as that extracted in the Pavillion area, is primarily methane,¹⁸ a potent greenhouse gas that is linked to climate change. But gas is also comprised of other VOCs. Researchers have shown that oil and gas development uses or emits hundreds of chemicals in the VOC family.¹⁹ In our report we are concerned primarily with a family of VOCs called BTEX (Benzene, Toluene, Ethylbenzene, and Xylenes) which are an inherent part of the mixture of natural gas, hydrocarbon gases, water and other compounds that are pumped out of underground reservoirs during gas production, known as gas condensate.²⁰ BTEX chemicals are also known to be hazardous to human health, even at low levels.²¹ One way to assess the potential health hazards of living and working near oil and gas site is to measure the presence of BTEX VOCs in the air and in our bodies.

VOCs are associated with a range of different immediate and long-term health problems, including eye, nose and

throat irritation, headaches, lower cognitive function, loss of coordination and nausea, damage to liver, kidney and central nervous system, and some VOCs are considered to be carcinogens. For example, benzene—a well-studied VOC—is considered by the International Agency for Research on Cancer (IARC) to be a group one carcinogen and can cause leukemia.²² Peer-reviewed research indicates a link between exposure to oil and gas chemicals and negative health effects on people who live and work close to oil and gas development sites.^{23,24} Studies also show elevated levels of preterm birth and lower birth weights in places closest to oil and gas development.²⁵

Non-cancer health effects that are significantly associated with ambient levels of exposure to BTEX chemicals include sperm abnormalities, reduced fetal growth, cardiovascular disease, respiratory dysfunction and asthmas.²⁶ Several hormones may be involved in these health outcomes, suggesting that BTEX chemicals and other VOCs

- 18 Gilman, J B, Lerner, B M, Kuster, W C, de Gouw, J A (2013). Source signature of volatile organic compounds from oil and natural gas operations in northeastern Colorado; *Environ Sci Technol.* 2013 Feb 5; 47(3):1297-305. doi: 10.1021/es304119a. Epub 2013 Jan 25. <http://www.ncbi.nlm.nih.gov/pubmed/23316938>.
- 19 The VOCs emitted will depend on variables such as the specific type of extraction or production activity; stage of production; what specific companies are involved and what chemical “recipe” they use; the company involved; and differences in geologic conditions at different sites (i.e. what chemical mixtures are used according to the type of underground shale formations in which oil and gas are contained). <http://www.endocrinedisruption.org/chemicals-in-natural-gas-operations/introduction> and <https://www.fracfocusdata.org>.
- 20 Natural-gas condensate is a low-density mixture of hydrocarbon liquids that are present as gaseous components in raw natural gas. Some gas species within the raw natural gas will condense to a liquid state if the temperature is reduced to below the hydrocarbon dew point temperature at a set pressure. For further information see: CONCAWE, Environmental science for the refining industry: https://www.concawe.eu/uploads/files/Additives_in_imported_Natural_Gas_Condensates-2008-04062-01-E.pdf. Impurities such as BTEX chemicals are present in the condensate portion of natural gas; it is not refined out and remains in the natural gas distributed to gas fired facilities and for home use. BTEX chemicals are also contained in oil condensate and continue to be present in crude oil refined materials.
- 21 Bolden, A L, Kwiatkowski, C F, Colborn T (2015). New Look at BTEX: Are Ambient Levels a Problem? *Environ Sci Technol.* 2015 May 5; 49(9):5261-76. doi: 10.1021/es505316f. Epub 2015 Apr 15.
- 22 IARC Monographs on the evaluation of carcinogenic risks to human, Volume 29 supplement 7.
- 23 Concerned Health Professionals of New York (2014). Compendium of Scientific, Medical, and Media Findings Demonstrating Risks and Harms of Fracking (Unconventional Gas and Oil Extraction), July 10, 2014. <http://concernedhealthny.org/compendium>.
- 24 Hays, J, Shonkoff, S B C (2016). Toward an Understanding of the Environmental and Public Health Impacts of Unconventional Natural Gas Development: A Categorical Assessment of the Peer-Reviewed Scientific Literature, 2009–2015, April 20 2016; <http://journals.plos.org/plosone/article?id=10.1371/journal.pone.0154164>. This paper demonstrates that the weight of the findings in the scientific literature indicates hazards and elevated risks to human health as well as possible adverse health outcomes associated with UNGD.
- 25 McKenzie, L M, Guo R, Witter, R Z, Savtiz, D A, Newman, L S, Adgate, J L (2014). Birth Outcomes and Natural Gas Development. *Environ Health Perspect*; DOI:10.1289/ehp.1408647R. <http://ehp.niehs.nih.gov/1408647r-final/#r5> and Birth outcomes and maternal residential proximity to natural gas development in rural Colorado *Environ Health Perspect* 122:412–417; doi: 10.1289/ehp.1306722. <http://ehp.niehs.nih.gov/1306722>.
- 26 Bolden, A L, Kwiatkowski, C F, Colborn, T, (2015). op.cit.

may have endocrine disrupting (hormone scrambling) properties as well.²⁷ Even very low levels of endocrine disrupting chemicals (EDCs)²⁸ are known to contribute to a range of health effects, in particular reproductive and developmental problems, at levels below existing safety limits.

People are not only exposed to BTEX and other VOCs in proximity to oil and gas production. They are present in vehicle exhaust fumes and cigarette smoke as well as in everyday household products made from derivatives of oil and gas.²⁹ BTEX and other VOCs are found in a wide array of everyday products such as paints and paint strippers, solvents, glues, cleansers and disinfectants, children's toys, pesticides, paints and protective coatings, fingernail polish, gasoline, aerosol sprays, wood, fiberglass, flooring materials, office equipment, PVC plastic, health and beauty products and more. Therefore people that live next to gas production facilities face greater potential exposure to VOCs from both gas production and everyday products, than the general population.

Of equal concern is the assessment of the total toxicity of VOCs in chemical mixtures. Little information exists about how VOCs in mixtures interact with each other and in the human body, but scientific research indicates that VOCs might interact in ways that ratchet up the risk of harm to humans.³⁰ In addition, VOCs in combination with other environmental factors may result in increased risk. For example VOCs may increase the toxicity of particulate matter in the air (e.g. soot)³¹ which is emitted by oil and gas development activities.³² Studies show that some VOCs may also combine with nitrogen oxide in



© Joaquin Sanchez

Many common household products contain harmful VOCs.

the presence of sunlight to create new chemical compounds considered to be harmful to human health.³³

Many factors, including the level of exposure, peak exposure, the length of time people are exposed to these chemicals and their individual vulnerability, influence how VOCs affect health. Government agencies, including the

27 Bolden et. al. (2015). op.cit.

28 "Endocrine disruption is the insidious trespass of man-made chemicals into every vital organ system in your body that comprises or is controlled by the endocrine system, such as the thyroid and parathyroid, pancreas, adrenals, thymus, male and female reproductive organs, the heart, digestive system, and skeletal system—all the systems that participated in how you were constructed in the womb and how you are functioning today." <http://www.psr.org/environment-and-health/environmental-health-policy-institute/responses/endocrine-disruption-public-health-and-national-and-international-security.html>.

29 Batterman, Stuart, Feng-Chiao Su, Shi Li, Bhramar Mukherjee, and Chunrong Jia, (2014). Personal Exposure to Mixtures of Volatile Organic Compounds: Modeling and Further Analysis of the RIOPA Data; Report #: 181, Publication Type: Research Reports; 2014-06-30; <http://pubs.healtheffects.org/view.php?id=421>. Knoppel, H, Schauenburg, H (1989). Screening of Household Products for the Emission of Volatile Organic Compounds. Environ. Int. 1989, 15 (1-6), 413-418. Wallace, L A, Pellizzari, E, Leaderer, B, Zelon, H, Sheldon, L (1987). Emissions of Volatile Organic Compounds from Building Materials and Consumer Products. Atmos. Environ. 1987, 21 (2), 385-393. Zhu, J, Cao, X L, Beauchamp, R. Determination of 2-butoxyethanol Emissions from Selected Consumer Products and its Application in Assessment of Inhalation Exposure Associated with Cleaning Tasks. Environ. Int. 2001, 26 (7-8), 589-597. Nazaroff, W W, Weschler, C J, (2004). Cleaning products and air fresheners: Exposure to Primary and Secondary Air Pollutants; Atmospheric Environment 38 (2004) 2841-2865. <http://citeseerx.ist.psu.edu/viewdoc/download?sessionid=16D732B37DFCD10658EF265F84454C36&doi=10.1.1.476.1547&rep=rep1&type=pdf>.

30 Batterman, et al (2014), op.cit., Brown D, Weinberger B, Lewis C, Bonaparte H. (2014). Understanding exposure from natural gas drilling puts current air standards to the test; Rev Environ Health. 2014;29(4):277-92. doi: 10.1515/reveh-2014-0002.

31 Ebersviller, S, Lichtveld, K, Sexton, K G, Zavala, J, Lin, Y H, Jaspers, I, Jeffries, H E (2012). Gaseous VOCs rapidly modify particulate matter and its biological effects—Part 1: Simple VOCs and model PM. Atmos Chem Phys Discuss. 2012;12(2):5065-5105. Epub 2012 Feb 14. <http://www.ncbi.nlm.nih.gov/pubmed/23457430>.

32 Brown et al (2014). op.cit.

33 Doyle, M, Sexton, K G, Jeffries, H, Bridge, K, Jaspers, I (2004). Effects of 1,3-Butadiene, Isoprene, and their Photochemical Degradation Products on Human Lung Cells. Environmental Health Perspectives. 2004;112(15):1488-1495. doi:10.1289/ehp.7022.

US EPA, the US Agency for Toxic Substances and Disease Registry (ATSDR) and the California Office of Environmental Health Hazard Assessment (OEHHA) have established regulations that set limits for acute exposure to some VOCs (for example, high-level exposure from an accident) or chronic exposures (for example, lower level exposures over the course of a work day or longer) in an attempt to prevent chemical-related illness. However, no safety levels have been established for the majority of chemicals associated with oil and gas production—which can number in the hundreds. Even when safety levels have been set, they typically do not take into account the exposure scenarios described in Pavillion and other oil and gas communities.

People living near oil and gas production activities—as opposed to workers who do not also live nearby—may be exposed to complex mixtures of VOCs at unknown, fluctuating levels, resulting in chronic low level exposures with periodic spikes at much higher levels, for 24-hours a day, possibly for years or even for decades. There is no current scientific analysis of the health effects that may result from such long-term exposures to VOC mixtures around oil and gas sites. Furthermore, there are currently no adequate methods to assess how the chemicals in this mixture may interact synergistically or additively in ways that may cause harm to human health.³⁴ Current research shows that the effects of chronic exposures to low levels of each of the BTEX chemicals, with periodic spikes, have been insufficiently incorporated into current safety standards for these chemicals (see Appendix 2, Table 5).³⁵

The scientific community has expressed concerns about its current incapacity to address the toxicity of mixtures. For example, research by Dr David Brown of the South-west Pennsylvania Environmental Health Project has documented that emissions vary at each well pad due to 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. He states,

BOX 1

How are Toxic Chemicals Emitted at a Gas Well Pad?

Toxic VOCs are emitted in a number of ways in the oil and gas development process. The Pavillion area, with its numerous gas production sites, became the basis for our investigation. Each piece of equipment used at or around a well pad to extract, process and transport oil and gas (including diesel trucks, drilling rigs, power generators, phase separators, dehydrators, storage water tanks, compressors and pipelines) is a potential emission source for methane, VOCs and other gases or particulate matter. Emissions of VOCs may occur at any stage of exploration or production by way of venting, flashing, or flaring which can also lead to fugitive or non-permitted emissions. When there are many wells in a small area, emissions from individual point sources can accumulate and become a substantial source of VOCs.³⁶

Storage tanks are just one example of how toxic chemicals are emitted at a gas well pad. Light hydrocarbons including methane and other VOCs, natural gas liquids and some inert gases are dissolved into condensate during storage. These chemicals may then vaporize or “flash out” and collect in the space between the liquid and the fixed roof of a storage tank and can be vented to the atmosphere as the liquid level in the tank fluctuates. Among the VOCs emitted are chemicals such as n-butane, pentane, propane, hexane, for example.³⁷ BTEX chemicals are also contained in this condensate and although they may not in general be at the highest levels by volume in the condensate, they are a cause for concern because of their well-established toxicity.

The life span of a single gas well, such as those in the Pavillion area, can extend from 30 to 50 years. This means that people living and working near these sites may be constantly exposed to toxic chemicals for many decades.

- 34 Mauderly, J L, and Samet, J M (2009). Is There Evidence for Synergy Among Air Pollutants in Causing Health Effects? *Environ Health Perspect*; DOI:10.1289/ehp.11654. <http://www.ncbi.nlm.nih.gov/pmc/articles/PMC2627851>.
- 35 Kassotis, C D, Tillitt, D E, Lin, C H, McElroy, J A, Nagel, S C (2016). Endocrine-disrupting Chemicals and Oil and Natural Gas Operations: Potential Environmental Contamination and Recommendations to Assess Complex Environmental Mixtures. *Environ Health Perspect* 124:256–264; <http://ehp.niehs.nih.gov/1409535>. ehp.1409535.
- 36 Gilman et al (2013). op.cit.
- 37 Zielinska, B, Fujita, E and Campbell, D (2011). Monitoring of Emissions from Barnett Shale Natural Gas Production Facilities for Population Exposure Assessment. National Urban Air Toxics Research Center (NUATRC), No. 19 2011. <https://sph.uth.edu/mleland/attachments/DRI-Barnett%20Report%2019%20Final.pdf>. Moore et.al. (2013). op.cit.



Using a FLIR camera to capture toxic chemical emissions at a produced water tank in Pavillion.

© Wilma Subra

“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.”³⁸

In addition, in 2012 the Air Pollution Control Division of the Colorado Department of Public Health and Environment conducted air sampling adjacent to natural gas well completion activities in Erie, Colorado.³⁹ The purpose of the sampling was to measure air emissions that may be associated with the well completion activities. The authors of the report concluded “the concentrations of various compounds are comparatively low and are not likely to raise significant health issues of concern. However, it should be noted the current state of the science is unable

to estimate the potential risks due to exposure from multiple chemicals at the same time, which may be higher.”

Of special concern are chronic exposures to low levels of chemicals as these occur in mixtures. A characteristic of endocrine disrupting chemicals is their capacity to cause harm at low levels. Dr Chris Kassotis states, “although toxicological studies often assess adverse outcomes from high-exposure scenarios relevant to occupational exposure, endocrinological studies can assess outcomes from low-level exposure that may be more relevant to humans living near oil and natural gas operations.”⁴⁰ With approximately 1,000 chemicals used in and produced by oil and gas operations,⁴¹ there is a critical need for methods to assess the EDC activity of these complex mixtures.

38 Brown et al (2014). op.cit.

39 Colorado Department of Public Health and Environment (CDPHE) (2012). Air Emissions Case Study Related to Oil and Gas Development in Erie, Colorado; CPDHE, Air Pollution Control Division, Technical Services Program, December 5, 2012. http://www.colorado.gov/airquality/tech_doc_repository.aspx?action=open&file=Erie_Air_Emissions_Case_Study_2012.pdf.

40 Kassotis, C D, et.al. (2016). op.cit.

41 US EPA (2015). Assessment of the Potential Impacts of Hydraulic Fracturing for Oil and Gas on Drinking Water Resources (External Review Draft). EPA/600/R-15/047. Washington, DC: US EPA. Available: <http://cfpub.epa.gov/ncea/hfstudy/recordisplay.cfm?deid=244651>.

CHAPTER THREE

DESCRIPTION OF STUDY METHODS

Implementing this innovative methods development research project—to assess the potential exposure to the hazards of oil and gas production—required a variety of monitoring tools and methods.

Our research team knew from previous studies that air monitoring tools had been successfully used to determine that exposure to toxic chemicals in air emissions from well pads was possible.⁴² We knew that exposure to these emissions was likely for individuals living close to well pads.⁴³ However, other than studies of workplace-related chemical exposures, very little research had been conducted to measure the degree to which people living near oil and gas well pads are being exposed.

In this study, we looked for the breakdown products of chemicals found in sampled air, by analyzing blood and urine specimens from local residents. Due to limited financial resources, we could collect and analyze only a small number of air and biomonitoring samples (see Box 3; The Sampling Process in Numbers); we did not have enough gear to utilize our complete array of monitoring tools at every pad and with every study participant. However, even with these limitations and the small sample size, we were able to use a variety of tools to indicate how VOC exposure pathways could be traced from the point of emission, to the air inhaled by a study participant, and then to chemical breakdown products (metabolites) measured in urine when these chemicals were excreted. This study is the first time, as far as we are aware, that such an exposure pathway process has been developed in connection with gas production.

Aside from our research team, eleven volunteers, all of them living in the Pavillion area, participated in this study.

The research team designed and implemented the study in accordance with Community Based Research Principles (CBRP)⁴⁴ and in collaboration with the study participants throughout the process.

In order to determine which chemicals emitted from gas development and production sites might be reaching local residents' bodies, we began by sampling air emissions at the well pads. We used a variety of monitoring tools (see Figure 5), while simultaneously assessing weather conditions, wind direction and wind speed to help determine whether these emissions might arrive in the vicinity of Pavillion area community members who live near the well pads. We then used the air monitoring tools to test for chemicals in the areas downwind from the well pads, during the time we collected air samples. During the air testing around the well pads, we also tested the air being inhaled by community members who were working and living downwind. Our final step was to collect blood and

“PEOPLE LIVING AND WORKING
in oil and gas fields deserve to know what chemicals from development activities are in their bodies. The test methods we used in this project could be further refined to help us understand what chemicals they are exposed to and how, so we can better protect people from harm.” — *Wilma Subra*

42 Macey et al. (2014). op.cit. and Coming Clean and Global Community Monitor (2014). op.cit.

43 Gilman et al (2013). op.cit. Symanski, E L, Stock, T H, Tee, P G, Chan (2009); Demographic, Residential, and Behavioral Determinants of Elevated Exposures to Benzene, Toluene, Ethylbenzene, and Xylenes among the US Population: Results from 1999–2000 NHANES. W J Toxicol Environ Health A. 2009; 72(14):915–24. doi: 10.1080/15287390902959706. <http://www.ncbi.nlm.nih.gov/pubmed/19557620>.

44 Community Based Research Principles provide a framework for mutually beneficial relationships between researchers and community members. See for example: <https://www.washington.edu/research/main.php?page=communityPrinciples>.

urine samples in people living and working in proximity to the well pads, at a time when airborne chemicals, inhaled by those people, might conceivably be “broken down” within the body and excreted.

Once VOCs enter the body, they are either exhaled or quickly broken down and eliminated through the urine, usually within a few hours. Therefore we collected urine and blood from participants about four hours after we collected air samples at gas production activity sites and air samples from the immediate environment of the participant.

In the Pavillion area, individuals and families are likely to live near more than one well pad, many less than a quarter of a mile away and some as close as a few yards. Seven biomonitored individuals live or work in an area with three natural gas production pads. Four biomonitored individuals live or work in an area with two natural gas production pads. While we monitored the air near gas

“IT TAKES A LOT OF COURAGE

for people to have their bodies tested for toxic chemicals. Thanks to these Pavillion study volunteers and our science collaborators, we have a new research method and test results that can help get their community, and other impacted communities the attention they need.” — *Wilma Subra*

production related activities, we fitted study participants with personal air monitors attached to their clothing or accessories, to identify and measure levels of VOCS in the air in their immediate environment.

CHAPTER THREE MONITORING TOOLS, SAMPLING METHODOLOGY AND KEY FINDINGS

AIR AND BIOMONITORING TOOLS

To measure harmful air emissions from gas development in the Pavillion area, we selected an assortment of standard, scientifically-proven air monitoring tools, each with a varying capacity to test for the presence and levels of chemicals of concern; VOCs.⁴⁵ There was some overlap in the list of chemicals each tool could test for, but not all tools could test for all

chemicals of concern and not all chemicals could be tested for at the same levels of detection. The selected air monitoring tools also utilized different methods for capturing air. Grab samples (30 seconds) were able to detect spikes (higher levels) of some chemicals whereas 24-hour and 8-hour air samples averaged out exposures so that intermittent spikes were not captured. Researchers collected air samples over a seven-day period in August 2014. See Appendix 1 for protocols and methods.

BOX 2

Air Monitoring Devices Used at Pavillion Area Well Pads



FLIR Gas FindIR infrared camera: an infrared camera or thermal imager that is used to record gas leaks and create video images of VOC emissions from equipment and infrastructure used in petrochemical operations.

© www.laboratoryequipment.com



Minirae 3000: an air monitoring device that measures the total amount of VOCs present in air while we were using the FLIR Gas FindIR camera around gas production related activities. A PID, or photoionization device, uses ultraviolet rays to detect a broad range of VOCs, such as benzene, methane, formaldehyde and other hydrocarbons which typically occur in oil and gas drilling and refining. © www.directindustry.com



Ambient Weather Model WM-5, V-1: a hand-held weather station to measure barometric pressure, temperature, wind current direction and other information important for determining how and where VOCs might travel in air currents.

© Ambient Weather*

Sorbent Tube: an air monitoring device that can be worn by individuals. It measures levels of VOCs in air directly surrounding an individual during the specific period of time. Participants in the study wore sorbent tubes for periods of one hour.



CONTINUED ON PAGE 18

45 US EPA (2015). Volatile Organic Compounds (VOCs) in Ambient Air using Summa Canister Sampling and Gas Chromatography (GC) Analysis. <https://www.epa.gov/sites/production/files/2015-06/documents/aircrf.pdf>. US EPA (1999). Determination of Volatile Organic Compounds in Ambient Air using Active. Sampling onto Sorbent Tubes, Second Edition, Compendium Method TO-17. <https://www3.epa.gov/ttnamti1/files/ambient/airtox/to-17r.pdf>. US EPA (2009). Technical Assistance Document for the National Air Toxics Trends Stations Program Revision 2, April 2009. <https://www3.epa.gov/ttn/amtic/airtox.html>. US EPA (1999a). Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition, Compendium Method TO-15 Determination of Volatile Organic Compounds (VOCs) in Air Collected in Specially-prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry (GC/MS) <https://www3.epa.gov/ttn/amtic/natts.html>. Watson N M, and Cooper D. Tube Sampling Versus Canister Sampling—the Pros And Cons of Each Approach Paper #-POSTER, Markes International Ltd., Gwaun Elai.



Aldehyde Badge: an air monitor that measures chemicals other than VOCs that were sampled with the summa canister or sorbent tube. These badges monitored air for aldehydes over an 8-hour period.

© ChemExpress™



Summa Canister: a stainless steel electro-polished passivated vessel used to collect a whole air sample. The sample may then be analyzed according to the EPA guidelines for the presence of VOCs. The canisters can be used to collect air samples for various lengths of time. In this study we used summa canisters to collect both 15 seconds “grab samples” and 24-hour ambient air samples. © www.entechinst.com



HDS (helium diffusion sampling) passive air monitor: an air monitor worn by study participants which averages out the levels of chemicals in air over a specified period (in this case 8-hour time periods). © www.entechinst.com

The summa canisters and sorbent tubes, aldehyde badges and HDS monitors were kept in their shipping containers in a designated staging area accessible only to science team members. After summa grab samples were collected, and the aldehyde badges, sorbent tubes and HDS monitors were utilized, they were shipped overnight to the appropriate laboratory. The science team (Wilma Subra and Deb Thomas) trained two assistants in sample collection, and supervised all air monitoring and sample shipping. They also ensured that records were kept about the time of sample collection, the location of sampling, and the type and code number of tool utilized, along with code numbers and the location of participants who wore the sorbent tubes and/or who were near or in areas where summa grab samples were collected. The science field team reviewed records at the end of each day of monitoring and transferred to a single computer accessible to only one of the team members after review to ensure entries were accurate.

Urine collection materials were purchased as recommended by the study’s analytical laboratories and kept in their shipping containers in the holding area until use. The science team had also consulted with key scientific advisors about type of blood vacutainers, type of stoppers and necessary storage and shipping details to ensure the urine and blood samples would remain viable.

The science team kept records for the time and location of the blood and urine samples collected, along with code numbers of the vacutainers and the participants. All samples were double-wrapped in zip lock bags, placed in ice chests immediately after collection, transferred to a freezer and frozen for 24 hours before being placed in ice chests packed with ice and shipped to the appropriate laboratory overnight.

A total of 12 natural gas well pads in the Pavillion area were monitored in areas where bio-monitored individuals lived and/or worked. The pads contained one or more of the following types of equipment:

BOX 3**The Sampling Process in Numbers****7 days of sampling, August 2014****12 well pads**

- FLIR camera documented real time emissions from apparatus from the 12 well pads, including separators, produced water tanks and metering stations.
- 4 PID (photo ionization device) readings at each of the 12 well pads, plus measurement of VOCs emitted from soil surrounding leaking well pad apparatus, when leaks were identified by real-time FLIR camera images.
- At 4 of the well pads, selected for proximity to irrigation fields, we used summa canisters to capture air samples to be analyzed for levels of individual VOCs.
- 6 aldehyde badges were placed overnight on selected well pad apparatus.

11 individuals from Pavillion community

- 40 individual ambient air samples—both HDS (helium diffusion samplers) and sorbent tube monitors, worn by participants.
- 27 urine samples and 27 blood samples from all participants during the seven day period.

1. One or more wells;
2. Individual separator units⁴⁶ serving each well;
3. One or more produced water tanks⁴⁷ (with and without carbon filter drums);
4. One or more metering stations with associated methanol tanks.

It's not always easy to identify the function or hazards that might be associated with well pad equipment. Because there is no external indicator, some well pad equipment—such as separator units and water tanks—might look harmless but could be venting highly toxic chemical emissions at any time.

AIR AND BIOMONITORING METHODOLOGY

We asked study participants to avoid using products or engaging in activities that would ordinarily expose them to VOCs, including BTEX chemicals, in an attempt to isolate VOC emissions that might only be coming from gas sources. For example, we asked each participant to avoid filling car or truck gas tanks, exposure to cigarette smoke, burning trash, driving farm equipment, or using pesticides and other household products containing VOCs for the duration of the study. It is difficult to avoid exposures to VOCs because these chemicals are ubiquitous, but we wanted to eliminate as many ordinary daily activity exposures as possible, to more directly attribute any VOCs found in ambient air samples (those samples taken from personal air monitoring equipment) or human biospecimens to gas production activities.

Based on agreements with the study participants, no information in this report will link individual results to individual participants or in any way identify individuals who participated in the study, or the location of their homes and places of work. The study team and community members agreed that the participants' privacy and desired anonymity is extremely important. The identified individual study results are the personal property of each participant and each participant is free to decide how he or she may want to discuss their own individual results with others. The Pavillion participants reviewed and approved the results from the study released in this report.

Only a limited number of analytical laboratories in the United States have the capability to test for VOCs at non-occupational levels (that is, outside workplace environment). The Tobacco Control and Research analytical laboratory based at the Center for University of California, San Francisco based, headed by Dr Neil Benowitz, MD, tested urine samples for the presence of metabolites (breakdown products) for some of the VOCs that the study team had identified as being of concern. Dr Benowitz' work has centered on chemicals associated with cigarette smoking and some of these chemicals (benzene, acrylonitrile) have also been found around gas production sites. Dr Chung-Ho Lin at the University of Missouri developed a new analytical method to test the Pavillion participants' urine

⁴⁶ Separator Unit: a separator is a vessel used to separate gas and liquid components from the fluids extracted from an oil or gas well.

⁴⁷ Produced water is water brought to the surface during oil and gas exploration and production. This produced water can contain salts, chemicals and naturally occurring radioactive materials. Chemicals are transferred to the water through long-term contact with the oil or gas or are chemical additives used during drilling and operation of the well.

samples for a wider range of VOCs and their metabolites and developed a new analytical method that could test samples for very low levels of chemicals of concern (see Appendix 1 for a description of Dr Chung Ho Lin's analytical method). Although there was some overlap, these two laboratories did not test urine samples for the same list of metabolites. As stated previously, this study is a methods development study and as such, utilized several analytical testing methods for both air and human bio-specimens in order to assess the suitability of various methods for use in further research.

Blood samples were analyzed by NMS Laboratories. NMS Laboratories were unable to detect levels of VOCs in our blood samples. Our assumption is that NMS protocols are unable to detect the low levels that might have been present in blood samples (see Appendix 1). Alternatively, VOCs may not have been present in the blood samples we collected, possibly because these chemicals break down quickly and are excreted in urine or no recent exposure had occurred.

Our methods development study design, as described above, sought to develop a method which could link emissions of VOCs from gas activity sites to human exposure downwind by: measuring air emissions from the point source of emissions; assessing wind speed and direction at the emissions source; measuring VOCs in the ambient air surrounding individuals who were working downwind from emission sources at the time of air sampling; and finally, measuring VOCs in the urine of these individuals—who may have been exposed to VOCs emitted from the nearby well pad, which might be associated with the VOCs identified in the air samples that were collected at emission sources and in the personal air monitoring devices.

Our model, which utilized a series of tools, each capable of testing for differing lists of VOCs and incorporating different methods for sample capture and analysis, provides an overview of possible monitoring methods. Our pilot study was intended to explore the methods and challenges of evaluating exposures to chemicals from gas production, with a view to refining the methods used in future projects. The results of this investigation must be viewed as a snapshot of air emissions from gas production sites and a clear warning sign of problems, not as results which can be generalized.

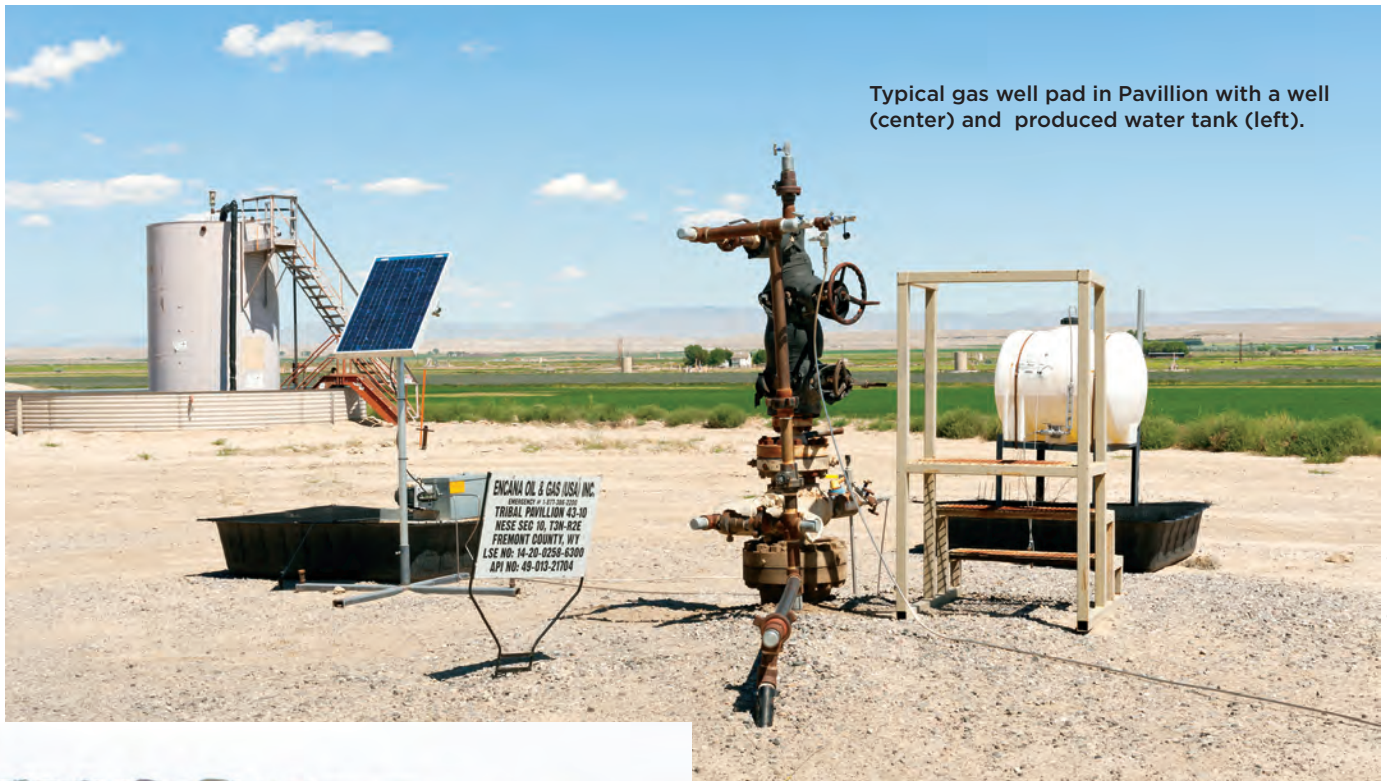
Description of sample collection protocol

The science team began the project by meeting with community members to explain the study and the benefits or disadvantages of participation. The team discussed study protocols and principles of community based participatory research,⁴⁸ emphasizing that the community would maintain the authority to release or not release information about the study or its results to the general public. The science team also made clear that individual participants would receive their own individual results along with aggregated results from the study and would be able to meet with the study's principal investigator to discuss their results.

Many of the residents in Pavillion have worked with oil companies currently engaged in gas production, or have friends or relatives that are employed by gas companies. The convening grassroots group, Pavillion Area Concerned Citizens, is small and many of its members have been severely impacted by gas production activities, according to their accounts. The eleven individuals who volunteered to participate in this pilot study are deeply motivated by these experiences.

1. To establish background levels of VOCs in the Pavillion area, we collected 24-hour air samples (which averages out exposures), using a summa canister, which we placed in the center of the testing area.
2. We mapped the areas where we wanted to do air and human monitoring, based on previous research conducted by Shale Test and consultations with community members. We identified well pads where we would use air monitoring tools, which were located in areas where study participants were also working and living. Given the density of well pads in Pavillion, we were able to identify areas where monitoring was most likely to produce useful information.
3. We developed a draft schedule for sampling, which began with air sampling around different pieces of equipment on our designated well pads. At some well pads we monitored air by using the FLIR camera to detect emissions and the Minirae to measure total volume of VOCs. We used a portable weather station to indicate the general speed and direction of the wind. At other well pads we also utilized summa grab samples, which were used for 15 to 30 seconds; these

48 Community Based Research Principles, op.cit.



Typical gas well pad in Pavillion with a well (center) and produced water tank (left).

© Jeremy Buckingham/Creative Commons



Sampling for chemical emissions at a produced water tank carbon filter drum in Pavillion. Credit: Wilma Subra

4. One or two hours after we collected air samples from the well pads, we collected personal air samples from study participants who wore either sorbent tubes or HDS samplers pinned to their clothing. Participants would typically have been wearing these samplers for an hour before collection. We were not always able to maintain a close schedule, mostly because of the unpredictability of ranching activities near well pads, such as the irrigation of fields as well as the length of time this takes.
5. We also collected a small number of air samples, using personal air monitors, at night, both indoor and outdoor, to give us information that might indicate differences between night-time and daytime exposures.
6. Approximately four hours after air samples were collected at the well pads and from personal air monitors, we collected blood samples from participants at our mobile biomonitoring van. We also collected spot urine samples from participants at this time.
7. First morning void urine samples were also collected from each participant. All human samples were immediately placed in ice filled chests and transported to a freezer, and later mailed overnight to the appropriate laboratory in an ice-filled chest.

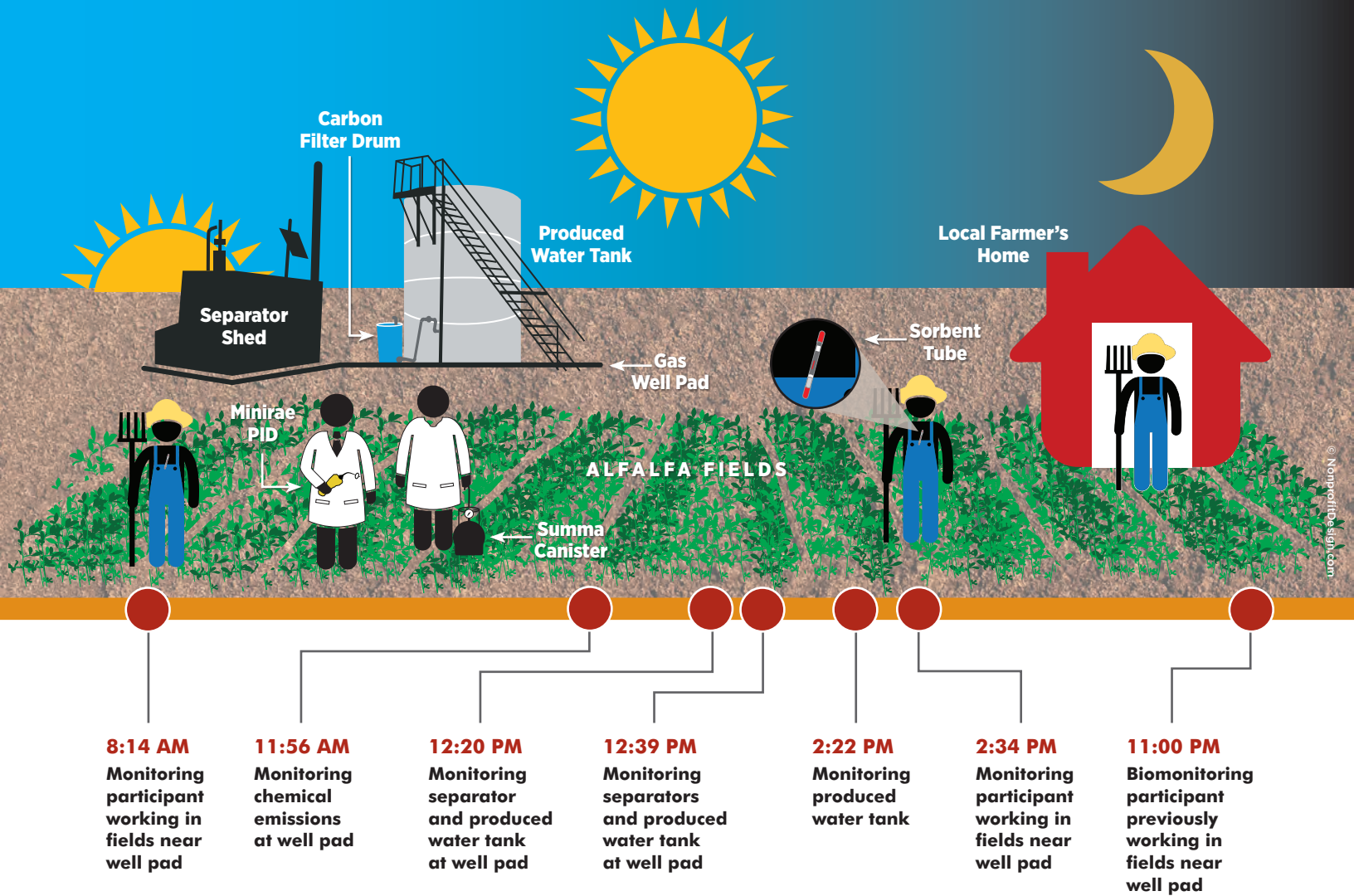
were analyzed for the presence and levels of VOCs, using an analysis called EPA-TO-15, which tests for over 200 VOCs. The well pads ranged from a few yards to approximately 50 yards away from homes and fields where ranchers would be irrigating and engaging in other ranching activities. Our portable weather stations would indicate when ranching activities might occur downwind from emission sources, (wind readings were only taken at well pads) but we knew that wind currents can easily vary and we could not be certain that a rancher or a family would be downwind from emissions when we collected personal air samples.

© Wilma Subra

FIGURE 2
Illustration of Pavillion Area Air and Biomonitoring Study Method

AUGUST 6, 2014

One Day's Monitoring of Chemicals from Gas Production in Pavillion Area



8. Financial resources constrained the number of personal air monitoring sorbent tubes, (which required batteries) and the number of available summa grab canisters. All samples were handled strictly according to protocol.
9. Ten months after the sample collection field work was completed and samples had been sent to laboratories for analysis, the science team met again with community participants to deliver aggregated and personal results at a closed meeting. Study participants were encouraged to make an appointment to discuss results with the study Principal Investigator.

10. Community members met separately to discuss the possibility of releasing a public report about the study.

Above is a sample chart illustrating our study design. Table 1 is an example of a daily monitoring schedule from our Pavillion research project provides results of air analysis from using a FLIR camera and a Minirae PID at a well pad, summa canister for ambient air, sorbent tubes worn by study participants and the results of analysis of urine specimens collected from an individual who was working in fields located near the well pad.

TABLE 1

Timeline for Gas Air and Biomonitoring Methods Development—One Example, August 6, 2014

Time	Location	Monitoring Tool	Results description	Results
8:14 AM	Fields near well pad.	Sorbent tube worn by study participant working in fields.	Sorbent tube found the following chemicals in ambient air collected in the early morning.	Toluene: 0.096 ppb benzene 0.038 ppb
8:14 AM—24-hour sample	Location central to well pads in order to measure background levels of VOCs.	Summa canister.	Average over 24 hours.	Toluene 0.090 ppb benzene <0.09 ppb
11:56 AM	Separator and produced water tank ⁴⁹ at well pad.	FLIR camera and Minirae PID.	Separator leaking along top of doors—VOCs from top of doors. Produced water tank—VOCs leaking at 3 locations. Thief Hatch (closed). Vent. Carbon Filter Drum.	VOCs 17.4 to 39 ppm VOCs 113 ppm VOCs 102.4 ppm VOCs 107.4 ppm
12:20 PM	Separator and produced water tank at well pad.	FLIR camera readings, Minirae PID.	Volatiles leaking out of ground adjacent to separator; Odors being released from ground near separator. Volatiles being released out of vent on produced water tank No emissions leaking out of hatch.	VOCs 37.1 ppm VOCs 482.7 ppm
12:39 PM	Top of the separator doors, well pad.	FLIR camera readings, Minirae PID . Emissions visualized from two separators leaking from top of doors.	Separator 1. Separator 2. VOC emissions from production water tank leaking from vent.	VOCs 9.5 ppm VOCs 33.7 ppm VOCs 58.8 ppm
2:22 PM	Produced water tank with carbon filter drum, one third full, well pad Strong Winds.	FLIR camera readings, Minirae PID. Wind speed measured by portable weather station.	Production water storage tank vent on top leaking . VOCs on the ground. Carbon Filter Drum.	VOCs 7.2 ppm VOCs 0.2 ppm VOCs 4.0 ppm
2:34 PM	Fields near well pad.	Sorbent tube worn by same study participant working in fields.	Chemicals found in ambient air collected mid-afternoon.	toluene 0.46 ppb benzene 0.091 ppb
11:00 PM	Participant previously working in fields near well pad.	Urine sample from same study participant.	Metabolites of chemicals were measured.	Toluene metabolite hippuric acid 605 ng/ml* Benzene metabolite tma 543 ng/ml.

ppb = parts per billion; ppm = parts per million

* ng/ml = nanograms per millilitre (the standard reporting method used by the CDC for biosamples)

KEY AIR MONITORING FINDINGS

From the samples taken with our variety of air monitoring tools, laboratories identified a total of 65 VOCs, including BTEX chemicals. Our findings reflect and complement other air monitoring studies previously conducted at oil and gas sites near Pavillion, and elsewhere in Wyoming and in the U.S. Of special interest are the chemicals

detected in summa canisters, which can identify specific VOCs and their concentrations; and sorbent tube samples which indicate chemicals present in the immediate proximity of the individual participants, which they were likely to have inhaled. Unfortunately there is no way that scientists can prove that chemicals detected at an emission source are the same chemicals detected in the air immediately

surrounding people.⁵⁰ In addition, differences in the monitoring devices and laboratory techniques meant we were not able to make apples-to-apples comparisons between the sample results. However the information is still helpful in establishing a methods for showing which chemicals were detected and where they were found, on the progression from emission source to people's bodies.

Levels of VOCs in Air and Environmental Screening Levels (ESLs)

Environmental Screening Levels (ESLs) are based on levels of toxic substances that public health agencies and environmental regulators have determined as warning signs for risk to human health. The air monitoring results from Pavillion have been analysed by Mark Chernaik with reference to these ESLs (see Appendix 2). Firstly ESLs apply to a specific duration of time (from short to long-term exposure) therefore applying ESLs for long term exposure to the VOC levels detected in air samples collected from Pavillion *requires an assumption that the air samples are representative of ambient air conditions that generally prevail at the location over long periods of time.* Secondly, ESLs only exist for a limited number of VOCs; an ESL has not been developed by public health agencies and environmental regulators for 36 of the 46 VOCs that were detected in air samples collected in sorbent tubes, nor have standards been developed for mixtures of VOCs to account for cumulative or synergistic effects.

The following tables show the findings for the 10 VOCs which have ESLs and highlights where the levels exceed any ESL⁵¹ (full references are in Table 5, Appendix 2). The results show that even the lowest levels of benzene and the average levels of xylene detected in the summa canisters exceeded the short-term ESL (Table 2). The highest level of benzene found in the sorbent tubes worn by participants (Table 3) also exceeded the long-term ESL, while the average levels of benzene and naphthalene exceeded the ESL for an increased risk of cancer.

TABLE 2
Levels of 10 VOCs of Concern Due to Hazard in Summa Canisters (15 minute grab samples), Aggregated Data

VOC levels detected in summa canisters (in ppb)			
Chemical	Lowest detected level	Average level	Highest detected level
acetone	BDL	BDL	BDL
2-butanone	BDL	BDL	BDL
hexane	0.61	3303	11000
ethylacetate	BDL	BDL	BDL
benzene	8.7	360	780
cyclohexane	0.66	3643	12000
toluene	0.3	1179	2400
ethylbenzene	BDL	5300	1300
xylenes	0.4	5388	18300
naphthalene	BDL	147.5	210

Key for Tables 2 & 3

- RED = VOC levels that exceed a short-term ESL.
- YELLOW = VOC levels that exceed a long-term ESL.
- ORANGE = VOC levels that exceed a level exposure which is estimated to increase a person's risk of cancer by more than 1 in 1 million.

BDL = below detection limit

ppb = parts per billion

TABLE 3
Levels of 10 VOCs of Concern Due to Hazard in Sorbent Tubes Worn by Participants (1 hour sample), Aggregated Data

VOC levels detected in sorbent tubes (in ppb)			
Chemical	Lowest detected level	Average level	Highest detected level
acetone	BDL	12.32	52.6
2-butanone	0.02	0.49	2.45
hexane	0.02	1.19	6.14
ethylacetate	BDL	0.97	6.21
benzene	BDL	0.41	1.12
cyclohexane	0.02	0.84	6.27
toluene	BDL	1.44	3.73
ethylbenzene	BDL	0.18	0.54
xylenes	BDL	0.84	2.75
naphthalene	0.01	0.08	0.36

49 A tank for water used in the oil and gas production.

50 This can be done with other techniques such as labelled compounds, but was not possible for this study as this method was not available.

51 These ESLs include: 1) Minimal Risk Levels (MRLs) developed by the U.S. Agency for Toxic Substances and Disease Registry (ATSDR); 2) National Ambient Air Quality Standards (NAAQS) and Reference Concentrations (RfCs) developed by the U.S. Environmental Protection Agency (USEPA); 3) Acute and Chronic Reference Exposure Levels (RELs) and Cancer Potency Factors (CPFs) developed by the California Office of Environmental Health Hazard Assessment (OEHHA); and 4) Ambient Air Quality Guideline Values developed by the World Health Organization (WHO)

KEY BIOMONITORING FINDINGS

A total of 16 chemicals or their breakdown products (metabolites) were found in the urine of study participants. Chemicals found in urine were:

- benzene
- toluene
- 2-heptanone
- 4-heptanone
- naphthalene

Metabolites were found in urine samples for the following chemicals:

- benzene
- toluene
- methylbenzene
- styrene
- xylenes
- NMP (N-methyl-2-pyrrolidone)
- 1,3-butadiene
- acrylonitrile, vinyl chloride and ethylene oxide (same metabolite)
- acrylonitrile (metabolite unique to acrylonitrile)
- propylene oxide
- crotonaldehyde
- acrylamide and acrolein

Some metabolites are considered breakdown products for more than one chemical. For example the metabolites for benzene are also metabolites for other chemicals, so their presence in urine may not indicate exposure to benzene. Metabolites for benzene may also change as levels of exposure increases, which must be considered when assessing exposure to benzene.⁵²

There are a number of complexities to account for, such as exposure pathways from well pads to people, which might account for differences in the detection of chemicals

between air monitors and the biospecimens. Many of the chemicals found in air cannot yet be tested for in human biospecimens (although researchers are developing analytical tools that may solve this problem in the future). It is also possible that some of the chemicals found in the air may have dispersed before they could be taken into the bodies of participants. We know that air currents are constantly shifting and participants were moving around; local residents and our team of researchers observed this in the Pavillion area. Chemicals can also degrade or transform into other chemicals through photochemical or other types of reactions in the atmosphere, with some reacting more quickly than others. In some cases, chemicals in participants' bodies may not have metabolized sufficiently to be excreted into urine. Although researchers predict that VOCs will be excreted in a matter of hours, they also know that individual metabolism rates can vary. Lastly, in some instances, perhaps the chemicals found in air samples were either not taken into the bodies of participants, or were not able to be identified because levels were too low to be detected.

Nevertheless, a comparison between the levels of VOC metabolites in Pavillion area study participants and the general population is very revealing. Mark Chernaik, study Science Advisor, has conducted such an analysis (see Appendix 3, Table 5) which finds that levels of trans, transmuconic acid (ttMA—a marker of benzene exposure) are significantly higher in the urine of Pavillion study participants than levels of this same chemical in the urine of the general US population, as measured by the CDC NHANES biomonitoring programme.⁵³ In the case of ttMA, levels in the urine of Pavillion residents studied is 10 times higher than the median level in the urine of the general population, as measured by CDC/NHANEs programme, and higher even than the median level of ttMA in refinery workers in Brazil (post-shift).⁵⁴

52 ATSDR (2007). Toxicological Profile for Benzene, August 2007; <http://www.atsdr.cdc.gov/toxprofiles>.

53 CDC (2015). Fourth National Report on Human Exposure to Environmental Chemicals, February 2015; www.cdc.gov/biomonitoring/pdf/FourthReport_UpdatedTables_Feb2015.pdf. CDC NHANES is the Centers For Disease Control and Prevention National Health and Nutrition Examination Survey.

54 Martins, I, and Siqueira, M E P B D (2004). Trans, Trans-muconic Acid in Urine Samples Collected in Three Periods from Benzene Handling Workers in a Brazilian Refinery. *Revista Brasileira de Ciências Farmacêuticas*, 40(2), 197–201.

TABLE 4

Levels of Chemicals in Urine Samples of Pavillion Residents, Wyoming (August 2014), µg/g Creatinine, Selected Findings

Chemical Metabolite	Parent Chemical	Median Level	Maximum Level
Hippuric acid	Toluene, cinnamaldehyde	322,959	1,197,549
Mandelic acid	Ethylbenzene, styrene	215	2466
4-Methylhippuric acid	Xylene	92	1395
2-Methylhippuric acid	Xylene	81	631
3-Methylhippuric acid	Xylene	99	643
Phenylglyoxylic acid	Ethylbenzene, styrene	53	411
trans, transmuconic acid	Benzene	369	2046
PMA (N-Acetyl-S-(phenyl)-L-cysteine)	Benzene	BDL	1.0
MHBMA (N-Acetyl-S-(2-hydroxy-3-butenyl)-l-cysteine)	1,3-butadiene	BDL	0.8
HEMA (N-Acetyl-S-(2-hydroxyethyl)-l-cysteine)	Acrylonitrile, vinyl chloride	1.3	3.6
CNEMA/CYMA (N-Acetyl-S-(2-cyanoethyl)-L-cysteine)	Acrylonitrile	1.3	31.9
3-HPMA (N-Acetyl-S-(3-hydroxypropyl)-l-cysteine)	Acrolein	388	7058
2-HPMA (N-Acetyl-S-(2-hydroxypropyl)-l-cysteine)	Propylene oxide	35	162
AAMA (N-Acetyl-S-(2-carbamoyl-ethyl)-l-cysteine)	Acrylamide	99	199
HPMMA (N-Acetyl-S-(3-hydroxypropyl-1-methyl)-l-cysteine)	Crotonaldehyde	235	630

■ YELLOW = Level that exceeds median in urine of general population
■ ORANGE = Level that exceeds 95th percentile in urine of general population
 µg/g = micrograms/gram

The high hazard of the chemicals emitted into the air, together with the findings that the levels of certain VOC metabolites in urine of the people studied are well above the levels in the general population, sends a clear signal

that action needs to be taken to prevent exposures, especially when all the limitations of the study listed above are also considered.

CHAPTER FOUR

OIL AND GAS CHEMICAL HAZARD ASSESSMENT METHOD

Through this study we have shown that harmful VOCs are present in the air, and that some of these chemicals are also present in the bodies of people who live and work in close proximity to oil and gas production. Numerous other studies have detailed the illnesses and diseases associated with exposure to VOCs and other emissions (e.g. ozone and methane).⁵⁵ Federal VOCs regulations are designed to prevent exposure to “unsafe” levels of some of these chemicals, to prevent illness and disease. However these risk-based standards may not fully address the hazards of these chemicals, or combinations of chemicals. Researchers are continuing to develop methods for assessing chemical mixtures, especially those mixtures that occur around oil and gas production activities and in particular mixtures of chemicals that are considered to have endocrine disruption capacities.⁵⁶ For many chemicals used in both conventional and unconventional oil and gas activities, communities and researchers have little or no data.⁵⁷

We used the GreenScreen® for Safer Chemicals⁵⁸ (GreenScreen) method to get a clear overview of the extent of the environmental and health hazards associated with oil and gas chemicals. GreenScreen, launched in 2007, sets the global standard for comparative chemical hazard assessment. Transparent, scientifically robust, and publicly available, GreenScreen is used by businesses such as HP and Nike to help inform chemicals management policies and product design and by state governments such as Maine and Washington as part of alternatives assessments to meet regulatory processes. GreenScreen is used in the US’s largest green building standard set by the US Green Building Council as well as the apparel industry’s global Zero Discharge of Hazardous Chemicals initiative. The GreenScreen method requires detailed scrutiny of all information

pertaining to a chemical’s hazard including the number of data gaps associated with that chemical. In addition the method also considers the hazards of the chemical’s breakdown products resulting in a highly precautionary approach to chemical screening. Because GreenScreen provides a rigorous and comprehensive overview of a chemical’s hazard in a clear and easy to read format, it has become the tool of choice for highly informed decision making.

GREENSCREEN® FOR SAFER CHEMICALS METHOD

GreenScreen categorizes chemicals into four benchmarks; each benchmark defines progressively safer chemicals, from *Benchmark-1 “Avoid—Chemical of High Concern”* to *Benchmark-4 “Prefer—Safer Chemical.”* A GreenScreen assessment is comprehensive and provides all the known information about a chemical and its environmental breakdown products, based on 18 hazard endpoints or categories of human health and environmental impact. In GreenScreen, a chemical’s hazard characteristics are defined by its potential to cause acute or chronic adverse effects in humans, environmental fate and toxicity, and certain physical/chemical properties that relate to worker safety. It does this by consolidating all the available data on a chemical’s inherent characteristics into a table of hazard endpoints, each ranked as high, moderate, or low. At a glance, the hazard tables show, for example, to what degree a chemical can be considered a carcinogen, a reproductive toxicant, an endocrine disruptor, or persistent in the environment.

From there, the hazard evaluations are further consolidated into a single benchmark that provides an easy means for comparing chemicals. GreenScreen is particularly valuable

55 See for example: McKenzie et. al. (2014). op.cit., Bolden et. al. (2015). op.cit.

56 Kassotis et. al. (2014). op.cit.

57 Bolden et. al. (2015). op.cit.

58 GreenScreen® for Safer Chemicals, op.cit.

because Benchmark-1 clearly defines the criteria for chemicals of high concern to human health and the environment consistent with international regulations such as Europe's Registration, Evaluation, and Authorisation of Chemicals (REACH).⁵⁹

GreenScreen assessments also identify data gaps; it is just as important to know when environmental or human health data do not exist for an endpoint. Lack of data does not imply safety. Ideally there would be comprehensive hazard data and knowledge of feasible environmental transformation or breakdown products for all chemicals. Unfortunately, this is seldom the case in either the chemical manufacturing arena, or in regard to fossil fuel chemicals.⁶⁰ A chemical with too many data gaps is classified as Benchmark-U "Unspecified Due to Insufficient Data."

HAZARD ASSESSMENT FINDINGS— GREENSCREEN BENCHMARK SCORES

GreenScreen hazard assessments of key chemicals associated with oil and gas production—including common BTEX chemicals—showed that many of these chemicals are highly toxic. GreenScreen Benchmark™ scores for chemicals found through biomonitoring are listed as follows:

12 chemicals found in urine were assessed as Benchmark-1 "Avoid Chemical of High Concern":

- Benzene
- Toluene
- o-xylene
- m,p-xylene
- xylenes which includes m-, o-, or p-xylene (isomers)
- Naphthalene
- Styrene
- 1,3 Butadiene
- Acrylonitrile
- Ethylene oxide
- Propylene oxide
- Vinyl chloride

Two chemicals found in urine were assessed as Benchmark-2 "Use but Search for Safer Substitutes":

- Ethylbenzene
- Acrolein

Two chemicals in urine were assessed as Benchmark-U "Unspecified Due to Insufficient Data":

- 2-heptanone
- 4-heptanone

The GreenScreen Hazard Summary Tables in Appendix 4 provide results for chemicals detected in both urine and air sampling. The hazard table for xylenes represents m,p-xylene as well as xylene. The complete GreenScreen assessments are available for [download](#).

BOX 4

Fracking Chemicals and GreenScreen

Evidence continues to mount on health and environmental impacts from the oil and gas industry's hydraulic fracturing (or "fracking") process use and release of chemicals.⁶¹ However the toxicity of the chemicals used is generally not well known; oil and gas companies' Confidential Business Information (CBI) requests shield the companies from releasing that information. In 2013, Clean Production Action analyzed chemicals used in hydraulic fracturing in the U.S.⁶² An initial screening assessment of 1100 chemicals and full GreenScreen assessments of 43 chemicals injected into fracking wells reveal that: 1) two-thirds of chemicals in widespread use in hydraulic fracturing have little or no information available on how hazardous they might be; 2) industry disclosure mechanisms are inadequate, while widespread use of 'trade secret' mechanisms thwart public oversight; 3) the industry is using more chemicals than previously listed on government databases; and 4) over 200 of those chemicals assessed were identified as substances of high hazard to both human health and the environment.

Although hydraulic fracking has been used as a method for extracting gas in Pavillion, in general, gas production in the area uses conventional methods, where the concern focuses on the toxic VOCs that are inherent to gas production.

59 European Commission (2016). REACH Regulation (EC 1907/2006); "No data no market": the REACH Regulation places responsibility on industry to manage the risks from chemicals and to provide safety information on the substances; http://ec.europa.eu/environment/chemicals/reach/reach_en.htm.

60 In the US, chemical manufacturers are not required to generate comprehensive test data before putting a chemical on the market; the vast majority of the more than 80,000 chemicals on the market have limited to no publicly available test data. The situation is changing in Europe since the introduction of REACH in 2007, but for now we live in a world of imperfect and incomplete chemical hazard data.

61 Macey et.al. (2014). op.cit. and Coming Clean and Global Community Monitor (2014). op.cit., Concerned Health Professionals of New York (2014). op.cit.

62 Penttila et. al. (2013). Submission: EPA Notice. Agency Information Collection Activities, Proposals, Submissions, and Approvals: Inform Hydraulic Fracturing Research Related to Drinking Water Resources. <https://www.regulations.gov/#/documentDetail;D=EPA-HQ-ORD-2010-0674-1770>.

CHAPTER SIX

CONCLUSIONS AND RECOMMENDATIONS

This report shows that the hazardous nature of volatile chemicals in gas condensate, which appears unavoidable in natural gas production, indicates that production cannot be carried out in a manner that truly protects workers or the public. These chemicals are present in air surrounding gas well head equipment and in the bodies of people living and working nearby. Many of the chemicals found in this study are chemicals of high concern and should be avoided. The high hazard of the VOCs emitted into the air, the fact that there are several examples where these chemicals exceed the Environmental Screening Limits for air, together with the findings that metabolites of some of these chemicals were in the urine of the people studied at levels that are well above those in the general population, is a cause for concern.

We also observed that the debate about oil and gas production is often focused on what can be done to make it safer, rather than taking a more precautionary approach⁶³ where the intrinsic hazards of the chemicals being emitted are taken into account (as in the hazard assessments that were done for this report), which asks whether or not oil and gas activities can be carried out safely, *period*.

The Precautionary Principle enables us to make decisions based not on irrefutable proof of cause-and-effect relationships but on prevention and protection, based on what we do know. The Pavillion study was not only an exercise in methods development; for the people living in the Pavillion area, who have lived among toxic chemicals from oil and gas development for decades, the study was a means of identifying the presence of toxic chemicals in the air and in their bodies, which could lead to better protection of their health and community. It is a basic human right for the community and for all people to be informed about

exposure to hazardous chemicals and to be protected from them.

Based on the monitoring research findings and the GreenScreen hazard assessment results, we recommend the following:

- **Encourage further biomonitoring research and use results to effectively prevent exposure.** Air monitoring data from this and previous studies show irrefutably, that oil and gas development is emitting highly toxic chemicals into the air that workers and families breathe each day. This data itself makes the case that people's health may be harmed. We have proven protocols for biomonitoring: the presence of the same chemicals in summa canisters, sorbent tubes and urine samples signals that air pollutants are getting into people's bodies. We believe this study is the first methods development of its kind, which can be a basis for additional research.
- Additional environmental monitoring and biomonitoring research by independent institutions should be conducted to help identify and understand the ways in which people and ecosystems are exposed to oil and gas chemicals, in order to reduce these exposures.
- Further research on the effects of chemicals associated with oil and gas development will also help understand the complex health impacts of these chemicals.
- State and federal agencies should utilize results from community-based research on the exposure pathways of toxic oil and gas chemicals, to more effectively reduce exposures and prevent harm to workers and community members from chronic, recurrent exposure to oil and gas chemicals and from oil and gas development as a whole.

63 A comprehensive definition of the precautionary principle is the Wingspread Statement on the Precautionary Principle from January 1998, which summarizes the principle this way: "when an activity raises threats of harm to the environment or human health, precautionary measures should be taken even if some cause and effect relationships are not fully established scientifically." http://www.sehn.org/Volume_3-1.html.

Fenton home and gas development site.



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- **Investigate the harmful impacts of cumulative exposure to multiple chemicals and how their toxicity may increase when they interact in mixtures, especially chemicals with endocrine disrupting effects, which may act at low levels.**
 - Additional research must be conducted by independent scientists, regulators and health professionals to further understand the harmful impacts of cumulative exposures from oil and gas chemicals and ubiquitous chemicals from other common (e.g. household, workplace and other industrial air emissions), in order to better protect public health.
- **Implement precautionary regulations, ensure disclosure and transparency.** Highly toxic chemicals present in the Pavillion area indicate that current environmental regulations are not adequately protecting community members from harm. While additional research can be helpful, regulatory agencies already have enough emissions data available to justify swift action to protect public health and the environment.
 - State and federal agencies must aggressively implement more protective, precautionary standards for chemical emissions, (e.g. for methane and VOCs; oil and gas fracking chemicals in water; and for toxic emissions at all phases of exploration and development).

These standards should apply not only to “new” or “modified” development activities but also to existing development.

- Companies that explore for, extract or process fossil fuels must fully and publicly disclose the chemicals used and emitted in all exploration and production activities at each phase of oil and gas production. Government agencies must mandate that oil and gas companies disclose all chemicals and constituents used in conventional and unconventional oil and gas development.
 - Government agencies such as the US Environmental Protection Agency (EPA) must ensure a transparent process, including community involvement, for the review and assessment of scientific information and data when setting protective standards.
-
- **Promote clean renewable energy sources and stop promoting natural gas as “clean” and “safe.”** The GreenScreen hazard assessment data shows that the chemicals released during oil and gas production—conventional and unconventional—pose high, inherent hazards to the environment and to people. Regulatory improvements to development activities (i.e. zoning setbacks, better industry safety practices) may alleviate some of these problems, however fundamental hazards will remain. Protecting workers, community members

“OUR BACKS ARE AGAINST A WALL, so we’ve decided to make a stand. I’m frequently asked why I don’t leave. We built our home with our own hands; our hearts are in the land. Fossil fuels development is a problem we can’t run from. After traveling across the US and the planet, I’ve seen the same problems caused by the invasion of the fossil fuels industry. I refuse to be a ‘cost of doing business.’”

— *John Fenton, local resident*

and the public from these hazards requires a comprehensive change in our energy system.

- Utilities, governments and businesses must invest in aggressive energy efficiency measures and clean, renewable energy sources to meet our nation's energy needs. Workers, small businesses and community members can work together to design and implement solutions that foster a healthy environment, safe jobs and strong economies so that communities that are currently economically dependent on fossil fuels are able to effectively transition to a 21st century sustainable economy.
- US and international governing institutions such as the United Nations must stop promoting natural gas as “clean” energy or a safe bridge fuel or alternative to other fossil fuels such as coal. The US and other world governments should instead invest in clean energy solutions that protect the health and well-being of all people.
- **Provide ongoing monitoring, health evaluation and site remediation to protect people already affected by oil and gas production.** The combination of monitoring data and hazard assessment data indicates that long-term and legacy contamination from long-term

oil and gas development in rural and urban areas⁶⁴ poses a health threat to residents and the public. The Pavillion/Muddy Ridge gas field consists of ageing and inadequately constructed wells, deteriorating infrastructure and known contamination that poses an even greater hazard as the field ages. The lack of government regulation and industry practices to address the legacy of contamination is a warning sign for other communities living with development and facing future development.

- Monitoring must continue through development and production, when wells are shut in and after wells have been plugged and abandoned, to ensure that the development no longer poses a hazard to the environment, people who live and work nearby and the public.
- Industry should be financially responsible for remediation of oil and gas development and production sites, as well as associated impacts and contamination off site, during drilling and production, when wells are shut in and after wells have been plugged and abandoned. Communities must not bear the ongoing burden of environmental contamination and toxic chemical exposures from industrial development.



Wyoming wind turbines generate clean energy.

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APPENDIX 1

PROFESSIONAL RESEARCH AND LABORATORY SERVICES

Professional research and laboratory services were provided by a number of laboratories. The various analytical techniques which were used are listed below, followed by details of the laboratories and their methodology.

ANALYTICAL TECHNIQUES USED

Headspace Gas Chromatography (GC)

A technique used for the concentration and analysis of volatile organic compounds. A headspace sample is normally prepared in a vial containing the sample, the dilution solvent, a matrix modifier and the headspace. Volatile components from complex sample mixtures can be extracted from non-volatile sample components and isolated in the headspace or vapor portion of a sample vial. An aliquot of the vapor in the headspace is delivered to a gas chromatography system for separation of all of the volatile components.

Gas Chromatography

The separation and analysis of different substances according to their different affinities for a standard absorbent. In the process a gaseous mixture of the substances is passed through a glass cylinder containing the absorbent, which may be dampened with a nonvolatile liquid solvent for one or more of the gaseous components. As the mixture passes through the absorbent, each substance is absorbed to a different extent and leaves a characteristic pigment. The bands of different colors left when all the gaseous mixture has moved through the absorbent constitute a chromatograph for analysis.

Mass Spectrometry (MS):

In order to measure the characteristics of individual molecules, a mass spectrometer converts them to ions so that they can be moved about and manipulated by external electric and magnetic fields. The three essential

functions of a mass spectrometer, and the associated components, are:

1. A small sample is ionized, usually to cations (a positively charged ion, i.e. one that would be attracted to the cathode in electrolysis), by loss of an electron.
2. The ions are sorted and separated according to their mass and charge.
3. The separated ions are then measured, and the results displayed on a chart.⁶⁶

Urine Analysis Protocol:

Dr Chung-Ho Li (University of Missouri)

Analysis of VOCs by SPME followed by GC-MS

To quantify the volatile organic compounds (VOCs) in the urine samples, including benzene, toluene, xylene, trimethylbenzene, the toluene-d8 was spiked into the samples as the internal standard, the VOCs were extracted by a headspace solid-phase microextraction (SPME) using a 85mm carboxen/polydimethylsiloxane fiber followed by the analysis with an Agilent 6890N gas chromatography coupled with an Agilent 5973N quadrupole mass spectrometer (GC-MS).

Analysis of Hydrophobic Metabolites by Liquid-Liquid Extraction followed by GC-MS

The hydrophobic metabolites in the urine samples were extracted by a water:dichloromethane (1:1, v/v) liquid-liquid procedure described by Lin (2007 and 2008). The identification and quantification of these metabolites were performed using a Varian 3400cx GC with a Hewlett Packard cross-linked methylsiloxane DB-5 capillary column (30 m x 0.25 mm I.D.) coupled with a Varian Saturn 2000 ion-trap mass selective detector (Varian Inc., Walnut Creek, CA).

65 (n.d.) *Mosby's Medical Dictionary, 8th edition.* (2009).

66 MSU, website. Mass Spectrometry. See sample charts under 2. The Nature of Mass Spectra. <https://www2.chemistry.msu.edu/faculty/reusch/VirtTxtJml/Spectrpy/MassSpec/masspec1.htm>.

Analysis of Polar Pollutants and their Metabolites by Liquid Chromatography Coupled with Tandem Mass Spectrometry

The concentrations of polar compounds and the metabolites in the urine samples, such as 2-hydroxy-N-methylsuccinimide, 2-methylhippuric acid, phenylglyoxylic acid and trans,transmuconic acid, were determined using Waters Alliance 2695 HPLC system coupled with Waters Acquity TQ triple quadrupole mass spectrometer (HPLC-MS/MS). The compounds were separated by a Phenomenex Kinetex C18 (100 mm x 4.6 mm; 2.6 mm particle size) reverse-phase column using electrospray ionization in either positive ion mode (ES+) or negative ion mode (ES-) with a capillary voltage of 1.5 kV. The molecular parent ions were screened and the product ions used for the quantifications were determined from the spectra of analytical standard solutions. Analytical data were processed using Waters Empower software (Waters Corp).

1. Lin, C H, Lerch, R N, Garrett, H E, George, M F: An Improved GC -MS/MS Method for determination of atrazine and its chlorinated metabolites uptake by forage plants-laboratory and field experiments. *Communications in Soil Science and Plant Analysis* 2007, 38:1753-1773.
2. Lin, C H, Lerch, R N, Garrett, H E, George, M F: Bioremediation of atrazine-contaminated soil by forage grasses: transformation, uptake, and detoxification. *Journal of Environmental Quality* 2008, 37:196-206.

NMS Laboratories Analysis: Headspace Gas Chromatography—2413B Inhalants Panel, Solvents and Gases—Blood

NMS did not detect levels for any of the VOCs tested for in the Pavillion blood samples. This may be because NMS Labs reporting levels are higher than the levels of VOCs that might have been present in blood samples. Commercial labs often use reporting levels rather than levels of detection. For example, NMS Laboratory reporting limit for benzene is 0.050 mcg/mL or 50 ng/mL.

The median level for benzene in blood in the US population (2001–2006) is 0.028 ng/mL, (CDC/NHANES Fourth Report_Updated Tables 2015), an amount below NMS reporting level for benzene.

OUR PILOT STUDY was intended to explore the methods and challenges of evaluating exposures to chemicals from gas production, with a view to refining the methods used in future projects.

Summa canister air sample analysis

(The analytical laboratory the study used does not give permission to be identified by name in general to community scientist research study reports without additional charges, which were not included in the study's budget.)

The method used by the study's analytical laboratory to analyze air samples is described below:

Summa Canister—EPA Method TO-15 is commonly used for the collection of volatile organic compounds (VOCs) in ambient and indoor air. EPA Method TO-15 is a procedure defined by EPA for air sample analysis (the Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition (EPA/625/R-96/010b), January, 1999). This procedure (GC/MS) is described in laboratory SOP VOA-TO15. (EPA/625/R-96/010b)

Method TO-15 utilizes a passivated (treated so that the canister inner service is nonreactive to chemicals) stainless steel canister (Summa canister) to collect an air sample. The Summa canisters are cleaned, prior to sampling, down to the method reporting limit. Once the air sample is collected and shipped to the lab for analysis, it is interfaced to a whole-air preconcentrator, a component that accumulates, concentrates and then releases the concentrated air sample into the **gas chromatograph/mass spectrometer analytical** system.

Sorbent Tube Analysis: INSTAAR Labs (Institute of Arctic and Alpine Research—Dr Detlev Helmig)

INSTARR uses FID/MS protocols for VOC analysis in air samples collected in sorbent tubes. FID (Flame Ionization Detector) is a method that can measure total volume of

VOCs in an air sample. MS is described elsewhere in appendix.

Sorbent tubes are the most widely used collection media for sampling hazardous gases and vapors in air, mostly as it relates to industrial hygiene. They were developed by the US [National Institute for Occupational Safety and Health](#) (NIOSH) for air quality testing of workers. Sorbent tubes are typically made of glass and contain various types of solid adsorbent material).

Commonly used sorbents include activated charcoal, silica gel, and organic porous polymers. Solid sorbents are selected for sampling specific compounds in air because they:

1. Trap and retain the compound(s) of interest even in the presence of other compounds
2. Do not alter the compound(s) of interest
3. Allow collected compounds to be easily desorbed or extracted for analysis

Sorbent tubes are attached to air sampling pumps for sample collection. A pump with a calibrated flow rate in ml/min is normally placed on a study participant's belt or other clothing, and it draws a known volume of air through the sorbent tube. Chemicals are trapped onto the sorbent material throughout the sampling period.

The absorbent tube is then placed in a heated chamber and purged with an inert gas. VOCs are thermally desorbed into a cryogenic trap, cryofocused onto the transfer line, separated by GC and analyzed by a positive ion electron impact Mass Spectrometer (MS).

APPENDIX 2

APPLICATION OF ENVIRONMENTAL SCREENING LEVELS TO LEVELS OF VOCS DETECTED IN AIR SAMPLES COLLECTED IN PAVILLION, WYOMING

Environmental Screening Levels (ESLs) are based on levels of toxic substances that public health agencies and environmental regulators have determined may pose a risk to human health. These ESLs include: 1) Minimal Risk Levels (MRLs)⁶⁷ developed by the US Agency for Toxic Substances and Disease Registry (ATSDR); 2) National Ambient Air Quality Standards (NAAQS)⁶⁸ and Reference Concentrations (RfCs)⁶⁹ developed by the US Environmental Protection Agency (USEPA); 3) Acute and Chronic Reference Exposure Levels (RELs)⁷⁰ and Cancer Potency Factors (CPFs)⁷¹ developed by the California Office of Environmental Health Hazard Assessment (OEHHA); and 4) Ambient Air Quality Guideline Values⁷² developed by the World Health Organization (WHO).⁷³

When applying ESLs to levels of volatile organic compounds (VOCs), it is important to consider two factors.

First, each ESL is developed to apply to a specific duration of time, ranging from short-term exposure periods (for example, one hour or one day) to long-term exposure periods (for example, one month, one year or a lifetime). USEPA Reference Concentrations and OEHHA Cancer Potency Factors are examples of ESLs that apply to very long-term exposure periods. Air samples collected in Pavillion, Wyoming in the latter half of 2014 are samples that were collected over very short-term periods—either instantaneously (for samples collected in Summa canisters)

or for roughly one hour (for samples collected in sorbent tubes). Therefore, application to VOC levels detected in air samples collected from Pavillion of ESLs for long-term exposure periods *requires an assumption that the air samples are representative of ambient air conditions that generally prevail at the location over long periods of time.*

Second, there is not an ESL for each VOC. Considering that there are literally millions of VOCs that might be present in the environment, public health agencies and environmental regulators prioritize their resources on developing ESLs for VOCs that are likely to be the most toxic. For example, of the 46 VOCs detected in air samples collected in sorbent tubes, public health agencies and environmental regulators have not developed an ESL for the following 36 VOCs:

- propene
- propane
- isobutane
- isobutene
- dichlorodifluoromethane
- 1-butene
- n-butane
- ethanol, isopentene
- trichlorofluoromethane
- 1-pentene
- 2-propanol
- pentane

67 An MRL is “an estimate of the daily human exposure to a hazardous substance that is likely to be without appreciable risk of adverse non-cancer health effects over a specified duration of exposure.” <http://www.atsdr.cdc.gov/mrls/mrlolist.asp>.

68 NAAQS “provide public health protection, including protecting the health of “sensitive” populations such as asthmatics, children, and the elderly.” <https://www.epa.gov/criteria-air-pollutants/naqs-table>.

69 An RfC is the “concentration of a chemical that one can breathe every day for a lifetime that is not anticipated to cause harmful noncancer health effects.” <https://www.epa.gov/iris>.

70 <http://oehha.ca.gov/air/allrels.html>.

71 http://oehha.ca.gov/air/hot_spots/tsd052909.html.

72 http://www.who.int/entity/phe/health_topics/outdoorair/databases/WHO_AAP_database_May2016_v3web.xlsx?ua=1.

73 <http://www.who.int/mediacentre/factsheets/fs313/en>.

- soprene
- 2,3-dimethylbutane
- 3-methylpentane
- 2-methyl-1-pentene
- methylcyclopentane
- 2-methylhexane
- n-heptane
- 4-methyl-2-pentanone
- methylcyclohexane
- 2-methylheptane
- 2-hexanone
- 4-methylheptane
- 2-hexanone
- 3-methylheptane
- octane
- nonane
- isopropylbenzene
- 1-pinene
- n-propylbenzene
- ethylmethylbenzene
- 1,3,5--trimethylbenzene
- 1,2,4--trimethylbenzene
- 1,2,3--trimethylbenzene.

Therefore, the ESL analysis omits discussion of the detected levels of these substances.

Table 5 below shows how ESLs were applied to VOC levels in air samples collected in Pavillion, Wyoming in August 2014.

The findings highlighted in red are VOC levels that exceed a short-term ESL. These are the most relevant to highlight since the air samples that were collected in sorbent tubes or summa canisters represent short-term air quality conditions.

Highlighted in yellow are VOC levels that exceed a long-term ESL. Application of these ESLs to the air samples collected in Pavillion requires an assumption that the air samples are representative of ambient air conditions that generally prevail at the location over long periods of time.

Highlighted in orange are levels of VOCs in excess of a level of exposure which increases a person's risk of cancer by more than 1 in 1 million. Application of these ESLs to the air samples collected in Pavillion also requires an assumption that the air samples are representative of ambient air conditions that generally prevail at the location over long periods of time.

Application of ESLs to VOC levels in air samples collected in Pavillion, Wyoming in August 2014 show that air quality was substantially impaired in the vicinity of the three well pads (42x-11, 22-12, and 14-03w) during that time.

Levels of benzene, toluene and xylenes in these samples exceed levels associated with adverse impacts to the central nervous system and the immune system for short-term exposures. Levels of cyclohexane in two of the three samples exceed levels associated with adverse impacts on fetal development for long-term exposures.

Levels of ethylbenzene in two of the three samples exceed levels associated with adverse impacts on kidney function for long-term exposures. Levels of hexane and naphthalene exceed levels associated with adverse impacts to the central nervous system for long-term exposures.

Application of ESLs to VOC levels in air samples collected in Pavillion, Wyoming in the latter half of 2014 also show that exposure of farmers to carcinogenic levels of benzene and naphthalene might present a public health risk. All but one of the levels of benzene and nearly half of the levels of naphthalene in air samples collected by farmers in sorbent tubes exceed levels associated with a more than 1 in 1 million excess risk of cancer for long-term exposure. However, it should also be noted that the average level of benzene in the air samples collected by farmers in sorbent tubes (0.41 ppb) is consistent with typical levels of benzene in rural areas (0.47 ppb).⁷⁴ In contrast, the average level of naphthalene collected by farmers in sorbent tubes (0.08 ppb = approximately 0.4 µg/m³) is substantially above typical levels of benzene in remote or rural areas (less than 0.001 ppb).⁷⁵

74 "The following daily median benzene air concentrations were reported in the Volatile Organic Compound National Ambient Database (1975–1985): remote (0.16 ppb), rural (0.47 ppb), suburban (1.8 ppb), urban (1.8 ppb), indoor air (1.8 ppb), and workplace air (2.1 ppb). The outdoor air data represent 300 cities in 42 states while the indoor air data represent 30 cities in 16 states (Shah and Singh 1988)." U.S. Agency for Toxic Substances and Disease Registry, (August 2007) "Toxicological Information Profile for Benzene."ASTDR (2007) op.cit.

75 "A mean naphthalene concentration of 0.129 ng/m³ was detected in ambient air at the Mississippi Sandhill Crane National Wildlife Refuge, Jackson County from May to September 1991 (White and Hardy 1994)." U.S. Agency for Toxic Substances and Disease Registry, (August 2005) "Toxicological Information Profile for Naphthalene." www.atsdr.cdc.gov/toxprofiles/tp67.pdf.

TABLE 5

Levels of 10 VOCs in Summa Canisters and Sorbent Tubes, Compared to ESLs

VOC levels detected in sorbent tubes (in ppb)											
Chemical	Lowest detected level	Average level	Highest detected level	ESLs short term		ESLs long term			ESLs for Cancer		
				ATSDR MRL-acute	OEHHA acute REL	ATSDR MRL-chronic	ATSDR MRL-intermediate	EPA RfC	OEHHA chronic REL	EPA	Cal OEHHA
acetone	BDL	12.32	52.6	26000	none	1300	1300	none	none	none	none
2-butanone	0.02	0.49	2.45	none	4500	none	none	1695	none	none	none
hexane	0.02	1.19	6.14	none	none	600	none	200	2000	none	none
ethylacetate	BDL	0.97	6.21	none	none	none	none	250	none	none	none
benzene	BDL	0.41	1.12	9.00	8.00	3.00	6.00	9.40	1.00	0.04	0.10
cyclohexane	0.02	0.84	6.27	none	none	none	none	1715	none	none	none
toluene	BDL	1.44	3.73	2000	9800	1000	none	1325	70	none	none
ethylbenzene	BDL	0.18	0.54	5000	none	60	2000	600	400	none	none
xylenes	BDL	0.84	2.75	2000	5000	50	600	23	200	none	0.92
naphthalene	0.01	0.08	0.36	none	none	0.7	none	200	2.0	none	0.056

VOC levels detected in summa canisters (in ppb)											
Chemical	Lowest detected level	Average level	Highest detected level	ESLs short term		ESLs long term			ESLs for Cancer		
				ATSDR MRL-acute	OEHHA acute REL	ATSDR MRL-chronic	ATSDR MRL-intermediate	EPA RfC	OEHHA chronic REL	EPA	Cal OEHHA
acetone	BDL	BDL	BDL	26000	none	1300	1300	none	none	none	none
2-butanone	BDL	BDL	BDL	none	4500	none	none	1695	none	none	none
hexane	0.61	3303	11000	none	none	600	none	200	2000	none	none
ethylacetate	BDL	BDL	BDL	none	none	none	none	250	none	none	none
benzene	8.7	360	780	9.00	8.00	3.00	6.00	9.40	1.00	0.04	0.10
cyclohexane	0.66	3643	12000	none	none	none	none	1715	none	none	none
toluene	0.3	1179	2400	2000	9800	1000	none	1325	70	none	none
ethylbenzene	BDL	5300	1300	5000	none	60	2000	600	400	none	none
xylenes	0.4	5388	18300	2000	5000	50	600	23	200	none	0.92
naphthalene	BDL	147.5	210	none	none	0.7	none	200	2.0	none	0.056

- RED = VOC levels that exceed a short-term ESL.
- YELLOW = VOC levels that exceed a long-term ESL.
- ORANGE = VOC levels that exceed a level exposure which is estimated to increase a person's risk of cancer by more than 1 in 1 million.

APPENDIX 3

VOCS AND METABOLITES IN THE URINE OF RESIDENTS OF PAVILLION

Table 6 below details the aggregate data of VOCs and their metabolites in the urine of Pavillion residents studied and contains composite information about these levels (median and max); it also contains information about levels of VOCs and VOC metabolites in the urine of the general population. Values are from the CDC NHANES dataset with the exception of values for hippuric acid (a marker of toluene exposure).⁷⁶ The CDC HANES did not test urine for the chemical parent.

The levels of hippuric acid (a marker of toluene exposure) and trans,transmuconic acid (a marker of benzene exposure) in the urine of residents of Pavillion are significantly higher than levels of these same chemicals in the urine of the general population.

For example, the median level of trans,transmuconic acid (ttMA) in the urine of residents of Pavillion is 10 times higher than the median level of ttMA in the urine of the general population. In addition, the median level of ttMA in the urine of residents of Pavillion is higher than the median level of ttMA in refinery workers in Brazil (post-shift).⁷⁷ The max level ttMA in the urine of residents of Pavillion is 4–5 times higher than the 95th percentile level of ttMA in the urine of the general population and even higher than the Biological Exposure Index (BEI) for ttMA established by the American Conference of Governmental Industrial Hygienists (ACGIH) of 500 µg/g creatinine.⁷⁸

Similarly, the median level of hippuric acid in the urine of residents of Pavillion is 80% higher than the level of this

chemical in the urine of the general population. The maximum level of hippuric acid in the urine of residents of Pavillion is more than 2 times higher than the level of this chemical in the urine of the general population. PMA (N-Acetyl-S-(phenyl)-L-cysteine)—another marker of benzene exposure—in the urine of residents of Pavillion is many times lower than levels of these same chemicals in the urine of the general population. The highest level of PMA in the urine of residents of Pavillion is 70% lower than the 95th percentile of PMA in the urine of the general population. However, there is no consensus in the scientific community about the validity of PMA as a reliable biomarker for benzene exposure.

Levels of the following substances in the urine of residents of Pavillion showed noticeable but inconsistent variations with levels of these substances in the urine of the general population: MHBMA (N-Acetyl-S-(2-hydroxy-3-butenyl)-L-cysteine), HEMA (N-Acetyl-S-(2-hydroxyethyl)-L-cysteine), CNEMA/CYMA (N-Acetyl-S-(2-cyanoethyl)-L-cysteine), 3-HPMA (N-Acetyl-S-(3-hydroxypropyl)-L-cysteine), 2-HPMA (N-Acetyl-S-(2-hydroxypropyl)-L-cysteine), AAMA (N-Acetyl-S-(2-carbamoylethyl)-L-cysteine), and HPMMA (N-Acetyl-S-(3-hydroxypropyl-1-methyl)-L-cysteine) (the last 7 rows of Table 6). However, the differences between Pavillion levels and levels in the general population seem random, and these substances are not markers for exposure to VOCs typically emitted by natural gas production wells (e.g. many of these substances are biomarkers for exposure to tobacco smoke, wood smoke, for diesel emissions).

76 CDC (2015) 4th report Feb. 2015 update; http://www.cdc.gov/biomonitoring/pdf/FourthReport_UpdatedTables_Feb2015.pdf. For hippuric acid: Siqueira, M E P & Paiva, M J N (2002). Hippuric acid in urine: reference values, *Revista de Saúde Pública*, 36(6), 723-727

76 Martins, I, & Siqueira, M E P B D (2004). Trans, trans-muconic acid in urine samples collected in three periods from benzene handling workers in a Brazilian refinery. *Revista Brasileira de Ciências Farmacêuticas*, 40(2), 197–201.

77 See: https://www.osha.gov/dts/osta/otm/otm_ii/pdfs/otmii_chpt2_appb.pdf.

TABLE 6

VOCs and Metabolites in Urine Samples of Pavillion Study Participants, Compared to the General Population

Level of chemical in urine samples of residents of Pavillion, Wyoming (August 2014), micrograms per gram of creatinine				Level of chemical in general population ⁷⁸	
Chemical Metabolite	Parent	Median (µg/g)	Max (µg/g)	Median (µg/g)	95th Percentile
Benzene	Benzene	0.022	0.385	No data	No data
Ethylbenzene	Ethylbenzene	0.012	0.271	No data	No data
m/p-Xylene	m/p-Xylene	BDL	0.118	No data	No data
Styrene	Styrene	0.089	0.531	No data	No data
O-xylene	O-xylene	BDL	0.274	No data	No data
Toluene	Toluene	0.256	2.917	No data	No data
4-Heptanone	4-Heptanone	19.869	214.953	No data	No data
2-Heptanone	2-Heptanone	2.216	10.358	No data	No data
Naphthalene	Naphthalene	0.210	1.078	No data	No data
Hippuric acid	Toluene, cinnamaldehyde	322,958.63	1,197,549.00	180,000.00	360,000.00
2-hydroxy-N-methylsuccinimide	N-Methyl-2-pyrrolidone (NMP)	64,852.71	218,422.00	No data	No data
2-pyrrolidone	N-Methyl-2-pyrrolidone (NMP)	309.165	1638.980	No data	No data
Mandelic acid	Ethylbenzene, Styrene	214.608	2466.240	158.00	513
4-Methylhippuric acid	Xylene	92.119	1394.593	212.000	1540
2-Methylhippuric acid	Xylene	80.975	630.937	35.200	248.000
3-Methylhippuric acid	Xylene	99.033	643.311	212.000	1540
a-naphthylglucuronide	Naphthalene	924.94	6809.76	No data	No data
b-naphthylsulphate	Naphthalene	8.65	2865.919	No data	No data
1-naphthol (1-naphthalenol)	Naphthalene	BDL	255.729	No data	No data
Phenylglyoxylic acid	Ethylbenzene, styrene	53.384	411.338	206.000	518
trans, transmuconic acid	Benzene	369.350	2045.534	76.9	473
PMA (N-Acetyl-S-(phenyl)-L-cysteine)	Benzene	BDL	0.977	BDL	3.030
MHBMA (N-Acetyl-S-(2-hydroxy-3-butenyl)-l-cysteine)	1,3-butadiene	BDL	0.840	BDL	3.700
HEMA (N-Acetyl-S-(2-hydroxyethyl)-l-cysteine)	Acrylonitrile, Vinyl chloride	1.320	3.615	0.941	4.750
CNEMA/CYMA (N-Acetyl-S-(2-cyanoethyl)-L-cysteine)	Acrylonitrile	1.295	31.922	1.830	256.000
3-HPMA (N-Acetyl-S-(3-hydroxypropyl)-l-cysteine)	Acrolein	388.475	7057.75	276.000	2190.000
2-HPMA (N-Acetyl-S-(2-hydroxypropyl)-l-cysteine)	Propylene oxide	35.046	162.473	50.800	284.000
AAMA (N-Acetyl-S-(2-carbamoyl-ethyl)-l-cysteine)	Acrylamide	99.091	199.188	49.500	199.000
HPMMA (N-Acetyl-S-(3-hydroxy-propyl-1-methyl)-l-cysteine)	Crotonaldehyde	235.118	630.465	398.000	3970.000

78 Data is all from CDC (2015) op.cit., except for Hippuric acid which is Siquiera et.al. (2002), op.cit.

APPENDIX 4

GREENSCREEN ASSESSMENTS OF CHEMICALS FOUND IN URINE OF STUDY PARTICIPANTS, PAVILLION

Note that the full GreenScreen reports are available at <http://cleanproduction.org/resources/entry/pavillion-report>.

GreenScreen Benchmark Score and Hazard Summary Tables

Abbreviations in all of these tables are as follows:

C	Carcinogenicity	SnR	Respiratory sensitization	SnS	Skin sensitization	vH	Very High
M	Mutagenicity	IrS	Skin irritation	CA	Chronic aquatic toxicity	H	High
R	Reproductive Toxicity	IrE	Eye irritation	P	Persistence	M	Moderate
D	Developmental Toxicity	AA	Acute aquatic toxicity	B	Bioaccumulation	L	Low
E	Endocrine activity	ST	Systemic toxicity	Rx	Reactivity	vL	Very Low
AT	Acute mammalian toxicity	N	Neurotoxicity	F	Flammability	DG	Data Gap

Hazard levels in *italics* reflect estimated (modeled) values, authoritative B lists, screening lists, weak analogues, and lower confidence. Hazard levels in **BOLD** font are used with good quality data, authoritative A lists, or strong analogues. The following color scheme also denotes the hazard classification for each hazard endpoint:

■ vL deep green	■ M yellow	■ vH deep red
■ L light green	■ H red	□ DG white

Benzene was assigned a **Benchmark Score of 1** (“Avoid—Chemical of High Concern”) as it has High Group 1 Human Toxicity (High carcinogenicity (C), mutagenicity (M), reproductive toxicity (R), and developmental toxicity (D)). This corresponds to GreenScreen® benchmark classification 1e in CPA 2011. There are no data gaps.

Group I Human						Group II and II* Human								Ecotox		Fate		Physical	
C	M	R	D	E	AT	ST		N		SnS*	SnR*	IrS	IrE	AA	CA	P	B	Rx	F
						SINGLE	REPEATED*	SINGLE	REPEATED*										
H	H	H	H	<i>M</i>	L	vH	H	M	H	L	<i>L</i>	H	H	H	H	<i>vL</i>	<i>vL</i>	<i>L</i>	H

Toluene was assigned a **Benchmark Score of 1** based on failure of Benchmark Rule 1e, due to High reproductive and developmental toxicity.

Group I Human						Group II and II* Human								Ecotox		Fate		Physical	
C	M	R	D	E	AT	ST		N		SnS*	SnR*	IrS	IrE	AA	CA	P	B	Rx	F
						SINGLE	REPEATED*	SINGLE	REPEATED*										
DG	L	H	H	<i>M</i>	L	M	<i>M</i>	M	H	L	DG	H	L	H	H	<i>H</i>	<i>vL</i>	L	H

o-Xylene was assigned a **Benchmark Score of 1** based on a High Group I human health endpoints (Developmental toxicity (D)). A data gap (DG) exist for respiratory sensitization (SnR). o-Xylene meets requirements for a GreenScreen® Benchmark Score of 1 despite the hazard data gaps. In a worst-case scenario, if ethylene oxide were assigned a High score for respiratory sensitization, it would still be categorized as a Benchmark 1 Chemical.

Group I Human						Group II and II* Human								Ecotox		Fate		Physical	
C	M	R	D	E	AT	ST		N		SnS*	SnR*	IrS	IrE	AA	CA	P	B	Rx	F
						SINGLE	REPEATED*	SINGLE	REPEATED*										
L	L	M	H	M	M	M	M	M	H	L	DG	H	M	H	M	vL	vL	L	M

Ethylbenzene was assigned a **Benchmark Score of 2** (“Use but Search for Safer Substitutes”) based on Moderate Group I human health endpoints (carcinogenicity (C), developmental toxicity (D), and endocrine activity (E)); High Flammability (F); and a score of very high single dose neurotoxicity (N). A data gap (DG) exist for respiratory sensitization (SnR). Ethylbenzene meets requirements for a GreenScreen® Benchmark Score of 2 despite the hazard data gaps. In a worst-case scenario, if ethylbenzene were assigned a High score for respiratory sensitization it would still be categorized as a Benchmark 2 Chemical.

Group I Human						Group II and II* Human								Ecotox		Fate		Physical	
C	M	R	D	E	AT	ST		N		SnS*	SnR*	IrS	IrE	AA	CA	P	B	Rx	F
						SINGLE	REPEATED*	SINGLE	REPEATED*										
M	L	L	M	M	M	M	M	vH	M	L	DG	H	M	H	H	M	L	L	H

Naphthalene was assigned a **Benchmark Score of 1** based on criteria 1e (high concern for Group I Human health endpoint: cancer and possibly endocrine activity). This Benchmark score meets the Data Gap analysis. Note this chemical is also flagged on a number of PBT lists, however no data was found to support a concern for bioaccumulation.

Group I Human						Group II and II* Human								Ecotox		Fate		Physical	
C	M	R	D	E	AT	ST		N		SnS*	SnR*	IrS	IrE	AA	CA	P	B	Rx	F
						SINGLE	REPEATED*	SINGLE	REPEATED*										
H	M	DG	L	M	M	vH	H	M	DG	M	DG	M	L	vH	H	M	L	L	M

Propylene oxide was assigned a **Benchmark Score of 1** based on High Group I human health endpoints (carcinogenicity (C), mutagenicity (M), and reproductive toxicity (R)). A data gap (DG) exist for respiratory sensitization (SnR) and chronic aquatic toxicity (CA). Propylene oxide meets requirements for a GreenScreen® Benchmark Score of 1 despite the hazard data gaps. In a worst-case scenario, if ethylene oxide were assigned a High score for respiratory sensitization or chronic aquatic toxicity it would still be categorized as a Benchmark 1 Chemical.

Group I Human						Group II and II* Human								Ecotox		Fate		Physical	
C	M	R	D	E	AT	ST		N		SnS*	SnR*	IrS	IrE	AA	CA	P	B	Rx	F
						SINGLE	REPEATED*	SINGLE	REPEATED*										
H	H	H	M	M	M	M	M	M	M	M	DG	H	H	M	DG	vH	vL	M	vH

1,3 Butadiene was assigned a **Benchmark Score of 1** based on high Group 1 human health endpoints (carcinogenicity, mutagenicity, reproductive toxicity). Data gaps (DG) exist for skin sensitization (SnS), respiratory sensitization (SnR), skin irritation (IrS) and chronic aquatic toxicity (CA). 1,3 Butadiene meets requirements for a GreenScreen® Benchmark Score of 1 despite the hazard data gaps. In a worst case scenario even if 1,3 Butadiene were assigned a High score for the data gaps it would still be categorized as a Benchmark 1 Chemical.

Group I Human					Group II and II* Human								Ecotox		Fate		Physical		
C	M	R	D	E	AT	ST		N		SnS*	SnR*	IrS	IrE	AA	CA	P	B	Rx	F
						SINGLE	REPEATED*	SINGLE	REPEATED*										
H	H	H	M	M	L	L	M	M	M	DG	DG	DG	L	M	DG	M	vL	M	H

Acrylonitrile was assigned a **Benchmark Score of 1** based on High Group I human health endpoints (carcinogenicity (C), mutagenicity (M), and reproductive toxicity (R)). A data gap (DG) exist for respiratory sensitization (SnR). Acrylonitrile meets requirements for a GreenScreen® Benchmark Score of 1 despite the hazard data gaps. In a worst-case scenario, if acrylonitrile were assigned a High score for respiratory sensitization it would still be categorized as a Benchmark 1 Chemical.

Group I Human					Group II and II* Human								Ecotox		Fate		Physical		
C	M	R	D	E	AT	ST		N		SnS*	SnR*	IrS	IrE	AA	CA	P	B	Rx	F
						SINGLE	REPEATED*	SINGLE	REPEATED*										
H	H	H	M	M	H	M	vH	M	H	H	DG	H	vH	H	M	H	vL	M	H

Acrolein was assigned a **Benchmark Score of 2** based on Moderate Group I human health endpoints (carcinogenicity (C), mutagenicity (M), and developmental toxicity (D)); very high Group II human health endpoints (acute mammalian toxicity (AT), single exposure systemic toxicity (ST), skin irritation (IrS), eye irritation (IrE)); high Group II* human health endpoints (repeat exposure systemic toxicity (ST)); very high ecotoxicity (acute and chronic aquatic toxicity (AA and CA)) and high flammability (F)). Data gaps (DG) exist for endocrine activity (E) and respiratory sensitization (SnR). Acrolein meets requirements for a GreenScreen® Benchmark Score of 2 despite the hazard data gaps. In a worst-case scenario, if acrolein were assigned a High score for endocrine activity it would be categorized as a Benchmark 1 Chemical.

Group I Human					Group II and II* Human								Ecotox		Fate		Physical		
C	M	R	D	E	AT	ST		N		SnS*	SnR*	IrS	IrE	AA	CA	P	B	Rx	F
						SINGLE	REPEATED*	SINGLE	REPEATED*										
M	M	L	M	DG	vH	vH	H	H	H	M	DG	vH	vH	vH	vH	vL	L	H	H

Vinyl chloride was assigned a **Benchmark Score of 1** based on high Group 1 human health endpoints (carcinogenicity and mutagenicity) and very high persistence along with high Group II* human health endpoints. Data gaps (DG) exist for skin sensitization (SnS), respiratory sensitization (SnR), skin irritation (IrS) and chronic aquatic toxicity (CA). Vinyl chloride meets requirements for a GreenScreen® Benchmark Score of 1 despite the hazard data gaps. In a worst-case scenario, if vinyl chloride were assigned a High score for the data gaps it would still be categorized as a Benchmark 1 Chemical.

Group I Human					Group II and II* Human								Ecotox		Fate		Physical		
C	M	R	D	E	AT	ST		N		SnS*	SnR*	IrS	IrE	AA	CA	P	B	Rx	F
						SINGLE	REPEATED*	SINGLE	REPEATED*										
H	H	M	M	M	L	L	H	M	H	DG	DG	DG	M	L	DG	vH	vL	M	H

Styrene was assigned a **Benchmark Score of 1** based on a high Group 1 human health endpoint (carcinogenicity). No data gaps exist for styrene.

Group I Human					Group II and II* Human								Ecotox		Fate		Physical		
C	M	R	D	E	AT	ST		N		SnS*	SnR*	IrS	IrE	AA	CA	P	B	Rx	F
						SINGLE	REPEATED*	SINGLE	REPEATED*										
H	M	L	M	M	M	M	M	H	H	M	M	H	H	H	M	M	vL	M	M

4-Heptanone was assigned a **Benchmark Score of U** (“Unspecified Due to Insufficient Data”) based on not meeting the data requirements for a benchmark 2 or higher score. Specifically, data do not exist for carcinogenicity and exists only for 2 of the 3 Group 1 Human Health endpoints. In a worst case scenario, if 4-heptanone were assigned a High score for the Group 1 Human Health data gaps it would be categorized as a Benchmark 1 Chemical.

Group I Human					Group II and II* Human								Ecotox		Fate		Physical		
C	M	R	D	E	AT	ST		N		SnS*	SnR*	IrS	IrE	AA	CA	P	B	Rx	F
						SINGLE	REPEATED*	SINGLE	REPEATED*										
DG	L	L	DG	DG	M	L	L	M	L	L	DG	M	M	M	M	L	vL	L	M

2-Heptanone was assigned a **Benchmark Score of U** based on not meeting the data requirements for a benchmark 2 or higher score. Specifically, data does not exist for carcinogenicity and exists for only 2 of the 3 Group 1 Human Health endpoints. In a worst case scenario, if 2-heptanone were assigned a High score for the Group 1 Human Health data gaps, it would be categorized as a Benchmark 1 Chemical.

Group I Human					Group II and II* Human								Ecotox		Fate		Physical		
C	M	R	D	E	AT	ST		N		SnS*	SnR*	IrS	IrE	AA	CA	P	B	Rx	F
						SINGLE	REPEATED*	SINGLE	REPEATED*										
DG	L	L	DG	DG	M	L	L	M	L	L	DG	M	M	M	M	vL	vL	M	M

Ethylene oxide was assigned a **Benchmark Score of 1** based on High Group I human health endpoints (carcinogenicity (C), mutagenicity (M), reproductive toxicity (R), and developmental toxicity (D)). The Benchmark 1 score is also based on very high persistence (P) along with very high Group II human health endpoint (single dose neurotoxicity (N)) or very high P along with high Group II* human health endpoints (repeat dose neurotoxicity (N)). A data gap (DG) exist for respiratory sensitization (SnR) and chronic aquatic toxicity (CA). Ethylene oxide meets requirements for a GreenScreen® Benchmark Score of 1 despite the hazard data gaps. In a worst-case scenario, if ethylene oxide were assigned a High score for respiratory sensitization or chronic aquatic toxicity it would still be categorized as a Benchmark 1 Chemical.

Group I Human					Group II and II* Human								Ecotox		Fate		Physical		
C	M	R	D	E	AT	ST		N		SnS*	SnR*	IrS	IrE	AA	CA	P	B	Rx	F
						SINGLE	REPEATED*	SINGLE	REPEATED*										
H	H	H	H	M	H	M	M	vH	H	M	DG	H	H	M	DG	vH	vL	H	H

WHEN THE WIND BLOWS

TRACKING TOXIC CHEMICALS IN GAS FIELDS AND IMPACTED COMMUNITIES

In 2014 a team of residents from the area of Pavillion, Wyoming, science and health experts, and environmental health groups, collaborated on a project to test the air and residents' bodies for chemicals known to be linked to oil and gas production. This is the first study which combines environmental sampling with the monitoring of body tissues or fluids (biomonitoring) of community members in very close proximity to gas production equipment and activities.

Through this research project, we designed and tested methods for environmental monitoring and exposure assessment in people living near oil and gas fields. We did this by using a variety of air monitoring tools with the capacity to test for VOCs, which are a large group of carbon-based chemicals that easily evaporate at room temperature. VOCs can be both naturally occurring and man-made.

Pavillion area community members hope to use the monitoring results to encourage legislators and regulatory agencies to protect residents' health and to help other communities facing existing or new oil and gas development avoid the health challenges that Pavillion area residents are facing. A precautionary approach to decision making is critical if we are to truly protect public health and the environment. For communities impacted by existing oil and gas development this needs to happen now and it is not too late to prevent future damage in communities which are threatened with new development.

The report is available online at <http://comingcleaninc.org>.

For more information related to this report, contact
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