Title

Investigating the Human Health Impact Zone and Exposures near Oil and Natural Gas Development and Storage during both Routine and Non-routine Operations

Author

Garcia-Gonzales, Diane Armida

Publication Date

2018

Investigating the Human Health Impact Zone and Exposures near Oil and Natural Gas Development and Storage during both Routine and Non-routine Operations

By

Diane A. Garcia-Gonzales

A dissertation submitted in partial satisfaction of the
requirements for the degree of
Doctor of Philosophy
in
Environmental Health Sciences
in the
Graduate Division
of the
University of California, Berkeley

Committee in charge:
Professor Michael B Jerrett, Chair
Professor John Balmes
Professor Rachel Morello-Frosch
Professor Allen Goldstein

Summer 2018

Investigating the Human Health Impact Zone and Exposures near Oil and Natural Gas Development and Storage during both Routine and Non-routine Operations

Abstract

Investigating the Human Health Impact Zone and Exposures near Oil and Natural Gas Development and Storage during both Routine and Non-routine Operations

by

Diane A. Garcia-Gonzales

Doctor of Philosophy in Environmental Health Sciences

University of California, Berkeley

Professor Michael Jerrett, Chair

Within the past decade, major technological advancements in oil and natural gas development have made extraction of hydrocarbon resources economically feasible. As the demand for oil and natural gas development increases, the public and regulatory agencies have become increasingly concerned about human and environmental impacts of the development and storage processes. Oil and natural gas operations are known sources of greenhouse gases and of emissions associated with adverse environmental and human health outcomes; however, research efforts aimed at understanding these impacts have been outpaced by the rapidly evolving technology and increased production efforts of the past decade. While recent research has provided insights into the impacts of oil and natural gas development, there is still limited information on the full range of potential exposures from the upstream process, and a dearth of literature on the impacts of emissions from natural gas storage.

Various attempts to identify and classify all products and chemicals used during the oil and natural gas development processes have resulted in disparate, and often contradictory, lists ranging from hundreds to thousands of chemical constituents. Chemicals of particular concern due to their potential to cause cancer and other serious health effects, have been categorized as hazardous air pollutants (HAPs) by the U.S. Environmental Protection Agency (U.S. EPA). To identify the full range of HAPs measured near upstream oil and natural gas development sites in recent scientific literature, we conducted a critical review of peer-reviewed research published between 2012 and 2018. From this review, we identified over 61 individual HAPs that have been investigated, of which 32 HAPs were collected as primary datasets. Additional efforts to recategorize sourced emissions found that the production phase, with its lengthy operation timeframe and episodic peak emission events, has the potential to emit the highest concentrations of associated HAPs over the longest time period. Results from chapter one provided the impetus for investigations included in the following chapters.

From the critical review conducted in chapter one, we identified a growing, yet still relatively small body of studies that investigates the relationship between the proximity of upstream oil and natural gas facilities and exposures to air pollutant emissions. With a dearth of scientific data, it is difficult to fully understand exposure risks and offer scientific guidance on specific adequate set-back requirements. In chapters two and three, we expanded our investigations to include the oil and natural gas air pollution exposure impact zones during upstream activities. From the

evidence elucidated from the previous chapter, we targeted active oil and natural gas wells in the production phase and measured several indicative HAP compounds. We deployed passive samplers at varying distances along transects through upstream oil and natural gas development facilities to understand emission related gradient behaviors. Results along the sampled transects in semi-rural Colorado, suggest benzene, toluene, and n-hexane reach background concentrations at around 220 meters from the facilities. Additional measurements of various sized particles suggest PM can be measured in ambient air at distances as far as 560 meters from the facility fence line.

While much of the focus has been on the oil and natural gas development in rural and semi-rural regions, few studies have focused on emissions and the impact on human health in the state of California, where there are approximately 58,000 active wells. Despite the presence of multiple competing sources and the difficulties associated with deployment in dense urban environments, we were able to identify gradient behavior along the transect downwind of the target facility; correlate target HAPs with the natural gas tracer compound, n-pentane; and identify the added air quality exposure burden from the targeted facility. From these investigations, distance decay gradient samples suggest benzene and n-hexane reach background concentrations between 125 and 150 meters from the facility fence line within this dense urban environment.

The 2015 Aliso Canyon natural gas blowout provided a unique research opportunity to further our investigations during an on-going anthropogenic disaster event. Armed with the findings from the previous chapters, we focused our investigations on HAP compounds and speciated particles. Initial results revealed higher and more variable concentrations of particles in the outdoor air at locations close to the blowout site compared to those farther away. Subsequent sampling of indoor environments found a characteristic "fingerprint" of metals in the indoor dust samples similar to samples taken at the blowout site. Canonical correlation analyses of this metal signature showed that newer homes and homes with professionally installed weather proofing materials installed as a result of the blowout had lower metal concentrations. Additionally, we found compelling evidence that several HAPs were elevated in the surrounding communities of Porter Ranch during the blowout event, and final attempts to plug the well were associated with particle emissions. Taken together, our results suggest that the blowout and attempts to plug the well had a discernable effect on the indoor air environments of sampled homes.

The full understanding of human health impacts from exposures to underground natural gas storage related emissions remain tenuous. To the best of our knowledge, the work contained within the listed chapters is the first to investigate gradient behaviors around oil and natural gas development in downtown Los Angeles, to measure and characterize the impact zone of speciated particles near upstream activities, and to characterize potential exposures from particles from an anthropogenic natural gas storage blowout event. The current results expand on the dearth of studies examining impacts from oil and natural gas development and storage emissions, yet the need for additional research remains of high importance. We anticipate these results will serve as a guide for future research and help develop necessary policies to protect communities at risk of exposures from both routine and non-routine emission events.

Dedication

This dissertation is dedicated to….

My beloved friend: True, deep friendship is rare and, when achieved, is usually the product of the numerous years of shared experiences; seldom are such deep bonds developed while in adulthood. Through providential circumstances on the first day of orientation, I was granted the exceptionally rare opportunity of developing such an instantaneous, yet interminable, connection with my academic colleague, Dr. Kelsi Perttula. Over the past six years, the amplifying love and respect I have felt for this cherished individual has only proved the bonds of true friendship are incalculable.

My mother and grandmother: When I started this journey, I returned to my childhood home in the Bay Area to live with my mother and grandmother, Sylvia Garcia and Armida Garcia. For the first two years of my PhD program, these two amazing women fed and housed me, allowing me to focus solely on my studies. Later, when I married and had my children, they continued their support by caring for their grandchildren and great-grandchildren while I commuted to and from campus. They asked for nothing in return, except to see me finish. For this reason, and so much more, my love for them is endless.

My family: To my husband, Aaron Cassidy, and our two children, Hudson Bear and Cala Wren, I thank you for giving me purpose. Words cannot adequately convey my deep sense of gratitude for your love. I am, because of you.

Table of Contents

List of Figures

List of Tables

Acknowledgments

There are no proper words to convey the depth of my gratitude for all those who have played essential roles in the completion of my graduate degree. Although my words may fall short, my profound appreciation for my family, friends, fellow students, professors, and staff within the division of Environmental Health Sciences endures. This dissertation is a cumulative manuscript of a six-year long academic endeavor, making it nearly impossible to include all those who have contributed to its completion; however, those whose names were not encompassed within the following words are no less appreciated for their love and support.

This research was inspired by my brilliant advisor, Dr. Michael Jerrett, who has dedicated his career to studying the relationship between our environment and public health, especially among the most vulnerable in our society. I have been humbled by the depth of his expertise and willingness to support my own research. Dr. Jerrett worked tirelessly with me in the field both in Colorado and California and contributed to my methodological approach in measuring gradient behavior and characterizing the ambient air near oil and natural gas development and storage sites. I am forever indebted for his support in my academic pursuits while reminding me of the importance of maintaining a healthy work-life balance. I cannot thank him enough for all that he has done for me throughout my academic career. It is because of him that I consider myself a scientist.

The other distinguished members of my dissertation and qualifying exam committees have been markedly supportive throughout the grueling journey towards my doctorate. Professors John Balmes, Rachel Morello-Frosch, Allen Goldstein, and Tom McKone thoroughly challenged my knowledge during both preliminary and qualifying exams, providing me with a strong foundation in which to build my research ideas. Through their support and guidance, I was provided an arsenal of research tools that helped me navigate through the many unexpected challenges experienced along the way. I succeeded only with their enormous support, wisdom, and compassion. I can only hope that I will inspire the next generation of environmental scientists similarly to the way they have and continue to inspire me.

This research would have never been possible without our collaborators at Alphasense and the University of Cambridge: Dr. Rod Jones, Dr. Olalekan Popoola, Dr. Vivien Bright, and Dr. Iq Mead. Their combined knowledge in electrochemical sensors and monitoring air quality has been critical for the front-end data collection and processing. I am extremely grateful for their continued interest in this research, long hours spent processing the collected datasets, willingness to share their expertise and input, and for their long-distance feedback for the many questions I've presented them over the years. Their commitment of creating and providing the research world with high-quality, lost-cost air quality sensors is unparalleled.

I owe a debt of gratitude to the Berkeley Center for Green Chemistry's National Science Foundation's Systems Approach to Green Energy IGERT program which provided a generous grant and academic support for my research. Dr. Megan Schwarzman and Dr. Marty Mulvihill recognized the importance of this research when I proposed it to them several years ago and provided crucial advice on the development of my study design. I admire their passion for interdisciplinary training for the next generation of scientists and am humbled to have been selected as a recipient of this prestigious fellowship. I am further indebted to the brilliant and perpetually affable, Dr. Seth Shonkoff and his colleagues at Physicians, Scientists, and Engineers (PSE) for Healthy Energy whom contributed towards my research endeavors through generous grants, invaluable feedback, and a comradery developed through the shared goal of environmental justice. My final chapter would have never commenced without the prompting of our friends at the 11th Hour Project, whose quick action and financial support provided me with a unique research opportunity rarely entrusted onto novice researchers.

I have been overwhelmed with the support I received during the data collection process. Without the broad support from multiple organizations, agencies, academics, and individual citizens, this research would have never been possible. The ingenious scientists involved with the DISCOVER-AQ campaign welcomed me into the group without hesitation, allowing me access to their monitoring sites, equipment, and data all to support the shared goal of understating air quality in the Northern Front Range. I thank all the support I received from University of Colorado at Boulder: Dr. Michael Hannigan, Dr. Ashley Collier, and Mike Russel- all helped me with the smooth deployment of all my air quality monitors during the summer of 2014. Two of my monitors were located at private locations, both of which proved crucial in providing data that supported my research findings. For this, I would like to thank William Pratt and Steven and Kim Schneider for being wonderful hosts and citizen scientists.

The California data collection portion of my research was successful only by the wonderful and supportive team at the Los Angeles Department of Public Health, the South Coast Air Quality Management District, Argos Scientific, and the California Air Resource Board. While I possess a scientific understanding of the impacts of air pollution on public health, it was only from my experience with the community of Porter Ranch that I truly understood the impacts our environment has on us as individuals. I am forever grateful for the support and trust afforded me by the local community affected by the natural gas blowout. It is my true hope that my research provides those affected with a better scientific understanding of exposures and encourages additional research in the area of air quality near natural gas storage. I also thank the tireless community organizers including Nikki Wong and Alex Nagy, who have the natural gift of inspiring others into action and bridging the world of science and community with the shared desire to understand our environment.

An especially wonderful aspect about academic life at Cal is the incredible abundance of brilliant student collaborators, both past and present, willing to share their knowledge to further scientific endeavors. I was fortunate to share an advisor with the brilliant Dr. Bernard Beckerman who provided his profound technical expertise and brilliant scientific insights into investigations of air quality and exposures. Courtney Schiffman, a talented biostatistician, contributed her knowledge in statistics to the development of the CCA analysis. The ever congenial, Dr. Ben Greenfield, provided his support by helping me with in-field deployments around the Northern Front Range. I was always confident in the quality of their professional input and pleased to have these amazing individuals among my academic cohort.

As a first-generation, non-traditional college student, navigating through the graduate program was both confusing and greatly intimidating, and I thank Norma Firestone, Estela Almanza, Dr. Kelsi Perttula, and Dr. Bhavna Shamasunder for providing me with critical emotional and academic support necessary for my success. Norma helped smooth my transition into academia, assisted with all aspects of the administrative process, and provided a rich and nourishing environment for me and my fellow EHS cohort. Kelsi, Estela, and Bhavna provided support and guidance in the culturally appropriate context unique to my academic experience. All four of these women are inspiring, talented, role models that I have been honored to call my friends.

Chapter 1: Hazardous air pollutants associated with upstream oil and natural gas development: A critical synthesis of current peer-reviewed literature

Authors:

Diane A. Garcia-Gonzales[1]

Seth B.C. Shonkoff[2,3,4]

Jake Hays[2,5]

Michael Jerrett[1,7,8]

[1] Environmental Health Sciences Division, 50 University Hall, School of Public Health, University of California, Berkeley, Berkeley, CA 94720. dgonzales98@berkeley.edu

[2] PSE Healthy Energy, 402 E. 67th St., New York, NY 10065.

[3] PSE Healthy Energy, 1440 Broadway, Suite 205, Oakland, CA 94612

[4] Department of Environmental Science, Policy, and Management, University of California, Berkeley

[5] Weill Cornell Medicine, 402 E. 67th St., New York, NY 10065

[6] Lawrence Berkeley National Laboratory

[7] Department of Environmental Health Sciences, Fielding School of Public Health University of California, Los Angeles

[8] Center for Occupational and Environmental Health, Fielding School of Public Health University of California, Los Angeles

A similar version of this manuscript has been submitted for review: Garcia-Gonzales D, Shonkoff S, Hays J, Jerrett M. 2019. Hazardous Air Pollutants Associated with Upstream Oil and Natural Gas Development: An Examination of the Current Peer-Reviewed Literature (in review). Annu. Rev. Public Health. 40

1.1 Abstract

Increased energy demands and innovations in upstream oil and natural gas (ONG) extraction technologies has allowed the United States to become one of the leading producers of petroleum and natural gas hydrocarbons in the world. The United States Environmental Protection Agency (U.S. EPA) lists 187 hazardous air pollutants (HAPs) that are known or suspected to cause cancer or other serious health effects. Several of these HAPs have been measured at elevated concentrations around ONG sites, but most have not been studied in the context of upstream development. In this review, we analyzed recent global peer-reviewed articles that investigated HAPs near ONG operations to (1) identify HAPs associated with upstream ONG development, (2) identify their specific sources in upstream processes, and (3) examine the potential for adverse health outcomes from HAPs emitted during these phases of development.

1.2 Introduction

Increased energy demands and innovations in upstream oil and natural gas (ONG) extraction technologies have enabled the United States to become the world's top producer of petroleum and natural gas hydrocarbons[1]. The U.S. Energy Information Administration[2] reported U.S. petroleum and other liquid fuels production reached 15.6 million barrels per day and dry natural gas production averaged 73.6 billion cubic feet per day in 2017; with projected increases in 2018 and 2019. In some areas, ONG extraction and development has expanded closer to residential communities, increasing risks of air, water, soil, noise, and light pollution exposures in proximate populations. Research suggests current setback standards – or distances in which the ONG industry can develop from water sources, residential structures, and other facilities – may not be sufficient to reduce potential risks to human health from ONG activities[3,4]. There is a growing, yet still relatively small body of studies that investigate the relationship between the proximity of these facilities and human health impacts. With a dearth of scientific data characterizing exposure risks, it is difficult to offer scientific guidance on specific adequate set-back requirements, despite the fact that an estimated 18 million people live within 1,600 meters (~1 mile) from an active ONG well[5]. Special disclosure exemptions from the federal Emergency Planning and Community Right to Know Act allows the ONG industry to withhold information regarding chemical constituents used, produced and emitted, further compounding the difficulty in the identification of chemical-related hazards and their associated exposure pathways.

Upstream processes consist of four broad phases of operation: (1) exploration, well pad and infrastructure construction; (2) drilling of the well and construction of associated surface and subsurface equipment and facilities; (3) well stimulation and completion; and (4) oil and natural gas production and processing. The current body of scientific literature suggests that upstream ONG development processes emit numerous air pollutants including methane, non-methane-volatile organic compounds (VOCs), particulate matter (PM), aliphatic and aromatic hydrocarbons, aldehydes, and nitrogen oxides, some of which are also precursors to tropospheric ozone and secondary organic aerosol (SOA) production. Upstream ONG development includes all phases and processes necessary to extract ONG hydrocarbons from subsurface reservoirs, excluding the transportation, transmission, storage, refinement and wholesale of refined products. Various attempts to identify and classify all products and chemicals used or emitted during the upstream ONG development process have resulted in disparate lists ranging from 343 to 1,177 unique chemicals[6–10]. Current research provides conflicting evidence over the concentrations of various pollutants in the air; however, a consensus exists regarding the presence of air pollutants that pose human health hazards[11–18].

Emissions of hazardous air pollutants (HAPs) from ONG are of particular concern as they are known or suspected to cause cancer or other serious health effects. Currently the Clean Air Act lists 187 HAPs for regulation[19], some which have been associated with ONG activities. The Committee on Energy and Commerce and the Endocrine Disruption Exchange have identified over 20 different HAPs, which have been associated with upstream ONG activities or processes[6,20]. While the number of studies examining the human health impacts of ONG development is growing, limited information exists on the role of HAPs in the upstream process and the health impacts of HAP related emissions[21–26].

The purpose of this review is to summarize the research conducted to date on the associations between HAPs and upstream ONG development. Specifically, we will pursue the following aims: to identify compounds that have been investigated near upstream operations within the peer-reviewed literature; to determine which of these compounds have been traced to a specific upstream phase, process, or source; and to examine the potential health hazards attributable to these HAPs. Our synthesis of the science is intended to inform future research priorities related to ONG development and to assist in public health protection.

1.3 Materials and Methods

We began with the inclusion of all 187 HAPs listed by the United States Environmental Protection Agency (U.S. EPA). Hydrogen sulfide (H_2S) was removed from the official list in 1991 but was included in our review due to its high toxicity at lower concentrations and prevalence in oil and gas development operations. From this point forward, when referring to HAPs, we include all 187 compounds listed by the U.S. EPA, plus H_2S for a total of 188 compounds. Given the rapid expansion of ONG development activities over the past few years, only peer-reviewed articles published between January 1, 2012 and February 28, 2018 were included in the current review. A number of HAPs have been measured and monitored near ONG operations as primary pollutants; however, some HAPs – including for example formaldehyde and acetaldehyde – are also secondary pollutants formed from the atmospheric transformation of precursor compounds[27]. While central to the question of HAP formation and atmospheric concentrations, HAP precursors fall outside of the scope of this review.

Keyword Search

We developed a list of keywords to assist in a comprehensive literature search of all upstream ONG processes and target pollutants. Due to the inconsistency of the terminology surrounding the upstream ONG development process, we cast a wide net to be inclusive of possible iterations when building the keyword search. These keywords included, but were not limited to, the term “fracking”, “fracturing”, “hydraulic fracturing", "oil and natural gas development", and common acronyms including "UNGD" and "ONG". In all, we incorporated 18 iterations and acronyms. Additionally, we included key words for transport media to ensure search results encompassed airborne compounds. We erred on the side of being overly inclusive and integrated broad group names including volatile organic compounds (VOCs), non-methane hydrocarbons (NMHC), and hazardous air pollutants (HAPs) during the search process. Keywords and search queries are provided in Table 1.1.

Electronic Database Search

We searched peer-reviewed journal articles within three electronic search databases in March 2018. First, we searched the Thomson Reuter's Web of Science database (http://www.webofknowledge.com) using their Advanced Search query tool. Boolean operators were used to narrow English language article search results by topic, and publication timeframe. We also searched PubMed (http://www.ncbi.nlm.nih.gov) to ensure our literature review included a comprehensive search of peer-reviewed journal articles focused on the human health dimensions of upstream ONG development. Results were narrowed by text words and publication timeframe. Search queries resulted in 639 and 1146 peer-reviewed journal articles in the Web of Science and PubMed, respectively. After comparing databases and eliminating duplicate articles, search results were then compared with PSE Healthy Energy's Repository for Oil and Gas Energy Research (ROGER) database[28], a nearly exhaustive database of peer-reviewed literature on shale gas development, which can be found on the PSE website at www.psehealthyenergy.org. Articles found in the ROGER database that were not included in searches from the electronic databases were added to the collection. A final count of 1,833 journal articles was then collected, organized, and evaluated using the inclusion/exclusion criteria.

Inclusion and Exclusion Criteria

We first scanned titles to remove papers for exclusion based on the following criteria: not written in English; were review, commentary, or response papers; and papers that did not investigate air quality near ONG development. After reviewing the abstracts and content of the remaining papers, we excluded studies that did not collect primary HAP measurements, modeled or "estimated" HAP concentrations, or conduct primary HAP analyses from secondary data sources. We focused on papers that described ground level or local-level pollutant concentrations and papers that focused on sourcing HAPs to upstream ONG operations. Several articles using concentrations of HAP compounds to model the formation of secondary non-HAP air pollutions were excluded if they did not directly investigate impacts of local-scale HAP compounds or their emission sources. A Preferred Reporting Items for Systematic Reviews and Meta-Analyses (PRISMA) flowchart shows how the inclusion/exclusion criteria resulted in the final article count (Figure 1.1).

1.4 Results

We identified a total of 37 peer-reviewed journal articles, published between January 1, 2012 and February 28, 2018 that met our inclusion/exclusion criteria (Table 1.2). All but one peer-reviewed article focused on ONG within the United States. Thirty-one articles (84%) included primary HAP measurements within eight states including Arkansas, Colorado, Ohio, Oklahoma, Pennsylvania, Texas, Utah, and Wyoming; remaining articles included primary data analyses from secondary data sources or publicly accessible datasets.

HAPs Identified within Review

The sample limit of detection (LOD) expresses the lowest concentration of the targeted analyte that can be distinguished within a given sample, instrument, or method. We use the sample LOD as our metric of interest instead of commonly referenced health-based comparison values for several reasons. First, the heterogeneity of sampling methodologies prevents direct comparison between concentration results[29]. Second, it is difficult to select a single health-based standard exposure timeframe that adequately represents the variety of sampling durations present in the reviewed literature (Table 1.3). Finally, many health-based standards are derived from limited datasets and inadequate conversion factors that do not appropriately define the risk threshold of sensitive populations nor does it address the risks of exposure to multiple HAPs concurrently and, thus, may inappropriately imply the absence of health risks. Despite these advantages, a LOD above health-based standards may erroneously imply low exposure risk when concentrations are not detected within the sample. To address these issues, it is advised to include LODs within the results, as not to mislead the reader. Failure to supply sample LODs encumbers accurate descriptions of atmospheric concentrations leading to underestimations of exposure, an issue we have found rife in the ONG literature.

To generalize results across all studies, we extracted the reported HAP concentrations from the article content, tables, or supporting information; we did not extract concentrations from graphs or figures. HAPs that were not found above the sample LOD were labeled as “Not Detected”. Of the 37 studies we reviewed, a total of 61 unique HAP compounds were measured near upstream ONG or investigated from secondary data sources. Forty-four HAPs were collected and reported in more than one article as primary data, of which, 32 were found above the sample LOD. Table 1.4 provides the full inventory of HAP compounds investigated within the collected literature. HAPs collected from primary data sources were further listed by the state in which they were investigated and included in Table 1.5.

Sources of HAP Emissions

The range of air pollutant emission sources identified in the reviewed literature include equipment (e.g. dehydrators, condensate tanks, etc.), activities (e.g. flashings, gauging flowback tanks, etc.), development phases (e.g. drilling, well stimulation, etc.), facilities (e.g. water treatment and recycling center, oil storage facility, etc.), and areas (e.g. dense ONG development regions). To simplify these broadly categorized emission sources, we re-categorized equipment, activities, and facilities into one of the four most appropriate upstream ONG phases: (1) exploration, well pad and infrastructure construction; (2) drilling of the well and construction of associated facilities; (3) well stimulation and completion; and (4) oil and natural gas production and processing. For example, air quality measurements collected from flowback were re-categorized into the third phase (well stimulation and completion) because it is a fluid often recovered as a result of well stimulation. Storage tanks and impoundments can be present at the well pad through multiple phases or be transported off site via trucks or pipeline networks. Due to the mercurial nature of upstream ONG storage and associated activities, they have been re-categorized into a separate “storage and impoundment” phase. Although these sources can be associated with emissions into other mediums such as soil and water, we are focused only on HAPs emitted into the atmosphere for the current review.

Occupational and on-site studies – including Brantley et al.[30], Esswein et al.[31], and Hildenbrand et al.[32] – where primary data was collected at the well pad, reported concentrations from point sources and often provided detailed information about the equipment or activities that occurred during the sampling period. Based on their detailed descriptions, we collected and re-categorized emissions into one of our five phases, when appropriate. Several studies including Macey et al.[18] and Colborn et al.[16] collected samples off-site but provided information about potential sources of HAP compounds in ambient air by detailing closest upstream ONG equipment or activities during the collection timeframe. We cautiously used these source descriptions as a guide for re-categorization but used our best discretion for inclusion. We further re-categorized HAP compounds using common off-site sourcing and attribution techniques including factor analyses[33–35], distance decay gradients[36], and sourcing ratios[37–42], among others. We recognize that these off-site techniques provide insights into possible origins but, unlike point source emission measurements, fall short of identifying a single causal source.

A complete summary of re-categorized HAP emissions from primary measurements within the reviewed literature is provided in Figure 1.2. We did not identify any HAPs that were sourced to emissions during the first phase of development (exploration, well pad and infrastructure construction). Additional HAPs that were associated with the upstream ONG industry, but not a specific phase, include acetaldehyde, acetonitrile, and tetrachloroethylene (not included in Figure 1.2).

Well Drilling and Construction of Subsurface Infrastructure

After the site has been cleared, a vertical well is drilled using gas-powered rigs and other ancillary equipment to reach depths of several hundred meters underground. If necessary, operators will continue to drill horizontally to increase subsurface extraction capacity (e.g., in the case of shale gas development). Drilling through intermediate geological formation on the way to the target formation may release trapped hydrocarbons that can migrate to the atmosphere[24,43]. Thus, both ancillary drilling equipment and subsurface pockets of gaseous fluids within intermediate geologic formation are a source of various HAP emissions into the ambient environment[44].

Compared to all other stages of development, Colborn et al.[16] measured the most chemical spikes in the ambient air from a stationary monitoring site located 1.1 km from a well pad during drilling activities in rural Colorado. Samples identified 12 Polycyclic Organic Matter (POM) compounds, including naphthalene, during a timeframe dominated by drilling activities. POM defines a broad class of compounds that includes polycyclic aromatic hydrocarbons (PAHs) formed primarily from combustion. Temporal patterns of emissions without supplementary sourcing analyses are arguably suspect, but additional sourcing ratio analyses of similar compounds found evidence of petrogenic sources during a range of upstream ONG activities in Ohio[41]. Additional mobile measurements in Pennsylvania detected acetaldehyde, acetonitrile, benzene, methanol, and toluene downwind from a drilling rig, but concentrations were not elevated above background, suggesting the rig was not operating at full capacity or the activities and equipment associated with the drilling phase were not the source of these pollutants and thus not included in our sourcing analyses[24].

Well Stimulation and Completion

The well completion phase encompasses all processes associated with preparing a newly drilled well for the production of oil and natural gas. This phase is relatively short in duration (3-15 days) but can include a variety of activities including flowback collection, flaring, work-overs, and completion venting. Once the well is drilled, casing is installed to stabilize the wellbore and provide zonal isolation to minimize subsurface migration of liquid and gaseous fluids, followed by perforation of the casing in the target hydrocarbon reservoir to allow for the flow of hydrocarbons into the well. In low-permeability reservoirs, where hydraulic fracturing and other stimulation is required to extract hydrocarbons, between 0.25 and 50 million gallons of water, chemicals, and proppant is injected down the well at a pressure high enough to increase the permeability of the target geology. When these stimulation fluids return to the wellhead, it is referred to as "flowback." Although chemical constituents from the geological formation are present in this flowback, these fluids are often distinguished from produced water which is produced shortly thereafter and often throughout the lifetime of active hydrocarbon production[45]. Since flowback is mostly limited to the current phase, we include emissions associated with flowback, and not produced water, which is reviewed in subsequent sections.

The term BTEX refers to the group of compounds: benzene, toluene, ethylbenzene, and total xylenes. These compounds occur naturally in petroleum and are released primarily through motor vehicles emissions, but also emitted naturally via volcanoes and forest fires. BTEX, 1,3-butadiene, n-hexane, cumene, styrene, and 2,2,4-trimethylpentane were identified around the perimeter of five well pads in Colorado during completions activities and, with the exception of styrene, cumene, and 1,3-butadiene, median concentrations were higher than background in ONG area samples[14]. Additional field sampling downwind of a well pad in Pennsylvania during flaring activities measured benzene, toluene, and n-hexane above the sample LOD and at concentrations higher than the upwind direction[46]. Additional occupational and off site measurements identified POMs (including naphthalene) and H_2S near flowback and work-over rigs[18,31]. BTEX compounds and n-hexane are found in vehicular emissions, drilling fluids, and fracturing additives. BTEX compounds, in particular, occur naturally in ONG formations and are largely sourced from processes that provide an opportunity for unsurfaced compounds to migrate upward and volatize into the ambient air. Therefore, many of the identified compounds in this section could be direct emissions from industry trucks, ancillary well pad equipment, flowback, or volatized from the chemical mixtures of stimulation fluid or general stimulation and completion activities[6,7,20,47]. With the current evidence we cannot identify the specific source activity or equipment, although ONG development appears to be the likely source.

Oil and Natural Gas Production and Processing

During the production phase, natural gas is collected from the well and processed with various ancillary equipment, including wellhead compressors, pneumatic devices, separators, and dehydrators. The production phase is the longest of all of the upstream phases. While shale may be depleted within 1-5 years, migrated oil reservoirs may still be producing after decades of use. In regions with oil deposits or wet gas, larger-molecular weight hydrocarbons, including aromatics, can be emitted during the production and processing phase, when target alkanes are separated from heavier compounds. Operating practices, spud date, and production volumes, however, can also heavily impact emissions from producing wells within the same shale play[24,48]. Therefore, without insight into reservoir composition and well pad operations, it is difficult to predict potential emission compounds and volumes or interpolate results to larger areas.

Wellheads, dehydrators, and separators are important sources of heavy VOC emissions during production and processing in regions rich in oil, wet gas, and condensate[35,49]. Point source measurements collected on a well pad in Colorado identified BTEX compounds, styrene, n-hexane, and 2,2,4-trimethylpentane near producing wellheads, dehydrators and separator units[30]. Off-site measurements in Texas and Wyoming identified similar emissions with an addition of cumene and H_2S near wellheads, separators, and produced water tanks and discharge canals[18,50]. Compressors used to maintain hydrocarbon flow were associated with emissions of BTEX compounds, 1,3-butadiene, methanol, formaldehyde, mercury, and n-hexane[18,24,33,50–52]. With the exception of mercury, these compounds are commonly emitted from continuously reciprocating natural gas fired engines, such as those used to power compressors, and their presence within the collected samples was not unexpected. Mercury, a trace component in natural gas condensate, is removed from the compressor process; thus, its emission and may actually be a result of ineffective mercury removal systems, and therefore is included in this phase[51].

Abnormal process conditions including control failures, design failures, and malfunctions upstream of the point of emission occur in only a small fraction of facilities, yet may be responsible for a significant portion of ONG related air pollution[53–55]. Fly-over measurements in the Haynesville and Marcellus Shale gas production regions found that only ~10% of facilities were responsible for up to ~40% of the total CH_4 emissions[56], and mobile measurements in the Barnett Shale area found only 4% of measured ONG facilities were responsible for a relatively large amount of the measured atmospheric mercury[51]. Within the current review, there were few air quality samples collected during abnormal ONG development process conditions, yet it is possible that they occurred without operator knowledge or public disclosure. For example, samples collected near production phase equipment described as “rusty” recorded concentrations up to 47 times higher than those described as in “good” operating condition, yet neither were identified as abnormal processes[30]. In the instance where infrared video captured a clear example of a leaking natural gas wellhead, elevated concentrations of benzene, xylenes, n-hexane, and toluene were measured on and off site, and near residential homes[57].

Storage Tanks and Impoundments

Storage tanks and impoundments are used to hold production and maintenance chemicals or condensate collected and separated during various phases. Chemicals stored at upstream ONG sites include chemical additives and mixtures for stimulation and various maintenance needs. Condensate is different from stored chemicals, flowback, and produced water as has been separated from extracted crude oil or natural gas matrices in preparation for additional processing or disposal. Emissions from storage and condensate tanks have been associated with H_2S, BTEX, n-hexane, styrene, methanol, and 2,2,4-trimethylpentane[30,49,58]. Many of the stored liquids are volatile and enter a gaseous phase as a result of increases in temperature and decreases in pressure. Workers in the upstream ONG industry, especially those working with flowback and condensate tanks, are at increased risk of exposure during routine gauging, measurement and oil flashing activities which provide an opportunity for stored liquids to volatilize and escape into the atmosphere. A number of occupational deaths have been reported among workers taking volume measurements of condensate tanks[59].

Such emission events are often brief but significant, especially in oil-producing areas[60], which may have a substantial impact on local air quality[38]. Storage tanks can be housed at the well site, providing additional emissions source points during the associated phase; however, they can also be stored at different locations, far from the well pad, or piped off site through transmission pipeline networks[37]. Many of the listed HAPs in this section were found at well pads during production but they were re-categorized into a separate current group due to the mercurial nature of storage activities.

Summary of Health Impacts from HAP compounds

HAP compounds are associated with multiple cancer and non-cancer health outcomes and have, in some studies, been detected near ONG sites at levels that exceed health-based standards and reference concentrations. The current ONG literature offers limited insights into specific etiological agents and health outcomes, with granular measurements of exposure often lacking. To better understand health risks and impacts from HAP exposures near upstream ONG development, we further evaluated the studies that included a health component in the analysis. Although exposure to any of the 188 listed HAP compounds may pose reason for concern, we identified several HAPs that were consistently found above sample LODs, above health benchmarks, or posed the highest risk from inhalation exposures. A summary of some of the key findings are provided in the following sections.

HAPs of Highest Concern

BTEX compounds are linked to several serious human health impacts including neurological damage, fetal defects, some cancers and hearing loss[61]. Ubiquitous in the environment, it is common for these compounds to exceed sample LODs in urban areas as a result of transportation and industrial processes[62]; however, many of the reviewed samples were collected near ONG activities in rural regions, where urban sources are likely to have minimal impact on ambient air quality. Several of the studies included in this review found rural BTEX concentrations to exceed those measured in dense urban areas and at concentrations that exceed the health-based standards, with some concentrations over 2,900 ppb[15,17,18,24,35,37,38,40,42,49,63–65]. Reference Effect Level (REL) is a reference exposure level from the Office of Environmental Health Hazard Assessment (OEHHA) of the California Environmental Protection Agency (Cal/EPA). The REL is a concentration of a single chemical at or below which adverse noncancer health effects are not anticipated to occur for a specified exposure duration. For reference, the 8-hour and chronic REL for benzene is 1.0 ppb[66]. Studies that report ambient BTEX concentrations below existing health-based standards, have implied that upstream ONG emissions of these compounds may not have a substantial impact on human health, yet ambient BTEX concentrations, below health benchmarks, have been associated with adverse health outcomes in numerous epidemiological studies[67–80].

While health-based air quality standards provide a guide in which to base regulatory thresholds, many standards are derived from animal models or occupational studies that apply inappropriate conversion factors leading to underestimates of the actual exposure risks, particularly to sensitive populations such as children and pregnant women. Recognizing the possible inadequacies of existing uncertainty factors for benzene, the Office of Environmental Health Hazard Assessment (OEHHA) recently applied a stricter REL to include additional protections to sensitive populations[66], yet questions remain over whether these updated standards are protective enough. Based on the existing evidence of exposure risks from chronic, low-level concentrations, current health non-cancer benchmarks, such as the OEHHA RELs may be insufficient for estimating health impacts from benzene-related exposures near upstream ONG development. Recognizing the cancer risks associated with benzene exposures, the World Health Organization (WHO) states that “no level of exposure can be recommended”[81].

Formaldehyde and acetaldehyde were found to be the most abundant carbonyl species when sampling ambient air near ONG facilities. The chronic RELs for acetaldehyde and formaldehyde are 80 ppb and 7 ppb, respectively[82]. While many of the observed concentrations were below health standards, the International Agency for Research on Cancer (IARC) has classified formaldehyde as a Group 1 carcinogen, meaning it causes cancer in humans[83] and, generally, does not have a threshold below which there is a safe level of exposure. Further, simplified health risk assessments and modeling estimates have suggested that formaldehyde and acetaldehyde are the dominant contributors to acute and chronic cancer risks[42,84]. The abundance of formaldehyde detection in ambient collected samples may actually indicate secondary atmospheric formation as the dominate source and not primary emissions released directly from an ONG point source. This may actually lead to under reporting in mandated state inventories that focus on primary emissions.

The natural gas and crude oil impurity, H_2S, is a colorless and flammable toxicant easily identifiable by its “rotten egg” odor. H_2S becomes detectable at concentrations as low as 0.5 ppb[85], chronically toxic at 8 ppb[86], and has a National Institute for Occupational Safety and Health (NIOSH) immediately dangerous to life or health (IDLH) concentration of 100 ppm[87]. Within the current review, H_2S has been measured in ambient air at various phases of upstream ONG development including separation, storage tanks, and discharge canals at concentrations exceeding those known to be safe[18,31,50,58]. Concentrations of H_2S above the odor threshold were measured just beyond the fence line in 8% of natural gas production sites in Texas during mobile measurements[50].

The simplest unsaturated aldehyde, acrolein, is fairly ubiquitous throughout the environment at concentrations above chronic non-cancer benchmarks[88–91]. Used as a biocide additive and H_2S scavenger in ONG operations, acrolein is also emitted from more common sources including incomplete combustion of petroleum products, tobacco smoke, and cooking activities. Due to the current health burden of exposure in the ambient environment, OEHHA identified acrolein as one of the top five most important pollutants of concern in California[92], and an additional exposure from ONG operations could compound the existing public health burden. Acrolein is difficult to measure accurately and controversy over prevailing sampling methods persists[93–95]. Exposure to acrolein may cause adverse health effects including eye, nose, and throat irritation, chest pain, and difficulty breathing[96]. In underground natural gas storage facilities, acrolein is the eighth highest emitted air pollutant in California and was found at elevated levels in indoor environments near the Aliso Canyon natural gas storage leak[97,98]. Acrolein is an important toxicant emitted in the upstream ONG process, yet methodological constraints limit the availability of reliable industry-related emission estimates and, consequently, obscures the understanding of the potential impact to human health.

Gaps in the Health Research

Recent health-based studies have uncovered a spatial relationship between upstream ONG and a range of health outcomes. Epidemiological and health-based studies have found increased risk and incidence of adverse birth outcomes near ONG activity compared to further away[99–102]. Similarly, studies that utilize distance metrics as proxies of exposure reported increased health risks for individuals living near ONG activity compared to further away[14,42,103]. These findings are corroborated by symptom surveys that found the number of reported symptoms was higher among residents living closer to well pads compared to those living further away[104]. Further, McKenzie et al.[105] paired in-situ air quality measurements with distance and cancer risk assessment. The study found that within 152 meters (~500 feet) of active oil and gas development, the cancer risk estimate was 8.3 cases per 10,000 individuals, greatly exceeding the EPA's upper threshold for acceptable risk (1 case in 10,000).

Despite findings of a spatial dimension of health data near upstream ONG development, measured pollutant concentrations, including concentrations of HAPs, were generally below health-based standards. It is unclear why ambient air samples have failed to capture concentrations above health benchmarks while epidemiological studies continue to find incidence of poor health outcomes increasing as distance from these operations decreases. Recent literature provides insights into methodological shortcomings that make investigations more prone to null findings. First, in-situ measurements of emissions collected at a distance from well pad activities are prone to effects of atmospheric degradation, dispersion, and disposition[106]; yet they are commonly, and inappropriately, extrapolated to describe local exposures. Studies that utilize data from standard air monitoring networks, like the Texas Commission on Environmental Quality[11,57,107] , may fail to capture concentrations that pose actual exposure risks as a result of such methodological biases.

Second, samples collected with short collection timeframes (e.g. “grab samples”) are only capable of detailing conditions at a particular “moment in time” and fail to capture the episodic peaks commonly associated at many stages of the upstream ONG development process[44]. Recent evidence suggests that abnormal process conditions or uncontrolled emission events from a small proportions of wells may better explain the complex exposure environment at both local and regional scales[53]. Studies that estimate exposures based on modeled emission rates may miss peak exposures from abnormal process conditions that are more accurately characterized via field sampling. Air quality studies that focus on granular geographic estimates of exposures via continuous, local-level monitoring better characterize ambient concentrations during brief peak emission episodes, common in upstream ONG development, that may be missed using as intermittent sampling methods at select stages[108].

Third, current exposure science does not adequately address potential risks associated with long-term, chronic, lower levels of exposure to air pollutants and[109], thus, health standards developed from inadequate uncertainty factors may not provide protection for human populations and especially for sensitive subpopulations including children, infants, and pregnant mothers. For some of the contaminants such as benzene, it is possible the lower dose exposures may still elicit health effects. Furthermore, many HAP compounds are associated with cancer endpoints that, even at low emissions levels, generally do not have a threshold below which there is a safe level of exposure. Therefore, health studies that only provide comparisons to non-cancer benchmarks may be misleading in their actual long-term health impacts.

Finally, health studies using single pollutant health-based standards may fail to provide accurate risk estimates for concurrent or close-succession exposures to multiple pollutants that may act biologically antagonistic or synergistic and additive. This is especially relevant in upstream ONG development where emission inventories and exploratory air quality analyses have identified a wide range of pollutants that are capable of being co-emitted. Without knowledge of a specific etiological agent or exposure pathway, it is possible that these studies are not sampling and analyzing the full range of biologically relevant ONG pollutants or investigating the most appropriate exposure pathways.

1.5 Discussion

We identified 61 HAPs that have been investigated in recent peer-reviewed research. Well stimulation (e.g., hydraulic fracturing) has received the greatest attention for its potential impact to human and environmental health[110]. In the context of HAPs, however, we did not find evidence to support the common assumption that this phase is associated with highest risk of exposure. Instead, we found that the production phase, with its lengthy operation timeframe and episodic peak emission events, has the potential to emit the highest concentrations of associated HAPs over the longest time period, especially in regions rich in oil, wet gas, and condensate. Emissions of HAP compounds from the production phase can be much higher if co-located with condensate storage and wastewater impoundments.

In general, measured pollutant concentrations, were below health benchmarks yet multiple health-based studies found evidence that a spatial relationship exists; concentrations of HAPs and incidence of cancer and non-cancer health endpoints are generally higher closer to operations than further away. This suggests several possible explanations: (1) spatial sampling methodologies fail to properly characterize exposures prior to atmospheric degradation, dispersion, and disposition of sampled pollutants; (2) ambient air sampling timeframes are inappropriate for capturing sporadic, peak emission events characteristic of upstream ONG; or (3) prevailing health benchmarks are inadequate for identifying exposures to chronic, low levels of pollutants, multiple chemical exposures, or from multiple exposure pathways.

This review has several limitations. First, some HAPs targeted for this review include broad-range categories (e.g. POM) that contain multiple constituents, of which, some may have been overlooked during the inclusion/exclusion review. Second, some activities and equipment are used in both upstream and midstream processes, and it was not always clear which was being measured when collecting primary data. For example, compressors can be used to transport hydrocarbons and other compounds off the well pad during upstream activities; however, the act of transportation would classify associated releases as midstream emissions. We used our best judgement when collecting and recategorizing HAP compounds, but without clarification from the authors, it is possible that we included some midstream processes in our reclassification efforts. Third, several studies included in our review suffered from methodological limitations resulting in over- or underestimated concentrations or summary findings. Although we attempted to recognize and address these inadequacies we may not have adjusted for all possible shortcomings in the reviewed literature.

Through our synthesis of the peer-reviewed literature we have identified the following research priorities: (1) increase research on HAPs near upstream ONG development with an emphasis on those that have not been extensively measured or reported on in the peer-reviewed literature, especially those that overlap with chemicals identified in state inventories or disclosures; (2) undertake detailed source attribution investigations of emissions using spatially and temporally appropriate measurements; (3) conduct detailed health studies that focus on granular estimates of exposures near upstream ONG development via personal and community-based monitoring; and (4) implement additional research on health impacts from chronic, low-level ambient HAP exposures. Adoption and implementation of these research priorities will help guide future policy aimed at the implementation of appropriate upstream ONG development control measures and protocols that will protect human and environmental health and decrease the impacts of the ONG industry.

1.6 Tables and Figures

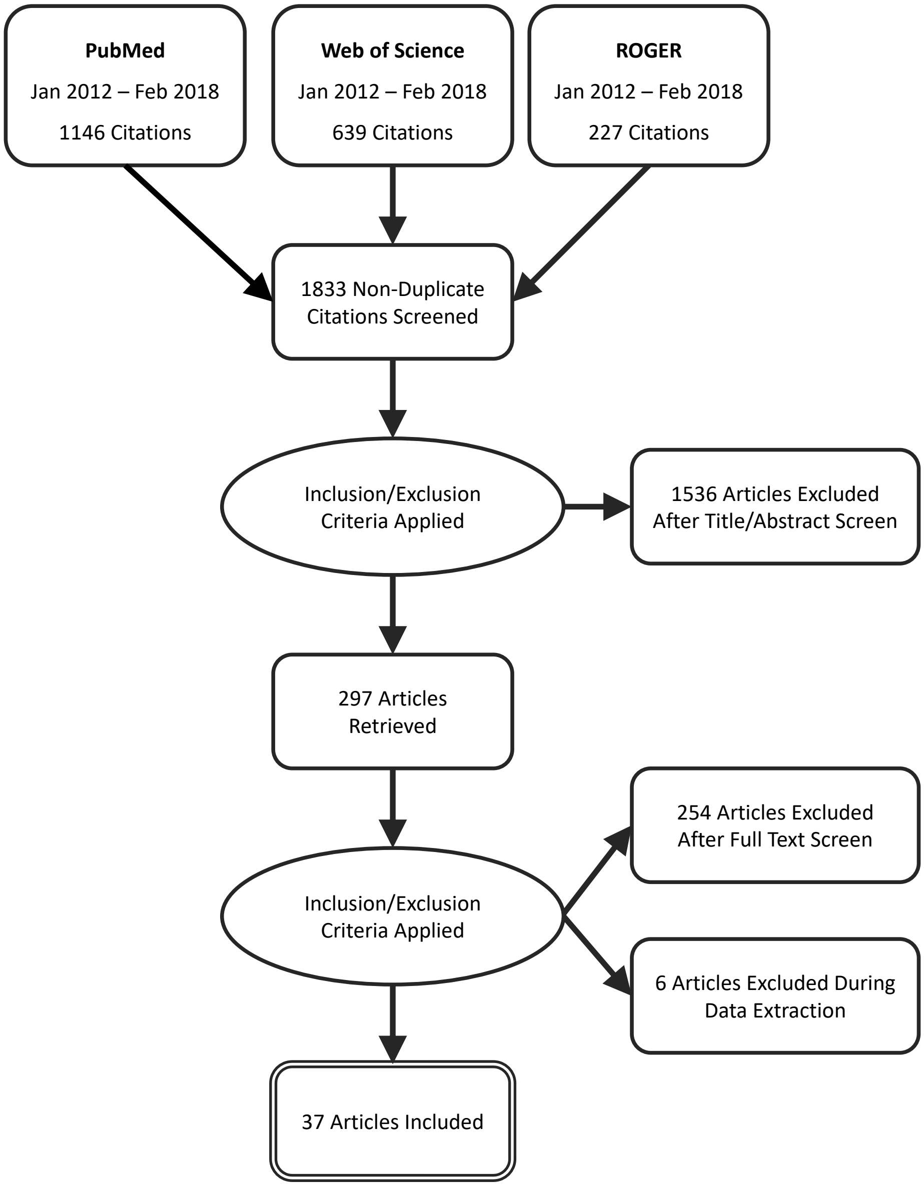
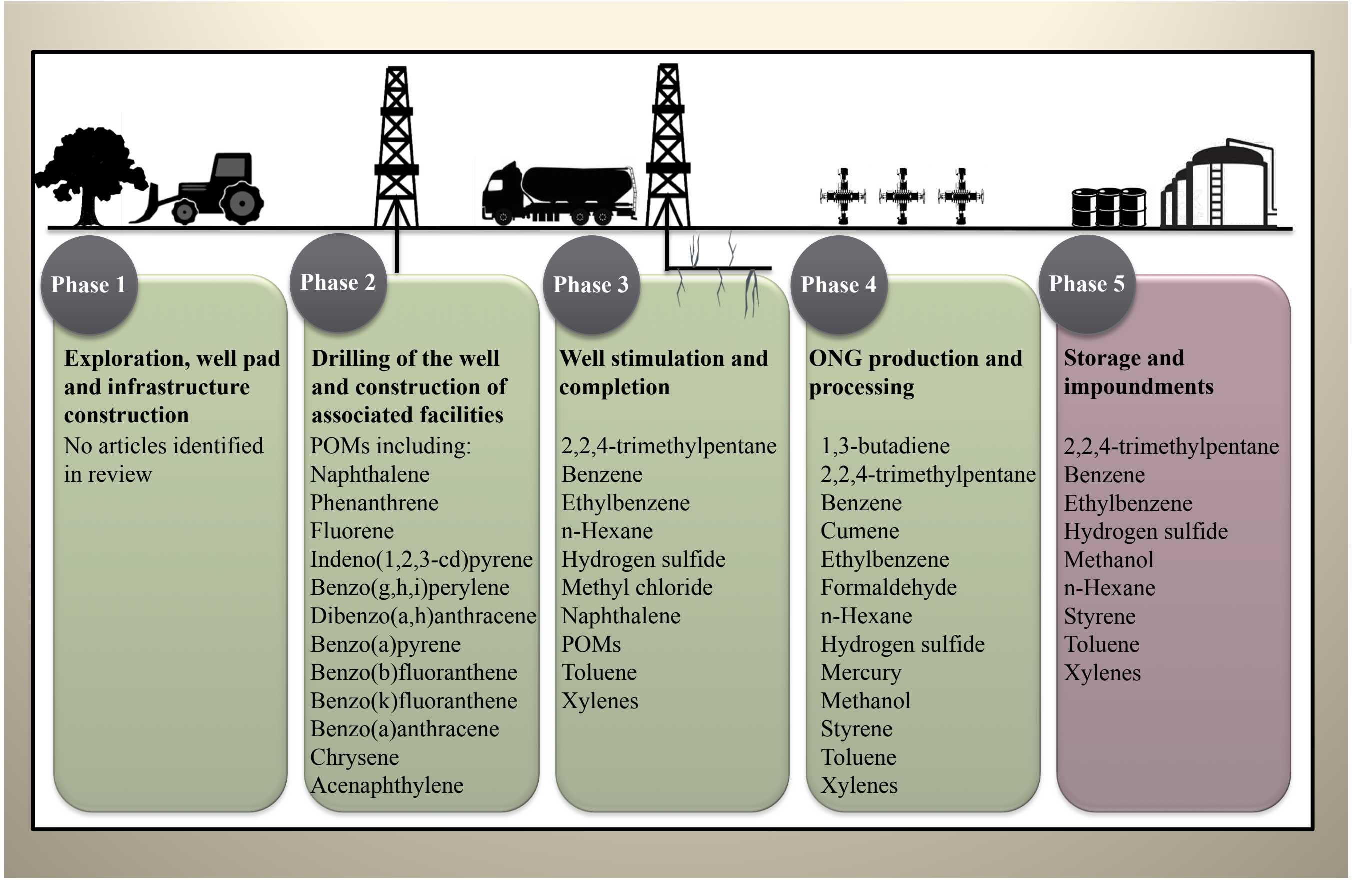


Figure 1.1: PRISMA flow diagram for HAP emissions near upstream ONG development.



Phase 1

Exploration, well pad and infrastructure construction

No articles identified in review

Phase 2

Drilling of the well and construction of associated facilities

POMs including:
- Naphthalene
- Phenanthrene
- Fluorene
- Indeno(1,2,3-cd)pyrene
- Benzo(g,h,i)perylene
- Dibenzo(a,h)anthracene
- Benzo(a)pyrene
- Benzo(b)fluoranthene
- Benzo(k)fluoranthene
- Benzo(a)anthracene
- Chrysene
- Acenaphthylene

Phase 3

Well stimulation and completion

- 2,2,4-trimethylpentane
- Benzene
- Ethylbenzene
- n-Hexane
- Hydrogen sulfide
- Methyl chloride
- Naphthalene
- POMs
- Toluene
- Xylenes

Phase 4

ONG production and processing

- 1,3-butadiene
- 2,2,4-trimethylpentane
- Benzene
- Cumene
- Ethylbenzene
- Formaldehyde
- n-Hexane
- Hydrogen sulfide
- Mercury
- Methanol
- Styrene
- Toluene
- Xylenes

Phase 5

Storage and impoundments

- 2,2,4-trimethylpentane
- Benzene
- Ethylbenzene
- Hydrogen sulfide
- Methanol
- n-Hexane
- Styrene
- Toluene
- Xylenes

Figure 1.2: Recategorized primary HAP measurements near upstream ONG development.

Table 1.1: Keywords used to build the Web of Science and PubMed search query.

List 1: Upstream ONG descriptors[a]	**List 2: Environmental medium descriptors**
Hydraulic fracking	Air
Hydraulic fracturing	Ambient
Hydrocarbon extraction	Hazardous Air Pollutant
Natural gas development	HAP
ONG	Non-methane hydrocarbon
O&NG	NMHC
O&G	Particle
Oil and gas development	Particulate
Oil and natural gas development	Volatile Organic Carbon
Shale development	VOC
Shale extraction	
Shale gas	
Natural gas field	
Natural gas production	
Unconventional gas development	
Unconventional natural gas development	
Unconventional oil and gas development	
UNGD	

[a] A Boolean search was completed by separating keywords within each list with an "OR" operator and including an "AND" operator in-between lists to narrow results.

Table 1.2: List and citations for all articles included in the current review.

Article #	Citation
1	McKenzie, Lisa M., Roxana Z. Witter, Lee S. Newman, and John L. Adgate. "Human health risk assessment of air emissions from development of unconventional natural gas resources." *Science of the Total Environment* 424 (2012): 79-87.
2	Gilman, Jessica B., Brian M. Lerner, William C. Kuster, and J. A. De Gouw. "Source signature of volatile organic compounds from oil and natural gas operations in northeastern Colorado." *Environmental Science & Technology* 47, no. 3 (2013): 1297-1305.
3	Steinzor, Nadia, Wilma Subra, and Lisa Sumi. "Investigating links between shale gas development and health impacts through a community survey project in Pennsylvania." *New Solutions: A Journal of Environmental and Occupational Health Policy* 23, no. 1 (2013): 55-83.
4	Swarthout, Robert F., Rachel S. Russo, Yong Zhou, Andrew H. Hart, and Barkley C. Sive. "Volatile organic compound distributions during the NACHTT campaign at the Boulder Atmospheric Observatory: Influence of urban and natural gas sources." *Journal of Geophysical Research: Atmospheres* 118, no. 18 (2013).
5	Bloomdahl, Ry, Noura Abualfaraj, Mira Olson, and Patrick L. Gurian. "Assessing worker exposure to inhaled volatile organic compounds from Marcellus Shale flowback pits." *Journal of Natural Gas Science and Engineering* 21 (2014): 348-356.
6	Bogacki, Marek, and Jan Macuda. "The influence of shale rock fracturing equipment operation on atmospheric air quality." *Archives of Mining Sciences* 59, no. 4 (2014): 897-912.
7	Bunch, A. G., C. S. Perry, L. Abraham, D. S. Wikoff, J. A. Tachovsky, J. G. Hixon, J. D. Urban, M. A. Harris, and L. C. Haws. "Evaluation of impact of shale gas operations in the Barnett Shale region on volatile organic compounds in air and potential human health risks." *Science of the Total Environment* 468 (2014): 832-842.
8	Colborn, Theo, Kim Schultz, Lucille Herrick, and Carol Kwiatkowski. "An exploratory study of air quality near natural gas operations." *Human and Ecological Risk Assessment: An International Journal* 20, no. 1 (2014): 86-105.
9	Eapi, Gautam R., Madhu S. Sabnis, and Melanie L. Sattler. "Mobile measurement of methane and hydrogen sulfide at natural gas production site fence lines in the Texas Barnett Shale." *Journal of the Air & Waste Management Association* 64, no. 8 (2014): 927-944.
10	Esswein, Eric J., John Snawder, Bradley King, Michael Breitenstein, Marissa Alexander-Scott, and Max Kiefer. "Evaluation of some potential chemical exposure risks during flowback operations in unconventional oil and gas extraction: preliminary results." *Journal of Occupational and Environmental Hygiene* 11, no. 10 (2014): D174-D184.
11	Li, R., C. Warneke, M. Graus, R. Field, F. Geiger, P. R. Veres, J. Soltis et al. "Measurements of hydrogen sulfide (H_2S) using PTR-MS: calibration, humidity dependence, inter-comparison and results from field studies in an oil and gas production region." *Atmospheric Measurement Techniques* 7, no. 10 (2014): 3597.
12	Macey, Gregg P., Ruth Breech, Mark Chernaik, Caroline Cox, Denny Larson, Deb Thomas, and David O. Carpenter. "Air concentrations of volatile compounds near oil and gas production: a community-based exploratory study." *Environmental Health* 13, no. 1 (2014): 82.
13	Pekney, Natalie J., Garret Veloski, Matthew Reeder, Joseph Tamilia, Erik Rupp, and Alan Wetzel. "Measurement of atmospheric pollutants associated with oil and natural gas exploration and production activity in Pennsylvania's Allegheny National Forest." *Journal of the Air & Waste Management Association* 64, no. 9 (2014): 1062-1072.
14	Rich, Alisa, James P. Grover, and Melanie L. Sattler. "An exploratory study of air emissions associated with shale gas development and production in the Barnett Shale." *Journal of the Air & Waste Management Association* 64, no. 1 (2014): 61-72.
15	Thompson, Chelsea R., Jacques Hueber, and Detlev Helmig. "Influence of oil and gas emissions on ambient atmospheric non-methane hydrocarbons in residential areas of Northeastern Colorado." *Elementa Science of the Anthropocene* 3 (2014).

16	Warneke, C., F. Geiger, P. M. Edwards, W. Dube, G. Pétron, J. Kofler, A. Zahn et al. "Volatile organic compound emissions from the oil and natural gas industry in the Uintah Basin, Utah: oil and gas well pad emissions compared to ambient air composition." *Atmospheric Chemistry and Physics* 14, no. 10977 (2014): e10988.
17	Zielinska, Barbara, Dave Campbell, and Vera Samburova. "Impact of emissions from natural gas production facilities on ambient air quality in the Barnett Shale area: A pilot study." *Journal of the Air & Waste Management Association* 64, no. 12 (2014): 1369-1383.
18	Brantley, Halley L., Eben D. Thoma, and Adam P. Eisele. "Assessment of volatile organic compound and hazardous air pollutant emissions from oil and natural gas well pads using mobile remote and on-site direct measurements." *Journal of the Air & Waste Management Association* 65, no. 9 (2015): 1072-1082.
19	Casey, Joan A., Elizabeth L. Ogburn, Sara G. Rasmussen, Jennifer K. Irving, Jonathan Pollak, Paul A. Locke, and Brian S. Schwartz. "Predictors of indoor radon concentrations in Pennsylvania, 1989–2013." *Environmental Health Perspectives* 123, no. 11 (2015): 1130.
20	Ethridge, Shannon, Tiffany Bredfeldt, Keith Sheedy, Stephanie Shirley, Glendora Lopez, and Michael Honeycutt. "The Barnett Shale: From problem formulation to risk management." *Journal of Unconventional Oil and Gas Resources* 11 (2015): 95-110.
21	Field, Robert A., Jeff Soltis, Michael C. McCarthy, Shane Murphy, and Derek C. Montague. "Influence of oil and gas field operations on spatial and temporal distributions of atmospheric non-methane hydrocarbons and their effect on ozone formation in winter." *Atmospheric Chemistry and Physics* 15, no. 6 (2015): 3527-3542.
22	Field, R. A., J. J. Soltis, P. Pérez-Ballesta, E. Grandesso, and D. C. Montague. "Distributions of air pollutants associated with oil and natural gas development measured in the Upper Green River Basin of Wyoming." *Elementa Science of the Anthropocene* 3 (2015).
23	Goetz, J. Douglas, Cody Floerchinger, Edward C. Fortner, Joda Wormhoudt, Paola Massoli, W. Berk Knighton, Scott C. Herndon et al. "Atmospheric emission characterization of Marcellus Shale natural gas development sites." *Environmental Science & Technology* 49, no. 11 (2015): 7012-7020.
24	Lan, Xin, Robert Talbot, Patrick Laine, Azucena Torres, Barry Lefer, and James Flynn. "Atmospheric mercury in the Barnett Shale Area, Texas: Implications for emissions from oil and gas processing." *Environmental Science & Technology* 49, no. 17 (2015): 10692-10700.
25	Swarthout, Robert F., Rachel S. Russo, Yong Zhou, Brandon M. Miller, Brittney Mitchell, Emily Horsman, Eric Lipsky, David C. McCabe, Ellen Baum, and Barkley C. Sive. "Impact of Marcellus Shale natural gas development in southwest Pennsylvania on volatile organic compound emissions and regional air quality." *Environmental Science & Technology* 49, no. 5 (2015): 3175-3184.
26	Eisele, Adam P., Shaibal Mukerjee, Luther A. Smith, Eben D. Thoma, Donald A. Whitaker, Karen D. Oliver, Tai Wu et al. "Volatile organic compounds at two oil and natural gas production well pads in Colorado and Texas using passive samplers." *Journal of the Air & Waste Management Association* 66, no. 4 (2016): 412-419.
27	Halliday, Hannah S., Anne M. Thompson, Armin Wisthaler, Donald R. Blake, Rebecca S. Hornbrook, Tomas Mikoviny, Markus Müller, Philipp Eichler, Eric C. Apel, and Alan J. Hills. "Atmospheric benzene observations from oil and gas production in the Denver-Julesburg Basin in July and August 2014." *Journal of Geophysical Research: Atmospheres* 121, no. 18 (2016).
28	Hildenbrand, Zacariah L., Phillip M. Mach, Ethan M. McBride, M. Navid Dorreyatim, Josh T. Taylor, Doug D. Carlton, Jesse M. Meik et al. "Point source attribution of ambient contamination events near unconventional oil and gas development." *Science of The Total Environment* 573 (2016): 382-388.
29	Marrero, Josette E., Amy Townsend-Small, David R. Lyon, Tracy R. Tsai, Simone Meinardi, and Donald R. Blake. "Estimating emissions of toxic hydrocarbons from natural gas production sites in the Barnett Shale region of Northern Texas." *Environmental Science & Technology* 50, no. 19 (2016): 10756-10764.

30	Maskrey, Joshua R., Allison L. Insley, Erin S. Hynds, and Julie M. Panko. "Air monitoring of volatile organic compounds at relevant receptors during hydraulic fracturing operations in Washington County, Pennsylvania." *Environmental Monitoring and Assessment* 188, no. 7 (2016): 1-12.
31	Paulik, L. Blair, Carey E. Donald, Brian W. Smith, Lane G. Tidwell, Kevin A. Hobbie, Laurel Kincl, Erin N. Haynes, and Kim A. Anderson. "Emissions of polycyclic aromatic hydrocarbons from natural gas extraction into air." *Environmental Science & Technology* 50, no. 14 (2016): 7921-7929.
32	Rich, Alisa L., and Helen T. Orimoloye. "Elevated atmospheric levels of benzene and benzene-related compounds from unconventional shale extraction and processing: human health concern for residential communities." *Environmental Health Insights* 10 (2016): 75.
33	Schade, Gunnar W., and Geoffrey Roest. "Analysis of non-methane hydrocarbon data from a monitoring station affected by oil and gas development in the Eagle Ford shale, Texas." *Elementa Science of the Anthropocene* 4 (2016).
34	Abeleira, A., I. B. Pollack, B. Sive, Y. Zhou, E. V. Fischer, and D. K. Farmer. "Source characterization of volatile organic compounds in the Colorado Northern Front Range Metropolitan Area during spring and summer 2015." *Journal of Geophysical Research: Atmospheres* 122, no. 6 (2017): 3595-3613.
35	Chen, Huan, and Kimberly E. Carter. "Modeling potential occupational inhalation exposures and associated risks of toxic organics from chemical storage tanks used in hydraulic fracturing using AERMOD." *Environmental pollution* 224 (2017): 300-309.
36	Goetz, J. Douglas, Anita Avery, Ben Werden, Cody Floerchinger, Edward C. Fortner, Joda Wormhoudt, Paola Massoli et al. "Analysis of local-scale background concentrations of methane and other gas-phase species in the Marcellus Shale." *Elem Sci Anth* 5 (2017).
37	Ghosh, Buddhadeb. "Impact of Changes in Oil and Gas Production Activities on Air Quality in Northeastern Oklahoma–Ambient Air Studies in 2015, 2016, and 2017." *Environmental science & technology* (2018).

Table 1.3: Summary of sampling methods and frequencies used in the reviewed articles.

Article	Method	Sample Frequency
Mckenzie et al. (2012)	Evacuated Summa passivated stainless-steel canisters, U.S. EPA Method TO-12	24-hr
Swarthout et al. (2013)	2-L electropolished stainless steel canisters; gas chromatographs (GC) equipped with two flame ionization detectors, two electron capture detectors, and a mass spectrometer	35-mins
Gilman et al. (2013)	Custom-built, two-channel gas chromatograph−mass spectrometer (GC-MS)	5-min
Steinzor et al. (2013)	Summa canisters, U.S. EPA's TO-14 and TO-15	24-hr
Bloomdahl et al. (2014)	Data provided by well operators, reports, and field samples and used in two models of volatilization	not specified
Bunch et al. (2014)	Automated gas chromatography (autoGC) samplers	40-min
	Canister samples, gas chromatography–mass spectrometry (GC-MS)	24 h
Colborn et al. (2014)	6-L summa canister, U.S. EPA TO-12/U.S. EPA Photochemical Assessment Monitoring Stations (PAMS) Protocol using gas chromatography/flame ionization detection (GC-FID), U.S. EPA Method TO-15 using gas chromatography/mass spectrometry (GC-MS)	4-hr, 6-hr
	Filter/Polyurethane (PUF), U.S. EPA Method TO-13 using gas chromatography/mass spectrometry (GC-MS)	24-hr
	2-4 Dinitrophenylhydrazine (DNPH) coated Silica Gel Cartridge, U.S. EPA Method TO-11A	4-hr, 6-hr
Rich et al. (2014)	6-L Summa canisters, American Society for Testing and Materials Method D-1357-95, U.S. EPA TO-14A using gas chromatograph/mass spectrometer (GC-MS)	24-hr
Pekney et al. (2014)	Gas chromatograph flame ionization detection (GC-FID) with thermal desorption	1-hr
Eapi et al. (2014)	Picarro G2204 cavity ring-down spectrometer (CRDS)	3-sec
Zielinska et al. (2014)	6-L Summa canister, gas chromatography/mass spectrometry/flame ionization detector (GC/MS/FID), U.S. EPA Method TO-15	grab samples, 1-hr, 7-day
	RAE Systems model PGM-7240, photoionization detector (PID)	not specified
	Teflon and quartz filter samples from portable Airmetrics MiniVol samplers	7-day
	Radiello diffusive samplers, thermal desorption-cryogenic pre-concentration method, high-resolution gas chromatograph/mass spectrometer GC-MS	7-day
	2,4-Dinitrophenyl hydrazine (DNPH) impregnated Sep-Pak cartridges, U.S. EPA Method TO-11	grab samples, 1-hr
Esswein et al. (2014)	SKC Pocket Pumps, Gilian low-flow personal sampling pumps, Anasorb CSC activated coconut shell charcoal sorbent tubes, NIOSH Methods 1500, 1501, and 1550	Full shift and area sampling
	ToxiRae, MiniRae 2000, MultiRae Plus with photoionization detectors (PIDs), UltraRAE 3000 PID	Direct reading and spot measurements
	TraceAir passive aldehyde badges, high-performance liquid chromatography (HPLC) with ultraviolet detection, modified NIOSH Method 2532	Direct reading and spot measurements

	SKC Pocket Pumps, Gilian low-flow personal sampling pumps, and SKC silica gel sorbent tubes, NIOSH Method 2000	Direct reading and spot measurements
	SKC XR-5000 personal sampling pumps, XAD-2 sorbent tubes, polytetrafluoroethylene (PTFE) filters, NIOSH Method 5506	Direct reading and spot measurements
Macey et al. (2014)	Evacuated sampling ("bucket") vessel, U.S. EPA Method TO-15 using gas chromatograph/mass spectrometer	2 or 3-min
	UMEx100 passive samplers, ASTM D 5504-08 using gas chromatograph equipped with a sulfur chemiluminescence detector	8-hr
Thompson et al. (2014)	6-L stainless steel Summa canisters with Veriflo flow controllers, U.S. EPA Method TO-14 using automated gas chromatograph-mass spectrometer/flame ionization detection (GC-MS/FID)	5-min, 3-hr, 24-hr
Warneke et al. (2014)	Proton Transfer Reaction Mass Spectrometry (PTR-MS)	0.5-sec
	Gas chromatograph-mass spectrometer (GC-MS)	5-min
Li et al. (2014)	Protontransfer-reaction mass-spectrometry (PTR-MS)	1-sec
	Picarro cavity ring down spectroscopy (CRDS) instrument	5-sec
Ethridge et al. (2015)	Thermo Scientific TVA 1000portable vapor analyzer with a flame ionization detector (FID)	not specified
	Thermo Scientific TVA 1000B with flame ionization detector (FID) and photo ionization detector (PID)	not specified
	RAE Systems AreaRAE Wireless Multi-Gas monitor	not specified
	RAE Systems MiniRAE 2000 and 3000 with photoionization detector (PID)	not specified
	UltraRAE 3000 with enhanced photo ionization detector (PID)	not specified
	Special emissions inventory provided by well operators	not specified
	Stationary automated gas chromatograph (AutoGC) with dual capillary columns and dual flame ionization detectors (FIDs), U.S. EPA Method TO-14	40-min
	SUMMA canister samples, thermal desorption into a gas chromatograph/mass spectrometer (GC/MS), modified U.S. EPA TO-15	1-hr, 24 hr
Goetz et al. (2015)	Proton-Transfer Reaction Mass Spectrometer (PTR-MS)	3-sec
Lan et al. (2015)	Tekran 2537A instrument with a cold vapor atomic fluorescence (CVAF) spectrometer	2.5-min
Swarthout et al. (2015)	2-L passivated stainless steel canisters	1-hr
	Proton-transfer reaction-mass spectrometer (PTR-MS)	2-min
Brantley et al. (2015)	Subatmospheric 6-L stainless steel canister with a valve and passivated interior, gas chromatography with flame ionization detection (GC-FID)	20-min
Casey et al. (2015)	Indoor radon sample inventory	not specified
Field et al. (2015)	Thermo Scientific 55i back-flush gas chromatographic system GC/FID	1-min
	Perkin Elmer OPA system gas chromatographic system GC/FID	grab, 1-hr, 24-hr, 3-day
Field et al. (2015)	Radiello diffusive samplers, thermal desorption/gas chromatography/mass spectrometry	3-7-day
	Prototype pocket diffusive samplers, thermal desorption/gas chromatography/flame ionization detection	3-days
Halliday et al. (2016)	Proton-transfer-reaction quadruple mass spectrometry (PTR-QMS) instrument	1-min

	NCAR Trace Organic Gas Analyzer (TOGA) gas chromatograph/mass spectrometer (GC/MS)	35-sec
	Whole air canister samples, gas chromatography (GC)	30-sec
Maskrey et al. (2016)	MultiRae Plus gas monitor (MultiRAE), photoionization detector (PID)	60-sec
	MultiRae ppbRAE 3000 TVOC monitor, photoionization detector (PID)	60-sec
	6-L Summa canisters, U.S. EPA Method TO-15	24-hr
Hildenbrand et al. (2016)	Mass spectrometer (MS) and residual gas analyzer	not specified
Paulik et al. (2016)	Low-density polyethylene (LDPE) passive samplers, Agilent 7890A gas chromatograph interfaced with an Agilent 7000 GC/MS-MS	3-4 weeks
Marrero et al. (2016)	2-L electropolished stainless steel canisters, multicolumn, multidetector gas chromatographic system	not specified
Eisele et al. (2016)	Passive samplers with PerkinElmer style tubes containing Carbopack X sorbent, PE Turbo Matrix ATD thermal desorption system followed by gas chromatography/mass spectrometry detection using an Agilent 6890N/5975 inert gas chromatography/mass spectrometry system (Methods 325A/B)	14-day
Schade & Roest (2016)	Automated gas chromatography (autoGC) samplers	40-min
Rich & Orimoloye (2016)	6-L Summa canisters with a certified 24-hour mass-flow regulator, U.S. EPA Compendium Method Toxic Organics (TO-14A)	24-hr
Abeleira et al. (2017)	Automated four-channel online gas chromatographic (GC) system with four different separation columns and four detectors	not specified
Chen & Carter (2017)	Calculated using various inventories	Estimates
Goetz et al. (2017)	Proton-Transfer Reaction Mass Spectrometer (PTR-MS)	3-sec

Table 1.4: Summary of all HAPs investigated within the reviewed studies.

	Casey et al. (2015)	Eapi et al (2014)	Lan et al. (2015)	Li et al. (2014)	Paulik et al. (2016)	Halliday et al. (2016)	Esswein et al. (2014)	Ghosh (2018)	Warneke et al. (2014)	Field et al. (2015a)	Hildenbrand et al. (2016)	Gilman et al. (2013)	Goetz et al. (2015)	Marrero et al. (2016)	Thompson et al. (2014)	Pekney et al. (2014)	Brantley et al. (2015)	Field et al. (2015b)	Rich & Orimoloye (2016)	Schade & Roest (2016)	Eisele et al. (2016)	Macey et al. (2014)	Swarthout et al. (2015)	Bloomdahl et al. (2014)	Steinzor et al. (2013)	Bogacki & Macuda (2014)	Abeleira et al. (2017)	Goetz et al. (2017)	McKenzie (2012)	Swarthout et al. (2013)	Zielinska et al. (2014)	Chen & Carter (2017)	Rich et al. (2014)	Ethridge et al. (2015)	Bunch et al. (2014)	Maskrey et al. (2016)	Colborn (2014)
benzene						+	+	+	+	+	+	+	+/-	+	+	+	+	+	+	++	+	+	+	++	+	++	+	+	+	+	+	++	+	+	++	+	+
toluene									+	+	+	+	+/-	+	+	+	+	+	+	++	+	+	+	++	+	++	+	+	+	+	+	++	+	+	++	+	+
xylenes*										+	+	+		+	+	+	+	+	+	++	+	+	+	++	+	++	+	+/-	+	+	+	++	+	+	++	+	+
ethylbenzene										+	+			+	+	+	+	+	+	++	+	+	+/-	++	+		+	+/-	+	+	+	++	+	+	++	-	+
n-hexane								+		+/-		+		+	+	+	+	+		++		+	+		+		+		+	+	+		+	+	++	+	+
styrene																+	+	-[1]	+	++	+		+/-	++					+	+	+		+	+/-	++	-	+
1,3-butadiene										+/-								-[1]		++	-	+							+		+			+/-	++	-	-
2,2,4-trimethylpentane																	+										+		+	+	+		+	+/-	++	-	-
formaldehyde																						+				++				++	+	++					+
acetaldehyde													+/-										+			++	+	+		+	+	++					+
carbon tetrachloride																					-			++	+									+/-	++	-	-
ethylene dichloride																								++	+								+	+/-	++	-	-
methanol							-		+				+										+					+		+		++					+
1,2,4-trichlorobenzene																			+					++									+			-	-
carbon disulfide																															+		+		++	-	-
methyl chloride																									+								+	+/-	++	+	-
methylene chloride																						-			+		+					++	+	+/-	++	+	+
tetrachloroethylene																					+				+		+						+	+/-	++		-
1,1,2-trichloroethane																								++										+/-	++	-	-
1,1,2,2-tetrachloroethane																																	+	+/-	++	-	-
1,4-dichlorobenzene(p)																			+														+			-	-
chlorobenzene																						+												+/-	++	-	-
chloroform																											+						+	+/-	++	-	-
cumene																						+							+			++		+/-	++	-	+
methyl chloroform																								++										+/-	++	-	-
naphthalene					+		+																			++						++	+				+
propylene dichloride																								++										+/-	++	-	-
trichloroethylene																									+								+	+/-	++		-
vinyl chloride																								++										+/-	++	-	-
acetonitrile													+/-										+					+		+							
acrolein																										++					-				++		-
ethylene dibromide																																		+/-	++	-	-
ethylidene dichloride																																		+/-	++	-	-
hexachlorobutadiene																																	+			-	-
methyl bromide																																		+/-	++	-	-
methyl tert butyl ether																																			++	-	-
1,4-dioxane																																++				+	-
bromoform																																				-	-
carbonyl sulfide																						+								+			+				
ethyl chloride																																				-	-
hydrogen sulfide		+		+			+/-															+															
radon	++																																				
mercury			+																																		
methyl isobutyl ketone																																++			++		-
propionaldehyde																															+						+
1,3-dichloropropene																																++		+/-		-	
acrylonitrile																						-															-
allyl chloride																																					-
benzyl chloride																																					-
chloroprene																																			++		
POM**					+		+																			++					+						+
propylene oxide																																++					-
vinyl acetate																																					-
vinyl bromide																																					-
dimethyl formamide																																++					
acrylamide																																++					
epichlorohydrin																																++					
acrylic acid																																++					
dichloroethyl ether																																++					
aniline																																++					
vinylidene chloride																																		+/-	++		

*xylenes include all isomers and mixtures

** Polycyclic organic matter (POM)

[1] Signal-to-noise ratio below threshold

🟩 Included in study	⬜ Not included in study
+ HAP found above sample LOD	+/- HAP not specficied if measured above sample LOD
- HAP not detected	++ HAP data extracted from secondary source

Table 1.5: Summary of HAPs by state included in analysis as primary data.

Arkansas

- 1,3-butadiene
- Acrylonitrile
- Benzene
- Carbonyl sulfide
- Chlorobenzene
- Cumene
- Dichloromethane
- Ethylbenzene
- Formaldehyde
- Hydrogen sulfide
- n-Hexane
- Toluene
- Xylenes

Colorado

- 1,1-dichloroethane
- 1,1,2-trichloroethane
- 1,1,2,2-tetrachloroethane
- 1,2,4-trichlorobenzene
- 1,3-butadiene
- 1,4-dichlorobenzene
- 1,4-dioxane
- 2,2,4-trimethylpentane
- 2,2,4-trimethylpentane
- Acetaldehyde
- Acetonitrile
- Acrolein
- Acrylonitrile
- Allyl chloride
- Benzene
- Benzyl chloride
- Bromoform
- Carbon disulfide
- Carbon tetrachloride
- Carbonyl sulfide
- Chlorobenzene
- Chloroform
- Cumene
- Ethyl chloride
- Ethylbenzene
- Ethylene dibromide
- Ethylene dichloride
- Formaldehyde
- Hexachlorobutadiene
- Hydrogen sulfide
- Methanol
- Methyl bromide
- Methyl chloride
- Methyl chloroform

Ohio

- 1,3-butadiene
- Acrylonitrile
- Benzene
- Carbonyl sulfide
- Chlorobenzene
- Cumene
- Dichloromethane
- Ethylbenzene
- Formaldehyde
- Hydrogen sulfide
- n-Hexane
- POMs
- Toluene
- Xylenes

Oklahoma

- Benzene
- n-Hexane

Pennsylvania

- 1,1,2-trichloroethane
- 1,1,2,2-tetrachloroethane
- 1,2,4-trichlorobenzene
- 1,3-butadiene
- 1,3-dichloropropene
- 1,4-dichlorobenzene(p)
- 1,4-dioxane
- 2,2,4-trimethylpentane
- Acetaldehyde
- Acrylonitrile
- Benzene
- Bromoform
- Carbon disulfide
- Carbon tetrachloride
- Carbonyl sulfide
- Chlorobenzene
- Chloroform
- Cumene
- Dichloromethane
- Ethyl chloride
- Ethylbenzene
- Ethylene dibromide
- Ethylene dichloride
- Ethylidene dichloride
- Formaldehyde
- Hexachlorobutadiene
- Hydrogen sulfide
- Methanol
- Methyl bromide

Texas*

- 1,1,2-trichloroethane
- 1,1,2,2-tetrachloroethane
- 1,2,4-trichlorobenzene
- 1,3-butadiene
- 1,3-dichloropropene
- 1,4-dichlorobenzene
- 2,2,4-trimethylpentane
- Acetaldehyde
- Acrolein
- Benzene
- Carbon disulfide
- Carbon tetrachloride
- Carbonyl sulfide
- Chlorobenzene
- Chloroform
- Chloroprene
- Cumene
- Ethylbenzene
- Ethylene dibromide
- Ethylene dichloride
- Ethylidene dichloride
- Formaldehyde
- Hexachlorobutadiene
- Hydrogen sulfide
- Mercury
- Methyl bromide
- Methyl chloride
- Methyl chloroform
- Methyl isobutyl ketone
- Methyl tert butyl ether
- Methylene chloride
- n-Hexane
- Naphthalene
- POMs
- Propionaldehyde
- Propylene dichloride
- Styrene
- Tetrachloroethylene
- Tetrachloroethylene
- Toluene
- Trichloroethylene
- Vinyl chloride
- Vinylidene chloride
- Xylenes

Utah

- Benzene
- Hydrogen sulfide
- Methanol

• Methyl isobutyl ketone • Methyl tert-butyl ether • Methylene chloride • n-Hexane • Naphthalene • POMs • Propionaldehyde • Propylene dichloride • Propylene oxide • Styrene • Tetrachloroethylene • Tetrachloroethylene • Toluene • Trichloroethylene • Vinyl acetate • Vinyl bromide • Vinyl chloride • Xylenes	• Methyl chloride • Methyl chloroform • Methyl tert butyl ether • Methylene chloride • n-Hexane • Propylene dichloride • Styrene • Tetrachloroethylene • Toluene • Trichloroethylene • Vinyl chloride • Xylenes	• Toluene
		Wyoming
		• 1,3-butadiene • Acrylonitrile • Benzene • Carbonyl sulfide • Chlorobenzene • Cumene • Dichloromethane • Ethylbenzene • Formaldehyde • Hydrogen sulfide • n-Hexane • Napthalene • POMs • Styrene • Toluene • Xylenes

* Includes data collected via the TCEQ monitoring network

Chapter 2: An investigation of the air pollution exposure impact zone around oil and natural gas operations in the Colorado Front Range

Authors:

Diane A. Garcia-Gonzales[1]

Michael Jerrett[1-3]

Affiliations:

[1] Environmental Health Sciences Division, 50 University Hall, School of Public Health, University of California, Berkeley, Berkeley, CA 94720. dgonzales98@gmail.com

[2]Department of Environmental Health Sciences, Fielding School of Public Health University of California, Los Angeles

[3]Center for Occupational and Environmental Health, Fielding School of Public Health University of California, Los Angeles

A similar version of this chapter will be submitted for publication to the journal of Environmental Science & Technology.

2.1 Abstract

Upstream oil and natural gas development (ONG) has expanded rapidly across the United States over the past decade, particularly in Colorado where natural gas and oil production has increased 35 and 434 percent, respectively, since 2006[111]. Research aimed at understanding the full range of health impacts from ONG development has been outpaced by the rapidly evolving technology and increased production efforts of the past decade. A growing body of evidence exists identifying an association between proximity from ONG development and potential health risks; however, the research has failed to feature any rigorous spatial analysis of pollutant levels, only suggesting that a spatial dimension exists. In this work, we investigate air pollutant gradient behavior around ONG facilities located within the semirural region of the Northern Front Range of Colorado in order to: 1) investigate the potential air pollution exposure impact zone and; 2) characterize ambient air quality in communities near upstream ONG development. Results from the current analysis suggest benzene, toluene, n-hexane, and n-pentane concentrations reach background concentrations around 220 meters from the facility fence line. Although limited, we found evidence that particles from ONG activities, particularly re-casing activities, may be measured in ambient air as far as 560 meters from the facility. While we have an adequate understating about particles near roadways, there is a dearth of scientific literature investigating the constituents of particles from upstream ONG development and their impact to human health. Correlations between n-pentane and measured hazardous air pollutants including benzene, n-hexane, and toluene, suggest that a broad range of pollutants are co-emitted during upstream ONG development and activities. These co-emissions may increase original estimates of health risks of exposure if compounds are biologically additive or synergistic, especially in environments with an already high pollutant burden, as seen with carbon monoxide at the Platteville sampling location.

2.2 Introduction

Upstream oil and natural gas development (ONG) has expanded rapidly across the United States over the past decade. Since 2006, the production of natural gas has increased 35 percent, while oil production has increased 434 percent in Colorado[111]. In the highest producing region of Weld County, natural gas and oil production has increased 258 and 815 percent respectively, over the same time period[111]. Existing research on chemicals and equipment associated with ONG development reveal a potential for adverse health outcomes and a number of studies have shown an association between proximity from site and potential health risks[14,16,41,42,99,101,102,104,105,112–119]. Most of these health studies, however, have not featured any rigorous spatial analysis of pollutant levels, only suggesting that a spatial dimension exists[120].

Research efforts aimed at understanding the full range of health impacts from ONG development has been outpaced by the rapidly evolving technology and increased production efforts of the past decade. Further complicating these efforts are that shale geologies, production volumes, development phases, well pad equipment, and chemicals vary between well pads. In an attempt to incorporate some of these variables, researchers have developed activity metrics when evaluating the impact of distance on health impacts[99,119]. These studies may elucidate the impacts using a comprehensive approach, yet these methodologies fail to identify specific etiologic agents or exposure pathways.

Given the sparse amount of literature on exposures to hazardous air pollutants near ONG operations and the potential for impacts on health, we investigated the air pollution exposure impact zones around ONG operations in Colorado's Northern Front Range (NFR). We measured four key volatile organic compounds (VOCs), common in ONG emissions, using passive samplers placed along a transect through two active well pads. Time weighted average concentrations were evaluated for evidence of a distance decay gradient. Studies have demonstrated gradient behavior in combustion related emissions where elevated emissions near roadways decreased to or near background levels as distance from the roadway increased[121–129]; however, few studies have repeated this methodology around ONG well pads, despite the need to understand the behavior and potential exposure pathways of well pad emissions. Additionally, we measured a broader range of gas phase species and size-speciated particulates to characterize the air quality of semirural environments in dense ONG regions. Therefore, the aim of this study was two-fold: (1) to investigate the potential air pollution exposure impact zone and; (2) characterize air quality near upstream ONG operations in semirural environments. Results identified potential exposures of populations residing at various distances from oil and natural gas operations and help guide policy around developing necessary setback requirements.

2.3 Methods

Sampling Site Description

The current study coincides with the 2014 "Deriving Information on Surface Conditions from Column and Vertically Resolved Observations Relevant to Air Quality" (DISCOVER-AQ) campaign. The DISCOVER-AQ campaign is a collaborative effort between the National Center for Atmospheric Research (NCAR), National Aeronautics and Space Administration (NASA), and several other institutions and has the aim of understanding the air quality of the NFR. Upstream ONG operations in the NFR mainly occur around the rural and semirural areas of Weld County. Sites were selected based on accessibility, host interest, and ability to represent a distance decay gradient without significant influence from confounding emissions sources (see map in Figure 2.1 for location of sampling sites).

A total of six sampling sites were selected for the current study and are numbered on the map in Figure 2.1: (1) Control; (2) Parkland Airport; (3) Boulder Atmospheric Observatory (BAO); (4) Longmont; (5) Platteville; and (6) Weld Tower. Four sampling sites (Control, BAO, Platteville, and Weld Tower) overlapped with the DISCOVER-AQ deployment locations and, thus, were co-located with other air quality monitors from the campaign. With the exception of the control, all sites were located within rural or semi-rural areas of Weld County. The control site, located in Boulder county, was geographically positioned away from all major competing pollution sources, with the closest producing well over one kilometer in distance.

Monitors deployed at the Parkland Airport sampling site were located in the yard of a single non-smoking residential home within a multi-acre, fly-in community with taxi easements and a private 4,200-foot aircraft runway located northeastern of the sampling site. Monitors deployed along the first transect at the Longmont sampling site targeted a producing ONG facility on a public-school campus, located between the parking lot and baseball fields. Hosts at both the Parkland Airport and Longmont sampling sites were advised to avoid activities that may expose the monitors to additional VOC emissions during the sampling timeframe. All other sampling locations overlapped with the DISCOVER-AQ campaign and were selected based on their distance from active ONG wells. BAO is a research facility in Erie, Colorado, maintained by National Oceanic and Atmospheric Administration's (NOAA) Earth System Research Laboratory (ESRL) Physical Sciences Division and is used for studying the planetary boundary layer. We selected this particular site for our second distance decay gradient because of the proximity of an active ONG well 260 meters west of the property boundary. During our sampling timeframe, the targeted facility was conducting re-casing activities: relining the inside of the drilled wellbore with steel pipe. We selected the rural Platteville site to characterize air quality in one of the densest ONG areas of the NFR; we selected both the Weld Tower and Parkland Airport sites to characterize air quality in ONG development regions with competing urban-related sources.

Data Collection

Passive TraceAir Badges

Passive samplers are inexpensive air quality sensors capable of measuring time weighted average concentrations from a variety of VOCs. They are commonly used in occupational settings but have shown success in ambient environments with longer exposure timeframes. The proven utility of passive samplers has been demonstrated across several ONG monitoring studies[18,31,36,41,63], but have not been used extensively for spatial gradient monitoring within the existing ONG literature. Passive TraceAir badges, from Assay Technology (http://www.assaytech.us/), are capable of collecting a panel of organic air pollutants through passive diffusion in a time-integrated manner. We deployed 30 passive TraceAir badges across all six sampling sites. To protect the samplers from the elements, all passive TraceAir badges were placed within an open-bottom, non-treated AllCan West (http://allstatecan.com/) tin can affixed to a metal fence post or existing structure at each site. A conceptual model of the distance decay monitoring set-up and sample of the passive TraceAir badge can be found in Figure 2.2.

At the BAO and Longmont sampling sites, we used several passive TraceAir badges to create transects through ONG well pads, similar to a study conducted near a major highway by Beckerman et al. (2008)[121]. At the Longmont sampling site, passive TraceAir badges were placed at the east and west sides of the facility's fence line. Five badges were placed along the eastern transect, several meters apart, up to 300 meters between the first and last passive badge. On the western side of the facility, one passive TraceAir badge was placed at the fence line and one additional badge was placed 100 meters further down the western transect. At the BAO sampling site, passive TraceAir badges were placed 230 meters from the eastern fence line, and an additional eight badges were placed at increasing distances along the eastern transect, up to 1,200 meters apart. On the western side of the facility, one passive TraceAir badge was placed 180 meters from the fence line and two additional badges were placed along the western transect, up to 300 meters apart.

Latitude and longitude coordinates were collected for each passive TraceAir badge using a Garmin eTrek GPS device. After 14 days in-field, samplers were collected and sent to Assay Technology laboratories in Ohio for analysis of n-pentane (CAS 109-66-0), n-hexane (CAS 110-54-3), benzene (CAS 71-43-2), and toluene (CAS 108-88-3). Badges were processed using a modified OSHA 7 method which included desorption in carbon disulfide with co-solvent and analysis by gas chromatography with flame ionization detector (GC/FID). Data was blank corrected and provided as average concentrations for period of time monitored.

Active Sensor Networks for Air Quality Monitors

Sensor Networks for Air Quality (SNAQ) monitors used for active air quality monitoring were developed at the Chemistry Department, University of Cambridge, UK. These monitors are capable of measuring carbon monoxide (CO), nitrogen oxide (NO), ozone (O_3), sulfur dioxide (SO_2), nitrogen dioxide (NO_2), and nitrogen oxides (NOx) gas phase species using electrochemical sensors developed by Alphasense (www.alphasense.com). In addition, SNAQ monitors measure carbon dioxide (CO_2) and total volatile organic compounds (tVOC) via optical sensors. A compact optical particle counter, designed and built at the Center for Atmospheric and Instrumentation Research at the University of Hertfordshire, also incorporated into the unit, measures aerosol concentrations every 20 seconds in the form of 16-bin histograms covering size ranges between 0.38 – 17.4 µm. Meteorological data including temperature, relative humidity (RH), wind speed and direction are also gathered by each node. Monitors contain a geographic positioning system (GPS) receiver and data was collected and stored via an onboard universal serial bus (USB) drive and manually downloaded on a weekly basis.

Six of the SNAQ monitors were deployed at five locations around Colorado and each was co-located with a passive TraceAir badge. Due to security concerns, a SNAQ monitor was not deployed at the Longmont sampling site. Two SNAQ monitors were co-located along the eastern transect at the BAO sampling site. All SNAQ monitors were placed in the field for approximately 3-4 weeks prior to collection.

Secondary Data Sources

Well production data for all sites was collected from the Colorado Oil and Gas Conservation Commission (COGCC) and summed for the month of August 2014. We used the geographic center of each well pad to create a buffer and determine density of producing wells within a half mile. For regional monitoring sites, we used the geographic coordinates of each SNAQ monitor to create buffers for density calculations. Wind speed and direction for the Longmont and BAO sampling sites were collected from MesoWest[130].

Data Analysis

Data from SNAQ monitors was post-processed at Cambridge University. Air quality and meteorological datasets were collected, saved as comma separated value (csv) files, and uploaded into R programming environment for data processing, visualization, and analysis. Data was analyzed using the open-source tools for air pollution data analysis, OpenAir[131], a Natural Environment Research Council (NERC) knowledge exchange project for the analysis of air pollution data (www.openair-project.org). Gas phase species and size-speciated particulates were analyzed using the OpenAir package for bivariate concentration polar plots and cluster analysis to identify and group similar characteristics by region, similar to previous source attribution efforts of various criteria air pollutants[132,133].

2.4 Results

Well Production Data

During the field campaign, Weld County sampling sites had an average of 18.4 producing wells within 0.5 miles (0.8 km) radius with an average gas production of 44,038 million cubic feet (Mcf) and oil production of 1,705 bbls (Table 2.1). Compared to all other sites, the Platteville monitoring site was located within in the highest density ONG field. Active wells within 0.5 miles from the Platteville monitoring site produced a total of 166,528 Mcf of gas, approximately three times more than all other Weld County monitoring sites combined over the same time period. This site also had the highest natural gas to oil production ratio (87 Mcf of gas per 1 bbls of oil). The BAO Tower site produced the most oil compared to the gas equivalent (1.69 Mcf for each 1 bbls of oil).

Passive TraceAir Badges

Summary Statistics and Correlation Analysis

The precision of passive TraceAir badge duplicates was ≤10%, with the exception of benzene and toluene at the Weld Tower sampling site where the duplicate samples were outside this range. Median two-week time weighted concentrations of all measured VOC species in Weld County were elevated above concentrations measured at the Control sampling site (Table 2.2). Passive TraceAir badges co-located with SNAQ monitors found a range of concentrations at each sampling site. Concentrations were highest in Platteville where mean concentrations of benzene, toluene, n-hexane, and n-pentane were 0.65, 0.73, 4.45, and 11.5 ppbv, respectively (data not included in table). Mean benzene concentration along the transect at the Longmont sampling site was significantly higher (0.60 ppbv) compared to the transect at the BAO sampling site (0.16 ppbv). Highest two-week time weighted concentration for a single passive TraceAir badge was measured at the Longmont sampling site (1.30 ppbv), where the targeted ONG facility was located on a public-school campus. Mean concentrations of toluene, n-pentane, and n-hexane were also higher along the transect at the Longmont compared to the BAO sampling site where toluene was below the sample limit of detection (LOD).

All measured VOC species from Weld County passive TraceAir badge samples were highly correlated (Table 2.3); however, the strength of these correlations varied slightly between sites. The relationship of all measured species at the Longmont sampling site showed a strong and significant positive correlation ($R^2 > 0.99$, p-value < 0.001). Weaker correlations between all measured VOC species were found at the BAO sampling site. Toluene was found below the sample limit of detection (< 2.0 ppbv) and, therefore, could not be included in the correlation analyses. Weaker correlations between n-pentane and n-hexane were measured at the BAO sampling site, although a relatively strong, positive correlation remained between n-pentane and benzene ($R^2 = 0.91$). Median toluene-to-benzene tracer ratios less than 1.0 at the Longmont sampling site further suggest minimal air quality impacts from urban and vehicle emission sources. Using half the sample limit of detection as the concentration of toluene to build tracer ratios, we found a median toluene-to-benzene ratio of 1.33 ppbv/ppbv at the BAO sampling site.

Spatial Gradient Monitoring

Passive TraceAir badges were deployed at increasing distances along the transects at the Longmont (Figure 2.3A) and BAO (Figure 2.3B) sampling sites in both the east and west directions. Wind data from MesoWest for the BAO (Station ID: D4448) and Longmont (Station ID: AR720) sampling sites were plotted with wind rose diagrams for the two-week deployment timeframe for the passive TraceAir badges. Visual inspection of the resulting diagrams revealed prevailing wind patterns originated from a southeast and southwest direction at the BAO and a northwest direction at the Longmont sampling sites; the sampled transects experienced approximately 10% of the total wind during the sampling timeframe.

Two-week time weighted concentrations for all VOC species were standardized using the maximum value of the respective VOC from the full transect in the denominator and presented as a percent of the maximum (Figure 2.4). Standardized results were plotted against distance (in meters) from the center of the targeted ONG facility in both directions. For the current work, we defined background concentrations as the concentration found at the furthest passive badge along the western transect (less dominate wind direction). Figure 2.4A plots the distance decay gradient at the Longmont sampling site where, the highest concentrations were measured along the more dominate (eastern) transect. On the western transect, concentrations of all measured VOCs were approximately 45% of the maximum value measured at samples collected closest to the facility and decayed an additional 10% between the first and second passive badge for benzene, n-hexane, and n-pentane; toluene was below the sample LOD at the sample furthest from the fence line. The eastern fence line measured the largest concentrations for all VOCs during the sampling timeframe. At this site, maximum two-week time weighted average concentrations of benzene measured 1.30 ppbv in the passive samples collected adjacent to the fence line. Between the first and second passive badges (35 meters), concentrations for all VOCs declined approximately 55% from the maximum value. Concentrations along this transect continued to decline until values neared background concentrations, around 220 meters from the ONG facility fence line.

Figure 2.4B represents distance decay gradient plots using standardized two-week time weighted average concentrations for measured VOCs at the BAO sampling site, where the targeted facility was re-casing drilled wells. Compared to the Longmont sampling site, samples collected along the transect at BAO revealed a narrower range of concentrations. Passive samplers were placed at the western and eastern edge of the property line, approximately 180 and 230 meters from the targeted ONG facility, respectively. Toluene was measured below the sample limit of detection within every sample collected during the sampling timeframe. The maximum benzene concentration of 0.18 ppbv was measured at the passive badge closest to the western fence line and decayed approximately 5% of the maximum value between the first and last passive badge along the western transect. Along the eastern transect, benzene measured background concentrations at the first passive sampler and remained relatively consistent along the transect. n-Pentane gradient behavior was similar to benzene, but concentrations neared background at slightly further distances. n-Hexane measured the largest decay between the first and second passive sampler along the eastern transect and again at further distances.

Characterization of Criteria Air Pollutants in Colorado

Concentrations of gas-phase species collected from the SNAQ monitors were similar across all monitoring sites with the exception of carbon monoxide (CO), where elevated concentrations were found well above measured background concentrations (Figure 2.5). Specifically, CO concentrations were elevated at sites with the highest density of gas wells, where median concentrations were approximately two to three times higher than median concentrations at the control site (Table 2.4). To elucidate potential emission sources, k-means cluster analysis of bivariate polar plot features (wind speed and wind direction) was used with CO concentrations at the Parkland Airport (Figure 2.6), Weld Tower (Figure 2.7), and Platteville (Figure 2.8) sampling sites. The number of clusters were selected to maximize sample size and describe all potential source pathways.

A six-cluster analysis of CO concentrations at the Parkland Airport site revealed an elevated CO source originating from the north/east of the sampling monitor, the direction of the airport runway, with a median CO concentration of 204.25 ppbv. All other clusters were analyzed in a time variation plot where peak concentrations are seen in the morning and late afternoon, similar to diurnal patterns from on-road vehicle emissions. A similar analysis was conducted at the Weld Tower site and revealed an elevated CO source originating from the north/west and in the direction of a major highway. Within this cluster, median CO concentrations of 117.63 ppbv were measured and a time series variation plot of all clusters revealed diurnal patterns similar, but more pronounced, than those seen in at the Parkland Airport sampling site.

The Platteville sampling location reported the highest concentrations of CO compared to the other sampling sites. A polar cluster analysis revealed two elevated CO clusters: a south/east cluster with a median CO concentration of 148.97 ppbv and an eastern cluster with a median CO concentration of 118.12 ppbv. A time variation plot of these two clusters revealed unique temporal patterns with peak CO concentrations most pronounced during early morning hours. Although the other clusters reflect temporal patterns similar to on-road vehicle emissions, peak morning concentrations were noticeably earlier than the other two sampling locations.

Additional analyses were conducted to further attribute potential sources using combustion tracer ratios and correlations to speciated particles. Both CO and NOx are commonly used tracer species for anthropogenic emissions, and their relationship can provide additional insight into potential combustion sources[134–137]. Peak [CO]/[NOx] ratios were identified within clusters with elevated CO concentrations at the Parkland Airport, Weld Tower, and, to a lesser extent, Platteville sampling locations. Moderate, positive correlations were identified between $PM_{2.5}$ and CO levels within peak [CO]/[NOx] ratio clusters at Parkland Airport and Weld Tower, where distances from likely sources were less than 0.80 kilometer, but these results were not replicated within any of the Platteville clusters.

BAO Tower PM

A ground-level CH_4 Picarro monitor was deployed at the BAO sampling site by Fischer's Group at Colorado State University's Department of Atmospheric Science as part of the DISCOVER-AQ mission. A time variation plot for CH_4 was created and provided in Figure 2.9 to show ambient concentrations over the available timeframe (July 31, 2014 – August 22, 2014). A cluster plot was created but did not reveal meaningful variations in the CH_4 dataset, and therefore, additional analysis between clusters was not pursued.

To better characterize distribution of PM in the dense ONG region and the relationship with CH_4, two SNAQ monitors were co-located at the BAO Tower sampling site approximately 335 meters apart (Figure 2.10). First, SNAQ 19 was deployed at the far west fence line of the BAO sampling facility (henceforth referred to as BAO Fenceline), approximately 230 meters east from the edge of the targeted ONG facility (denoted within the red polygon in Figure 2.10). Second, SNAQ 11 was deployed near the BAO tower (henceforth referred to as BAO Tower), approximately 560 meters east from the edge of the targeted ONG facility. Multiple wind directions contributed to the overall particle means (Figure 2.11), but the southwest wind quadrant dominated source direction for PM collected at the BAO Fenceline, south of the targeted ONG facility. A similar pattern was found in the BAO Tower sampling location with the addition of the southeast wind quadrant.

We isolated a single cluster from the previous cluster analysis with CH_4 concentrations originating from the direction of the ONG facility (cluster 2 in Figure 2.12). This cluster captured a small sample ($n = 169$) of infrequent mean CH_4 concentrations throughout the sampling timeframe. Data from both SNAQ monitors were averaged into one-minute mean concentrations and merged with CH_4 measurements from the Picarro based on date and time. To account for varying dispersion rates in the atmosphere and distance between co-located monitors, we lagged the particle and CH_4 data by up to 20-minutes prior to the merge. Moderate, positive correlations were identified (Figure 2.13) between PM_1 and CH_4 in multiple lags created at the BAO Fenceline sampling site and at one lag in the BAO Tower sampling location for the targeted cluster. Although the sampling size within the cluster was small and PM concentrations were not elevated above concentrations measured in the other clusters, the coefficients of determination were fairly consistent between monitors and increased significantly when relative humidity was added to the model (Table 2.5). Similar results were found when speciated particles (with a diameter ranging between 0.43 – 0.97 μm) were substituted into the model (data not shown).

2.5 Discussion

Inexpensive passive TraceAir badges provided reliable results comparable to measurements from previous research and co-located monitors from the DISCOVER-AQ campaign, especially for benzene. Mean benzene concentrations of 0.16 ppbv were measured at the BAO sampling site, similar to concentrations reported by Swarthout et al. (2013), where one-hour 2L electropolished stainless steel canister samples reported a mean concentration of 0.19 ppbv[48]. Additionally, a mean benzene concentration of 0.60 ppbv at the Longmont sampling site was similar to a mean concentration of 0.57 ppbv reported by Thompson et al. (2014) where 24-hour and 3-hour integrated 6-L stainless steel Summa canister samples were used to measure VOCs in ambient air near residential homes in the cities of Erie and Longmont, Colorado[65]. Finally, a mean benzene concentration of 0.65 ppbv at the Platteville sampling site (data not shown) was similar to a mean concentration of 0.53 ppbv measured via a co-located one-second time resolution PTR-QMS[40]. Concentrations of toluene, n-pentane, and n-hexane varied more between studies, but mean and median concentrations of all Weld County passive TraceAir badge samples were well within the range of samples reported by Swarthout et al. (2013) and Thompson et al. (2014)[48,65].

Strong correlations with light alkanes and poor correlations with combustion tracers have indicated that n-pentane is likely associated with emissions from ONG development in the NFR, with some estimates of nearly 100% attributable to these activities[15,17,34,40,65,138]. With approximately 3.0 tonnes emitted per hour in the NFR[138], we included n-pentane in the current analysis for its ability to act as a tracer compound. At the Longmont sampling site, strong correlations between benzene, toluene, and n-hexane with n-pentane indicate the VOCs measured at the Longmont sampling site were predominantly influenced by ONG activity, very close to multiple athletic fields on a public-school campus. Further analysis of toluene-to-benzene (T:B) tracer ratios found values < 1.0, further suggesting minimal air quality impacts from urban and vehicle emission sources, where the closest major road was over one kilometer to the east of the targeted facility. At the BAO sampling site, weaker correlations between n-pentane and n-hexane suggest the presence of competing emission sources or dispersion at greater distances, although a strong, positive correlation remained between n-pentane and benzene ($R^2 = 0.91$). Using half the sample limit of detection as the concentration of toluene to build tracer ratios, we found a median T:B ratio of 1.33 ppbv/ppbv at the BAO sampling site, similar to previous work in which wind direction analyses suggested advection of the Denver plume[48].

Benzene, n-hexane, and toluene are classified as hazardous air pollutants (HAPs) by the U.S. EPA due to their serious health effects, some with known carcinogenic properties[19]. Benzene, in particular, has been associated with various adverse health outcomes including hematological, immunological, and reproductive effects[139]. Ambient air quality studies near ONG operations have found benzene as the major contributor to the increased cumulative cancer risks near active wells[14]. At the Longmont sampling site, two-week time weighted average concentrations of benzene remained elevated at 0.41

ppbv at the furthest distance measured from the targeted ONG facility (440 meters from the eastern fence line). With the exception of Detroit and Los Angeles, benzene concentrations at this semi-rural public school in Longmont exceeded those found in all urban cities measured by Baker et al. (2008)[62].

Measured concentrations at the Longmont sampling site were concerning for several reasons. First, the maximum time weighted average concentration of benzene exceeded the 8-hour and chronic Reference Effect Level (REL) set by the Office of Environmental Health Hazard Assessment (OEHHA) of the California Environmental Protection Agency (Cal/EPA)[66]. The REL is a concentration of a single chemical at or below which adverse noncancer health effects are not anticipated to occur for a specified exposure duration. While such health-based air quality standards provide a guide in which to base regulatory thresholds, it is possible that actual health risks of exposure are higher for sensitive populations such as children. This sampling site is located on a public-school campus, near outdoor sport facilities, where children experience increased respiratory volumes during athletic activities. The observed benzene concentration is expected to elicit adverse health outcomes, but these risks may be further exacerbated within children with higher respiratory volumes[140,141]. Second, correlations between n-pentane and measured HAP compounds suggest influence by ONG activity, but further denote emissions from a wider range of air pollutants. A review of the available peer-reviewed literature on air pollutants measured and sourced to upstream ONG development found multiple HAP compounds emitted during various phases of development including ethylbenzene, styrene, methanol, formaldehyde, and cumene[142]. While the review focused on the compounds suspected to cause cancer or other serious health effects, the full range of unique products and chemicals associated with these processes may be in the hundreds[6–10]. Co-emissions may increase health risks of exposure if pollutants are biologically additive or synergistic, yet little research exists on health effects of co-exposures. Third, the transect was not placed in the prevailing wind direction, thus, the measured concentrations may be significantly underestimated during the sampling timeframe.

At the Longmont sampling site, the symmetrical decay along the sampled transect suggests diffusion from a stationary source; thus, combined with results from the correlation analysis, this finding implies the targeted ONG facility at the Longmont sampling site is the dominant source of measured VOCs. Zielinska et al. (2014) deployed passive samplers at varying distances from an active natural gas well and a compressor station located in the Barnett Shale in Texas[36]. Results indicated that most of the measured VOCs decayed to background concentration levels within 100 meters of both facilities. Results from the current analyses found concentrations reached background around 220 meters from the active ONG facility fence line, but these results may be underestimated since the transects experienced only 10% of the normal prevailing winds during the sampling timeframe. At the BAO sampling facility, measured concentrations were likely at or near background concentrations since the closest passive samplers were placed ~200 meters in both directions and the transects experienced only 10% of the normal prevailing winds during the sampling timeframe. Furthermore, toluene was below the sample LOD in all collected passive badges and concentrations for benzene and n-hexane did not vary significantly between samples. Results from the distance decay gradient indicate that the passive samplers along the measured transect may have been placed outside the zone of impact; however, we found limited evidence that particles from ONG activities may be measured in ambient air as far as 560 meters from the targeted facility.

Ancillary equipment and infrastructure associated with upstream ONG development including compressor stations, generators, truck engines, and drilling rigs have been identified as sources of combustion related emissions with potential of contributing to human and environmental health risks[110,143–147]; however, these emission sources have proven difficult to distinguish from on-road traffic emissions and other urban sources[48]. The common traffic emission tracer compound and greenhouse gas, CO, was measured at concentrations significantly higher in the dense ONG development area of Platteville compared to all other sampling sites. We applied cluster analyses, time variation plots, and ratios of tracer compounds to identify potential sources. At the Parkland Airport and Weld Tower sampling sites, most CO clusters contained [CO]/[NOx] ratios consistent with those emitted by different fuel types and diurnal temporal patterns analogous to daily traffic patterns suggest contributions from traffic emissions[148]. There were two exceptions that fell outside the [CO]/[NOx] ratios range for combustion sources. The first was the peak CO cluster originating from the direction of the small private aircraft runway north/east of the Parkland Airport monitoring location with a [CO]/[NOx] ratio of 15.43 ppbv/ppbv, consistent with emission ratios from taxying aircraft[149]. The second, measured at the Weld Tower sampling site, was a slightly elevated CO concentration cluster originating from the direction of a large multilane highway, possibly indicating contributions from larger diesel combustion engines. Furthermore, moderate, positive correlations were identified between $PM_{2.5}$ and CO levels within peak [CO]/[NOx] ratio clusters at Parkland Airport and Weld Tower, where distances from combustion sources were less than 0.80 kilometers.

At the Platteville site, peak CO clusters were associated with [CO]/[NOx] ratios consistent with those emitted by different fuel types; however, this rural sampling location was located far from any major roadways: the closest major roadway, U.S. Highway 85, is located approximately 7.7 kilometers due east. Furthermore, these clusters measured CO concentrations that peaked at early morning hours and were not correlated with any speciated particles. During the DISCOVER-AQ campaign, a collocated monitor by Thompson's Group identified a similar peak CO source in the southwest wind quadrant[40]. Results indicated that observed peak CO concentrations are likely emitted from a stationary source, and not from mobile vehicle emissions. In this rural sampling location, at a distance from any major roadway and a temporal pattern distinctive from on-road vehicle emissions, our data corresponds with these results. It is possible that idling diesel trucks or other non-mobile combustion sources from the local ONG industry may contribute to the elevated CO at the Platteville sampling site; however, without additional data, a specific source could not be elicited from the current analyses.

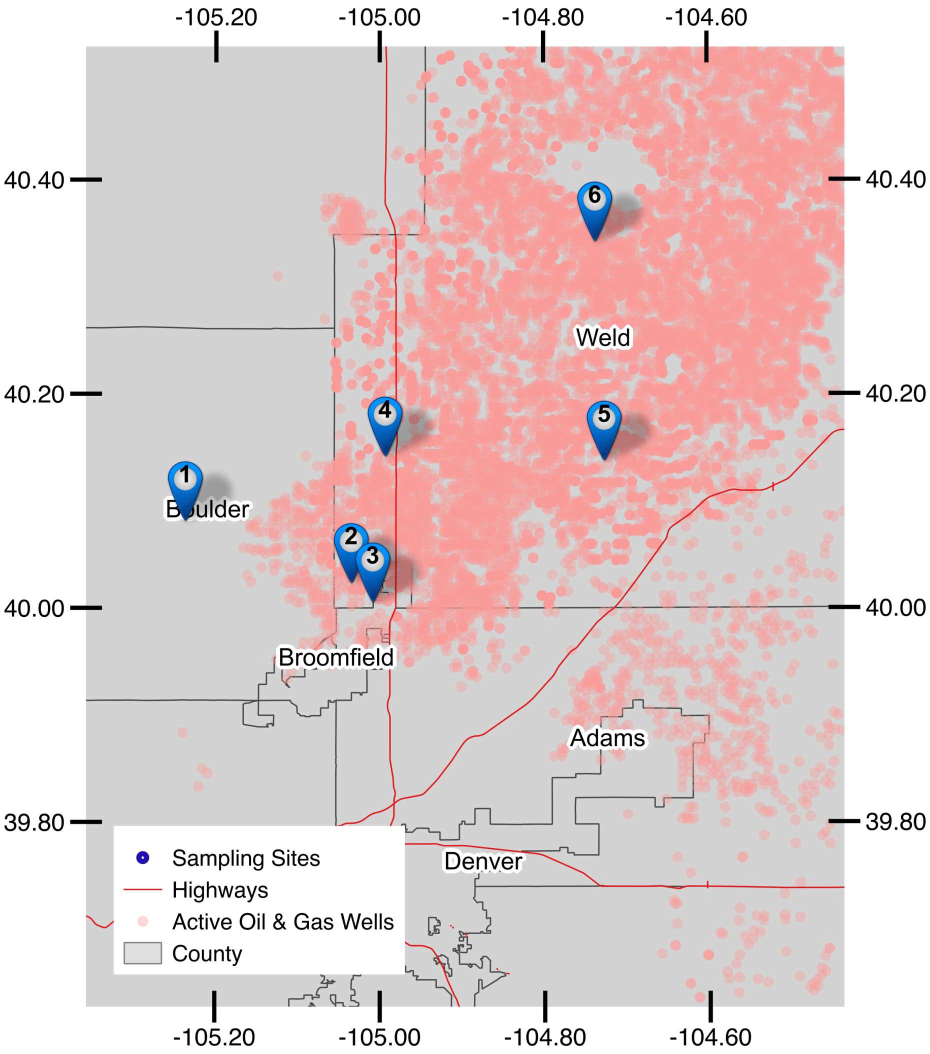
2.6 Conclusion

From this study, we identified a zone of impact near ONG facilities in semi-rural areas of the NFR for select VOCs. Results from the current analysis suggest measured HAP concentrations near background levels around 220 meters from the facility fence line; however, beyond 220 meters, concentrations of these VOCs remain elevated at concentrations higher than most urban sites. With the exception of one fence line sample at the Longmont sampling site, all two-week time integrated concentrations of individual compounds were below RELs; however, single pollutant health-based standards may fail to provide accurate risk estimates, especially for sensitive subpopulations. Although limited, we found further evidence that particles from ONG activities, particularly re-casing activities, may be measured in ambient air as far as 560 meters from the facility. While we have an adequate understating about particles near roadways, there is a dearth of scientific literature investigating the constituents of particles from upstream ONG development and their impact to human health. Particle concentrations in the targeted cluster, however, were not elevated above concentrations measured in other clusters from the same monitor. Correlations between n-pentane and measured hazardous air pollutants including benzene, n-hexane, and toluene, suggest that a broad range of pollutants are co-emitted during upstream ONG development and activities. These co-emissions may increase original estimates of health risks of exposure if compounds are biologically additive or synergistic, especially in environments with an already high pollutant burden, as seen with carbon monoxide at the Platteville sampling location.

In review of the current results, we recommend additional research on the ONG development exposure impact zone to better understand the relationship between proximity and health risks. Additional research is needed on health impacts from chronic, low-level ambient HAP exposures and exposures from multiple concurrent or close-succession toxic VOCs to more accurately characterize environments near ONG facilities. Findings of HAP concentrations above health benchmarks in close proximity to a public-school reflects the critical need for increased research on exposures from ONG facilities, especially on impacts to sensitive populations. We hope that the current analysis will help guide the development of necessary policy for setback requirements and, thus, minimize potential health risks of populations residing near ONG operations.

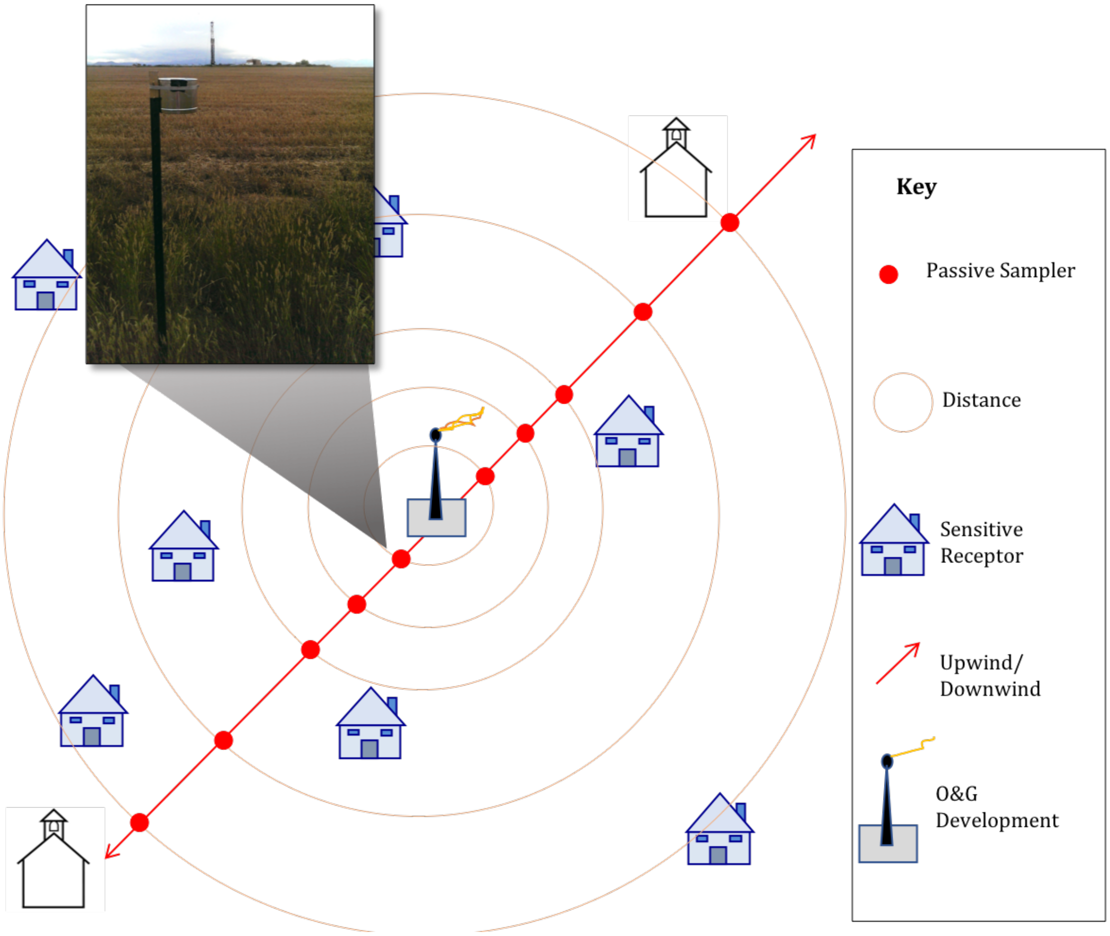
2.7 Tables and Figures

Figure 2.1: Map of air sampling locations and ONG wells in the Northern Front Range.



Air sampling locations are referenced as follows: (1) Control; (2) Parkland Airport; (3) BAO; (4) Longmont; (5) Platteville; and (6) Weld Tower. Geographic shapefiles are from the Colorado Department of Local Affairs, the Colorado Online Transportation Information System, the Colorado Oil and Gas Conservation Commission, and the Colorado Department of Public Health and Environment.

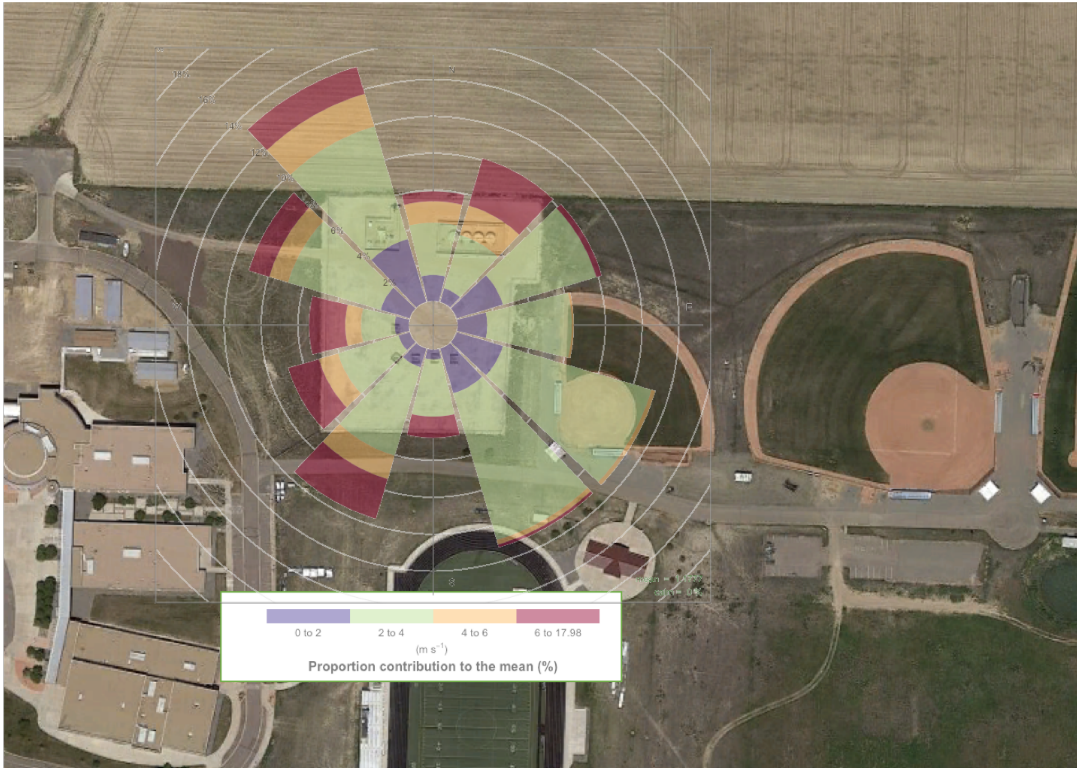
Figure 2.2: Conceptual model of a transect through an active site to capture gradient behavior of ONG related emissions.



The imbedded photo is a sample set-up of a TraceAir badge deployed at the BAO sampling site. Photo was taken at the BAO sampling site where an ONG rig can be seen in the distance.

Figure 2.3: Wind rose diagrams for BAO and Longmont sampling sites (August 1-14, 2014).

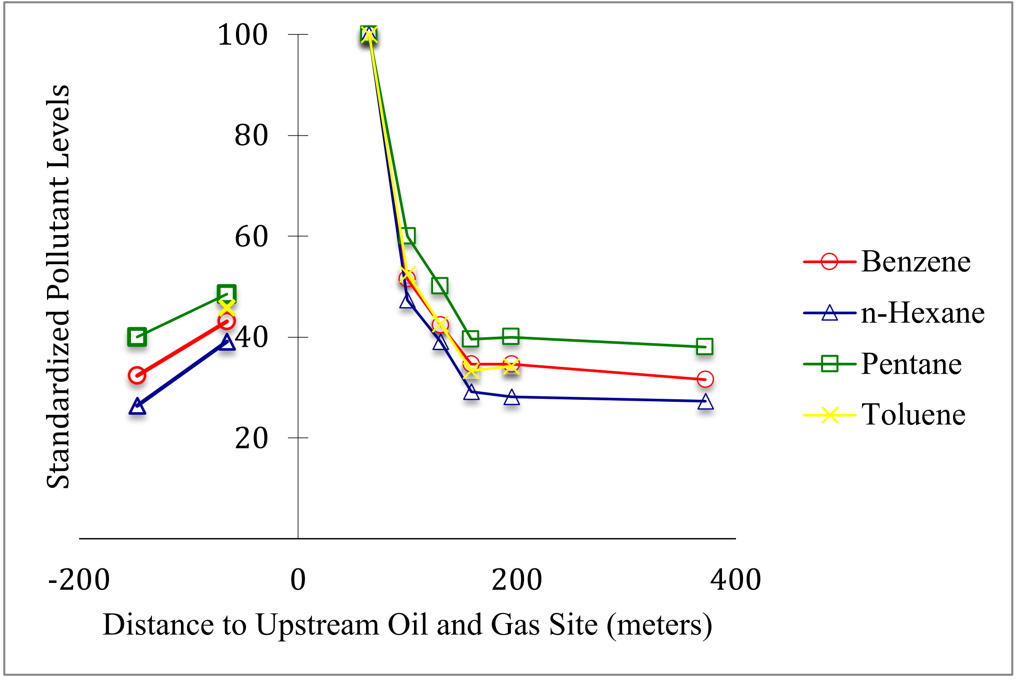
A. Longmont Sampling Site



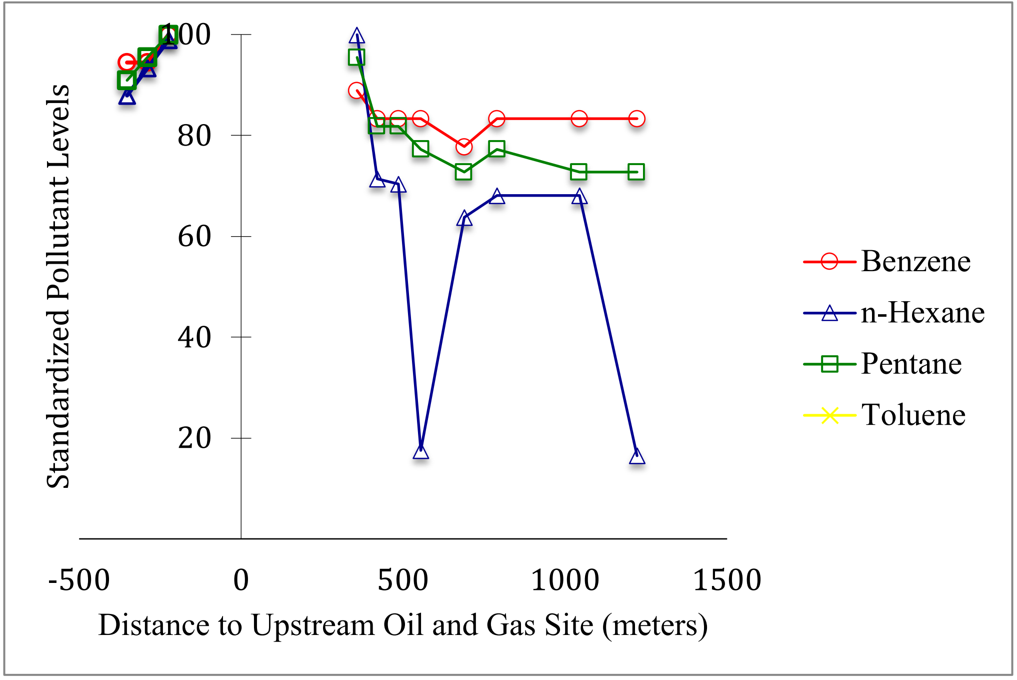
B. BAO Sampling Site

Figure 2.4: Plots of standardized two-week time weighted average passive TraceAir badge concentrations along the and BAO sampling site transects.

A. Longmont Sampling Site[a]



B. BAO Sampling Site[a]



[a] Quadrant one represents concentrations along the eastern transect and quadrant two represents concentrations along the western transect on both plots.

Figure 2.5: Timeplot for CO at all sampling sites in Colorado.

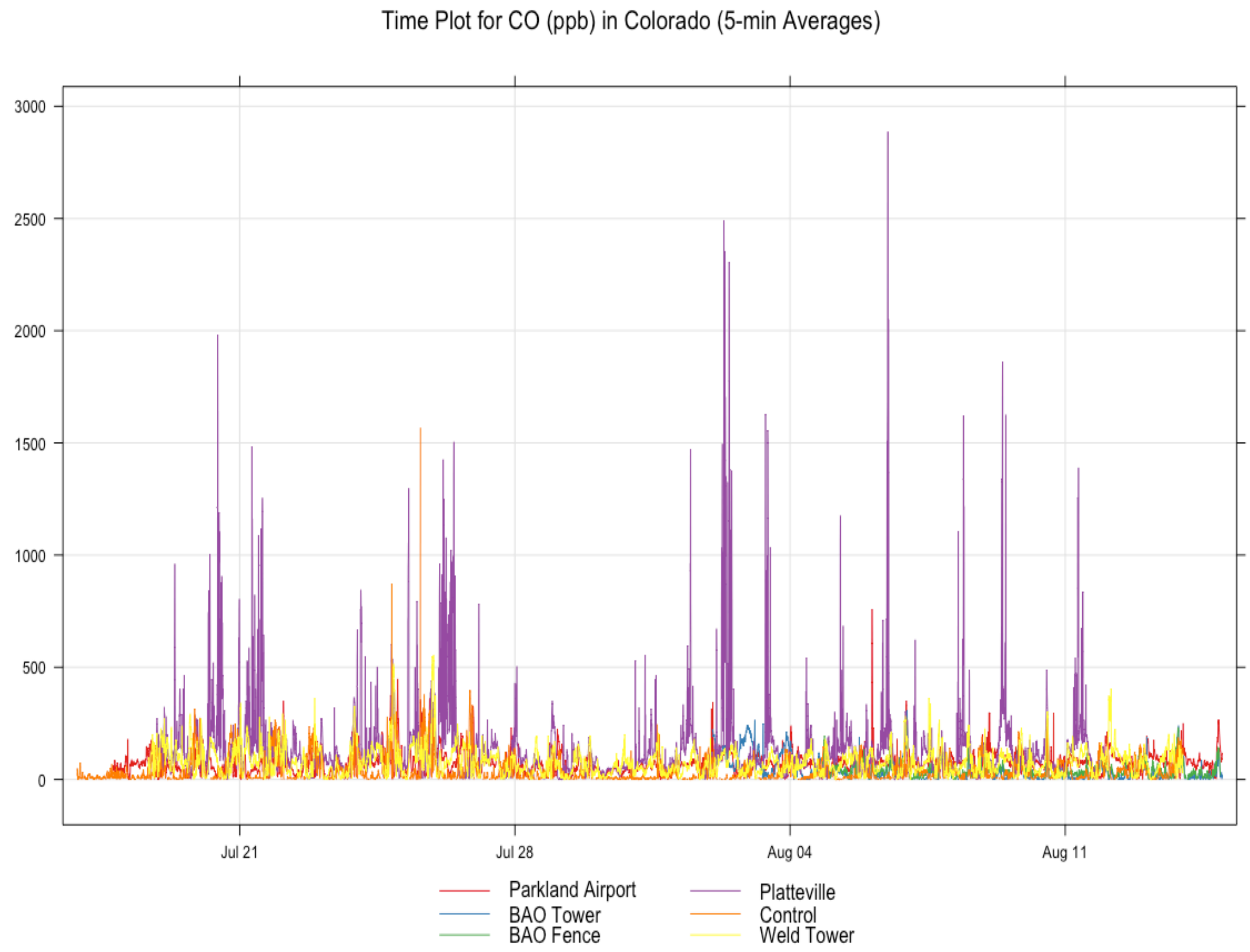
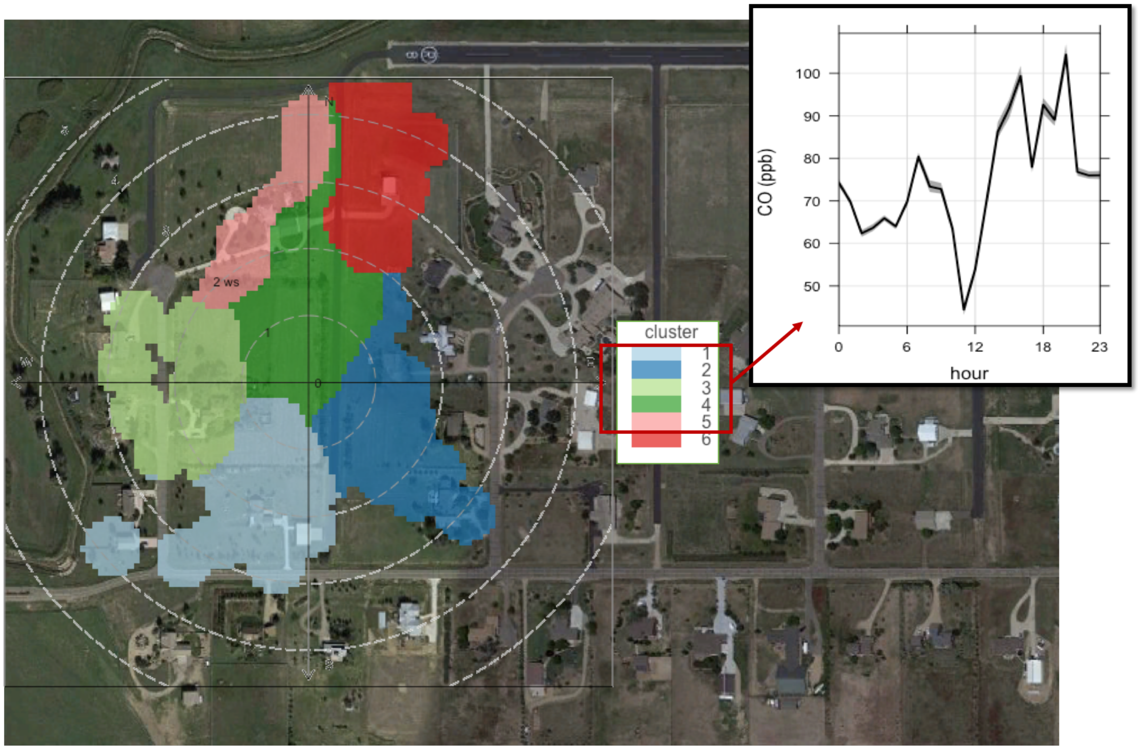


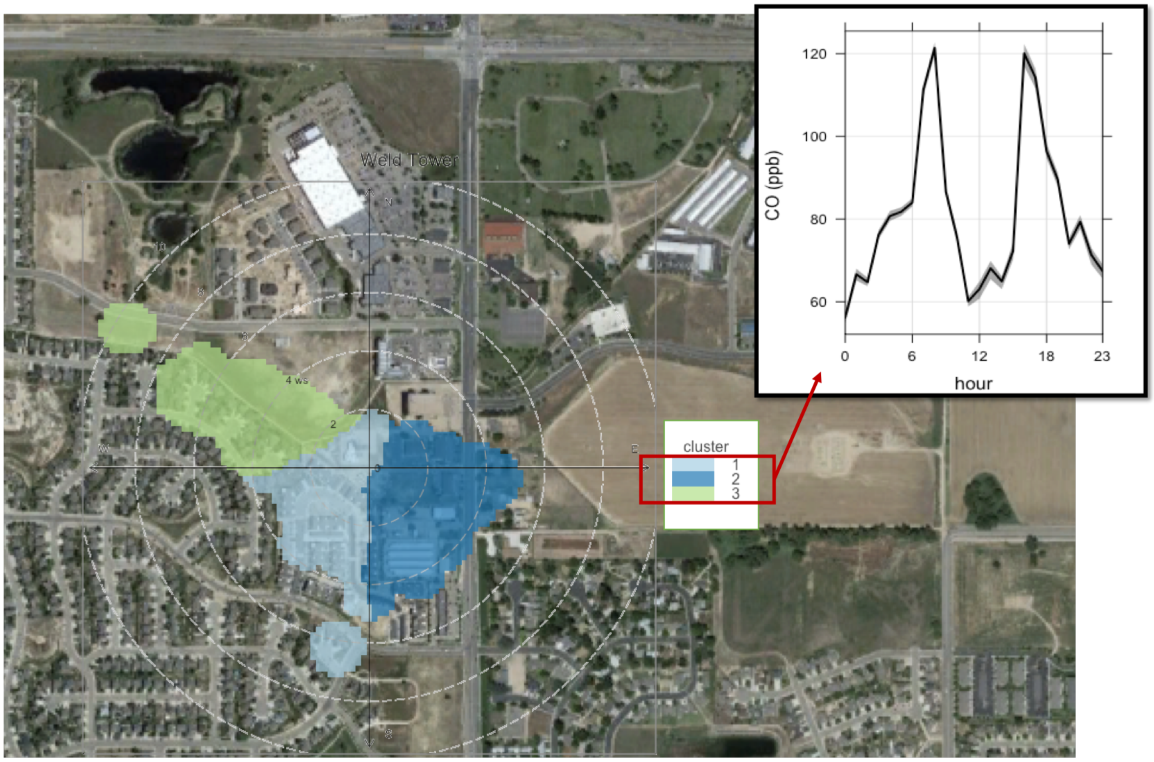
Figure 2.6: K-means cluster analysis of CO at the Parkland Airport sampling site and correlations between CO and PM_1, $PM_{2.5}$, and PM_{10}.



Cluster	n	Median [CO]	CO/ NOx	PM_1 (μg/m^3)		$PM_{2.5}$ (μg/m^3)		PM_{10} (μg/m^3)	
				Median	R^2	Median	R^2	Median	R^2
1	9,279	55.93	2.04	1.37	< 0.01	2.70	0.02	15.70	0.05
2	1,571	84.86	3.62	1.23	< 0.01	2.54	0.03	10.93	0.05
3	191	82.73	2.51	1.62	< 0.01	3.02	0.03	17.45	0.03
4	101,166	69.72	4.65	0.85	< 0.01	2.15	0.02	9.36	0.04
5	22	68.08	1.35	4.75	< 0.01	6.73	0.05	22.18	0.05
6	56	204.25	15.43	1.47	0.12	4.20	0.44	33.81	0.04

CO concentrations provided in ppb; [CO]/[NOx] concentrations provided as ppbv/ppbv

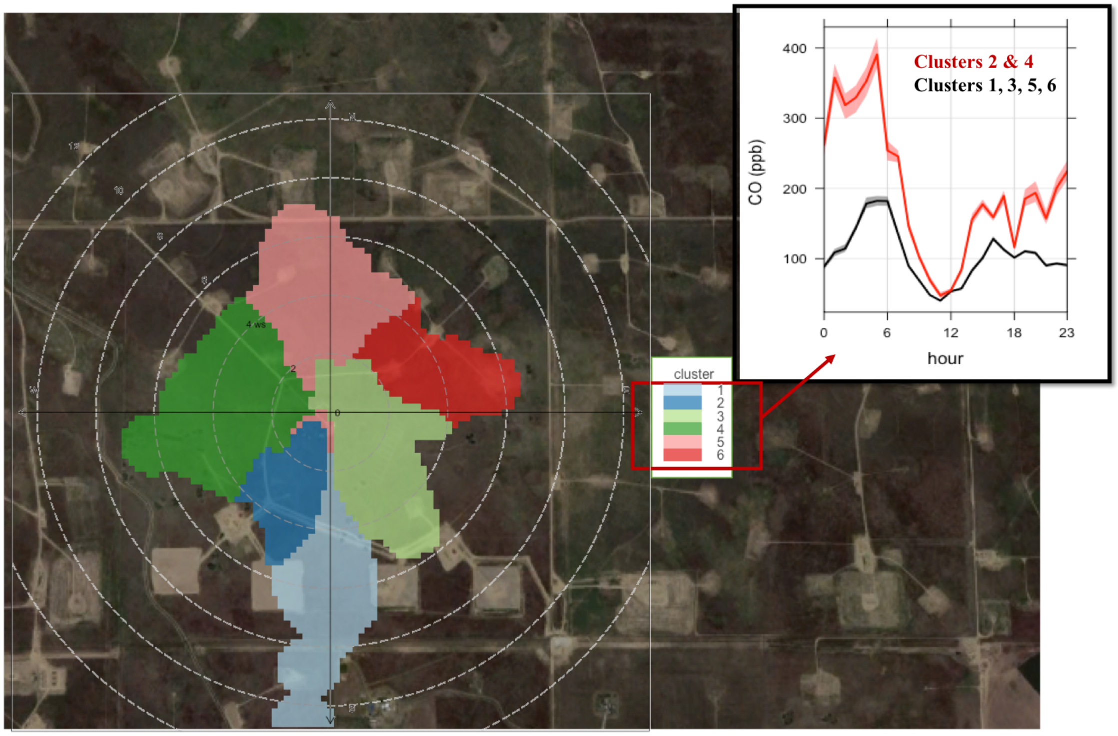
Figure 2.7: K-means cluster analysis of CO at the Weld Tower sampling site and correlations between CO and PM$_1$, PM$_{2.5}$, and PM$_{10}$.



Cluster	n	Median [CO]	CO/ NOx	PM$_1$ (μg/m^3)		PM$_{2.5}$ (μg/m^3)		PM$_{10}$ (μg/m^3)	
				Median	R^2	Median	R^2	Median	R^2
1	62,829	75.77	1.62	1.27	< 0.01	2.95	0.02	11.39	< 0.01
2	38,696	60.95	1.51	1.55	0.02	3.20	0.02	16.02	< 0.01
3	1,112	117.63	5.32	2.16	0.28	4.21	0.37	13.78	0.05

CO concentrations provided in ppb; [CO]/[NOx] concentrations provided as ppbv/ppbv

Figure 2.8: K-means cluster analysis of CO at the Platteville sampling site and correlations between CO and PM$_1$, PM$_{2.5}$, and PM$_{10}$.



Cluster	n	Median [CO]	CO/ NOx	PM$_1$ (μg/m^3)		PM$_{2.5}$ (μg/m^3)		PM$_{10}$ (μg/m^3)	
				Median	R^2	Median	R^2	Median	R^2
1	3,653	96.74	3.79	1.39	< 0.01	3.41	< 0.01	13.24	< 0.01
2	23,242	148.97	4.23	1.01	0.01	2.52	< 0.01	7.20	< 0.01
3	31,123	67.97	2.33	1.49	< 0.01	3.56	< 0.01	13.06	< 0.01
4	10,004	118.12	4.00	1.08	< 0.01	2.86	< 0.01	10.37	< 0.01
5	27,903	96.89	3.54	1.11	< 0.01	2.84	< 0.01	12.34	< 0.01
6	545	74.90	2.30	1.68	< 0.01	3.60	< 0.01	12.23	0.01

CO concentrations provided in ppb; [CO]/[NOx] concentrations provided as ppbv/ppbv

Figure 2.9: Time variation analysis of CH_4 concentrations at the BAO Tower.

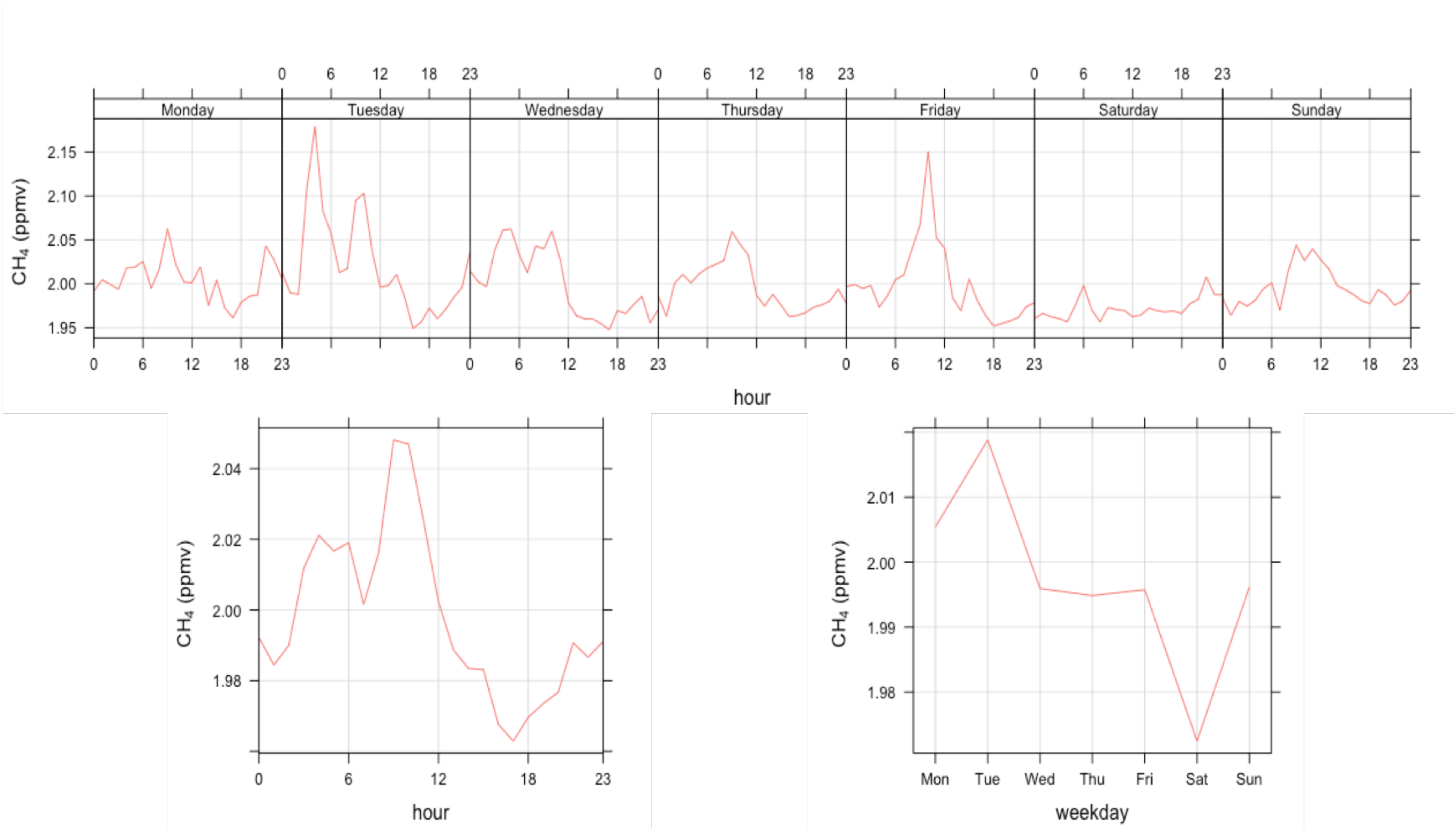
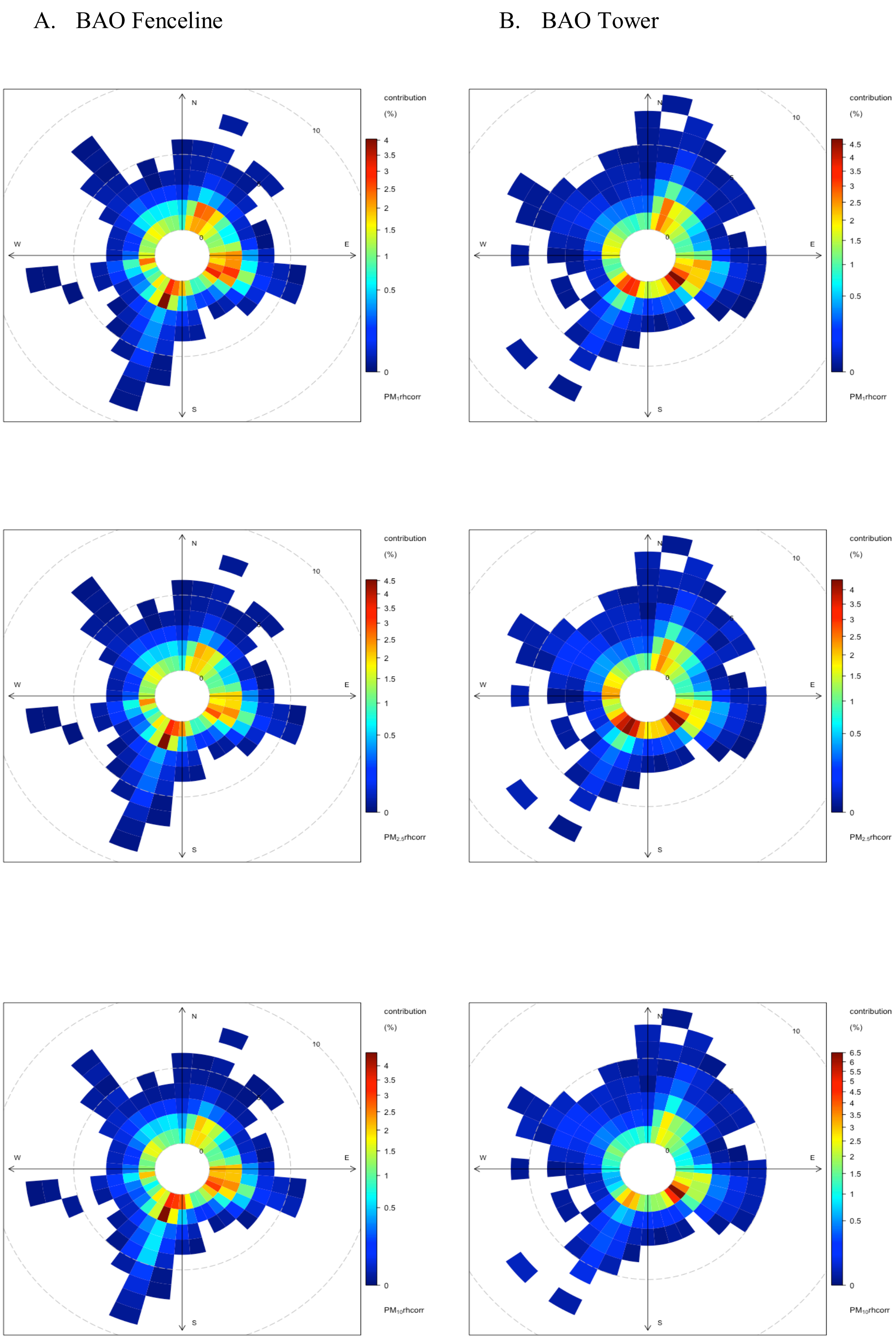


Figure 2.10: Location of SNAQ and Picarro CH_4 monitors at the BAO sampling site.

Monitors are identified by red dots and active ONG facility within the red polygon.

Figure 2.11: Weighted mean polar frequency plots for PM_1, $PM_{2.5}$, and PM_{10} at both BAO sampling sites.



A. BAO Fenceline

B. BAO Tower

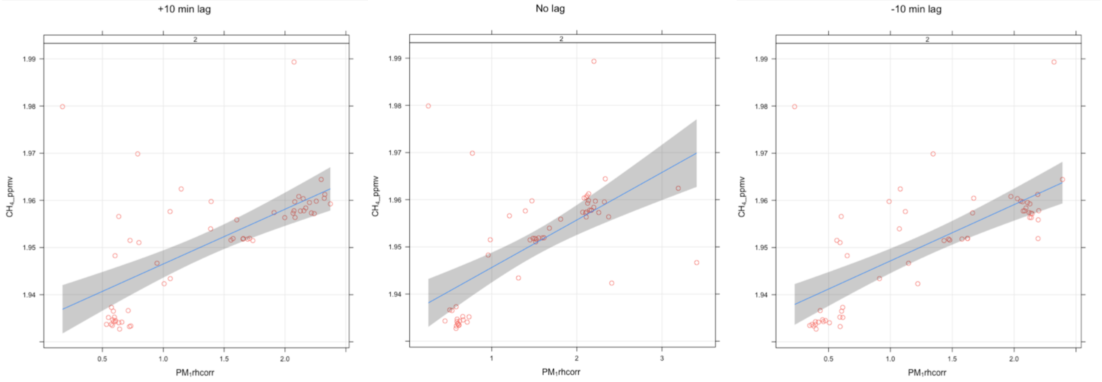
Figure 2.12: K-means cluster analysis of CH_4 at the BAO Tower.

Targeted upstream oil and gas development facility is identified within the red polygon.

	n	CH_4 (ppm)	CO (ppb)	(R^2)
Cluster 1	8,028	1.97	112.99	0.31
Cluster 2	169	1.94	99.34	0.49
Cluster 3	20,508	1.99	119.67	0.24
Cluster 4	392	1.97	112.93	0.28
Cluster 5	308	1.96	104.43	0.65

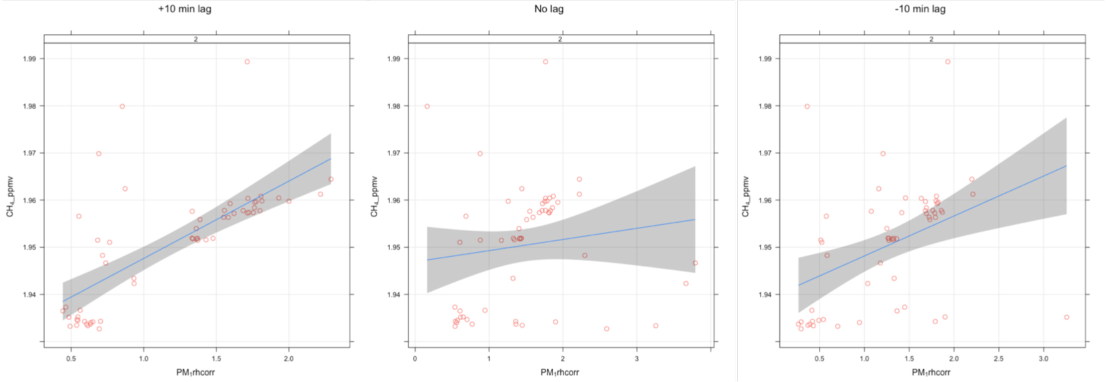
Figure 2.13: Correlation lags for CH_4 and PM_1 at two separate SNAQ monitors deployed at BAO: (A) BAO Fenceline and (B) BAO Tower with 10-minute CH4 data lag (left), no lag (middle), and 10-minute particle lag (right) merge.

A. BAO Fenceline Correlation Lags



$R^2 = 0.40$ ($p < 0.0001$) $R^2 = 0.36$ ($p < 0.0001$) $R^2 = 0.47$ ($p < 0.0001$)

B. BAO Tower Correlation Lags



$R^2 = 0.40$ ($p < 0.0001$) $R^2 < 0.001$ ($p = 0.32$) $R^2 = 0.16$ ($p < 0.01$)

Table 2.1: Site production information for all monitored sites.

Sites	**# Wells** (within ½ miles)	**Gas (Mcf)***	**Oil (bbls)****	**Gas/Oil**
Control	0	0	0	NA
BAO	16	5,525	3,265	1.69
Longmont	22	21,476	1,794	11.97
Parkland Airport	16	16,183	1,160	13.95
Weld Tower	12	10,478	393	26.66
Platteville	26	166,528	1,914	87.01

*Gas production is reported in 1,000 cubic feet (Mcf) volumes pressure.

**Oil is reported in barrels (bbls), which is equivalent to 42 U.S. gallons.

Table 2.2: Summary statistics for passive TraceAir badges at the Control site, all Weld County sampling sites, and badges collected within the Longmont and BAO transects.

	Range	Median	Mean	Mean Swarthout (2013)[a]	Thompson (2014)[b]
Control (n = 1)					
Benzene	NA	< 0.08	< 0.08	0.19	0.57
Toluene	NA	< 0.40	< 0.40	0.30	0.43
n-Hexane	NA	< 0.16	< 0.16	1.10	0.82
n-Pentane	NA	0.44	0.44	2.01	2.55
Weld County (n = 29)					
Benzene	0.14 – 1.30	0.17	0.34	0.19	0.57
Toluene	0.40 – 1.20	0.55	0.61	0.30	0.43
n-Hexane	0.15 – 11	0.91	2.17	1.10	0.82
n-Pentane	1.60 – 20	2.10	5.16	2.01	2.55
Longmont (n = 8)					
Benzene	0.41 – 1.30	0.50	0.60	0.19	0.57
Toluene	0.40 – 1.20	0.53	0.62	0.30	0.43
n-Hexane	2.90 – 11	3.75	4.63	1.10	0.82
n-Pentane	7.60 – 20	8.85	10.40	2.01	2.55
BAO (n = 14)					
Benzene	0.14 – 0.18	0.15	0.16	0.19	0.57
Toluene	NA	< 0.40	< 0.40	0.30	0.43
n-Hexane	0.15 – 1.00	0.64	0.65	1.10	0.82
n-Pentane	1.60 – 2.20	1.80	1.84	2.01	2.55

Data provided in ppbv. Non-detects are denoted by the “less than” sign, followed by the sample limit of detection.

[a] Swarthout, Robert F., Rachel S. Russo, Yong Zhou, Andrew H. Hart, and Barkley C. Sive. "Volatile organic compound distributions during the NACHTT campaign at the Boulder Atmospheric Observatory: Influence of urban and natural gas sources." *Journal of Geophysical Research: Atmospheres*118, no. 18 (2013).

[b] Thompson, Chelsea R., Jacques Hueber, and Detlev Helmig. "Influence of oil and gas emissions on ambient atmospheric non-methane hydrocarbons in residential areas of Northeastern Colorado." *Elem Sci Anth* 3 (2014).

Table 2.3: Correlation analysis for all Weld County passive TraceAir badges and subset badges at the Longmont and BAO sampling sites.

	Benzene	Toluene	n-Hexane	n-Pentane
Weld County (n = 29)				
Benzene	1	0.95**	0.99**	0.98**
Toluene	0.95**	1	0.91**	0.85**
n-Hexane	0.99**	0.91**	1	0.98**
n-Pentane	0.98**	0.85**	0.98**	1
Longmont (n = 8)				
Benzene	1	> 0.99**	> 0.99**	> 0.99**
Toluene	> 0.99**	1	> 0.99**	> 0.99**
n-Hexane	>0.99**	> 0.99**	1	> 0.99**
n-Pentane	> 0.99**	> 0.99**	> 0.99**	1
BAO (n = 14)				
Benzene	1	NA	0.65	0.91**
Toluene	NA	1	NA	NA
n-Hexane	0.65	NA	1	0.78**
n-Pentane	0.91**	NA	0.78**	1

*p-value < 0.01
**p-value < 0.001

Table 2.4: Median values for select criteria air pollutants and ratios in Colorado.

	CO (ppb)	**NOx (ppb)**	**CO/NOx**	**PM$_1$ (µg/m^3)**	**PM$_{2.5}$ (µg/m^3)**	**PM$_{10}$ (µg/m^3)**
Control	33.57	28.38	1.23	1.11	1.33	4.35
BAO Tower	39.19	44.85	0.88	1.55	2.24	10.56
BAO Fence	36.27	50.76	0.78	1.71	2.00	8.05
Parkland	69.12	15.65	4.37	1.20	1.81	8.14
Platteville	99.30	30.29	3.34	1.56	2.42	9.22
Weld Tower	70.53	45.73	1.60	1.78	2.58	10.85

Table 2.5: Linear regression model for PM_1 in cluster 2 at BAO with a + 10 min lag for SNAQ data.

	Coefficient			Model	
	CH_4	CO	RH	R^2	p-value
A. BAO Fence					
Model 1	35.74	NA	NA	0.40	< 0.001
Model 2	NA	NA	-0.06	0.70	< 0.001
Model 3	NA	0.05	NA	0.70	< 0.001
Model 4	23.63	NA	-0.05	0.87	< 0.001
Model 5	15.85	0.01	-0.04	0.88	< 0.001
B. BAO Tower					
Model 1	31.13	NA	NA	0.49	< 0.001
Model 2	NA	NA	-0.04	0.56	< 0.001
Model 3	NA	0.04	NA	0.69	< 0.001
Model 4	23.19	NA	-0.03	0.81	< 0.001
Model 5	17.37	0.01	-0.03	0.82	< 0.001

Chapter 3: Using distance decay gradients to measure the air pollution exposure impact zone around oil and natural gas facilities in the dense urban downtown area of Los Angeles

Authors:

Diane A. Garcia-Gonzales[1]

Michael Jerrett[1-3]

Affiliations:

[1] Environmental Health Sciences Division, 50 University Hall, School of Public Health,

University of California, Berkeley, Berkeley, CA 94720. dgonzales98@gmail.com

[2]Department of Environmental Health Sciences, Fielding School of Public Health

University of California, Los Angeles

[3]Center for Occupational and Environmental Health, Fielding School of Public Health

University of California, Los Angeles

This chapter has been formatted to follow the guidelines of a submission to the journal of Environmental Research as a "Report from the Field".

3.1 Abstract

In this work, we investigate air pollutant gradient behavior around an upstream oil and natural gas (ONG) facility located within the densely populated urban community in downtown Los Angeles. Despite difficulties associated with air quality measurements methodologies in urban environments, we were able to identify gradient behavior around the target ONG site and distinguish added air quality burden of several volatile organic compounds associated with ONG development.

3.2 Introduction

Upstream oil and natural gas development (ONG) has expanded rapidly across the United States over the past decade. While much of the focus has been on the ONG extraction and development in rural regions, many extraction facilities operate in densely-populated urban areas. Few studies have focused on emissions and the impact on human health in the state of California, where there are approximately 58,000 active ONG wells[5], many of which are located in the Los Angeles area. Approximately 1.7 million individuals live within one mile of an active ONG well within the Los Angeles Basin[150]. Research on chemicals and equipment associated with ONG development reveal a potential for adverse health outcomes, and a review of the current literature suggests an association between proximity from ONG site and potential health risks[142]. Most of these health studies, however, have failed to feature any rigorous spatial analysis of pollutant levels, only suggesting that a spatial dimension exists.

Los Angeles residents already experience a high health burden from poor air quality, where exposure to urban air pollution, including traffic emissions, increases risk for multiple adverse health outcomes[151–153]. Studies have demonstrated gradient behavior in combustion-related emissions; pollutant levels are elevated near roadways and decrease to or near background levels as distance from the roadway increased, with some studies suggesting most of the impacts occur within 500 m of major highways[121,125,129]. Few studies have repeated this gradient monitoring approach around ONG facilities, despite the need to understand the behavior of related air emissions, especially those located within highly dense urban communities.

Given the sparse literature on exposures to air pollutants near ONG operations and the potential for impacts on health, particularly in urban areas, here we investigate air pollutant gradient behavior around an ONG facility located in downtown Los Angeles. The consequences of exposure to ONG-related emissions have not been adequately studied and, thus, the current investigation on gradient behavior is warranted. Despite the economic impact of ONG production within California, it is imperative to understand the risks associated with exposures from these activities to minimize potential exposures, particularly in densely populated areas, and guide future regulation.

3.3 Methods

Site Selection

To understand gradient behavior of ONG related emissions in Southern California's urban environment, a facility was selected near downtown Los Angeles, in the Jefferson community. The Jefferson drill site is an active ONG facility that has been in operation since 1964 and operates 20 active oil and gas wells with a total gas production of 8,890 million cubic feet (Mcf) of natural gas and 8,553 barrels (bbls) of oil in February 2016, the month of the current sampling deployment. According to U.S. Energy Information Administration's average daily oil and natural gas production volume per well for 2016, the Jefferson drill site is among the top 9% of gas producing and top 34% of oil producing wells in California[154].

The Jefferson drill site (Figure 3.1) is situated in the middle of a vulnerable community, where wellheads are as close as 60 feet from residential homes. This site is located due south of Highway 10 (~1.2 km) and east of Highway 110 (~2 km), along a major bus route and is surrounded by a myriad of competing emissions sources including several restaurants, laundry mats, dry cleaners, a recycling center, and two gas stations (all within 1 km). The site was selected due to the high level of operational activity at the facility, residential proximity, the existence of an established neighborhood advocacy group, and the ability to create a distance decay gradient through the site along the prevailing wind directions. A total of 11 households were recruited to host air quality samplers for 14 days. Hosts were selected from non-smoking households and advised to avoid activities that may expose the monitors to additional VOC emissions including, but not limited to, burning firewood, barbeques, and the operation of yard equipment with combustion engines (e.g. gas-powered lawn mowers).

Passive TraceAir Badges

Commercially available passive samplers do not require a power source and are generally inconspicuous when deployed. As such, these samplers can be utilized ubiquitously across multiple site locations in dense urban environments where security might be a concern. For the current study, we used passive TraceAir badges (Assay Technology), which are capable of collecting a panel of organic air pollutants through passive diffusion in a time-integrated manner. We deployed 15 TraceAir passive badges around 11 residential homes near the Jefferson drill site. To protect the samplers from the elements, all passive badges were placed within an open bottom non-treated AllCan West (http://allstatecan.com/) tin can affixed to a metal fence post or existing structure at each site.

Three passive TraceAir badges were placed along the western transect up to 230 meters from the center of the facility. Six passive TraceAir badges were placed along the eastern transect up to 225 meters from the center of the facility. An additional passive badge was used as a control and placed at a residential home 680 meters northwest of the facility, away from the prevailing wind direction. For quality assurance and control, the remaining passive badges were used as either field duplicates, field blanks, or travel blanks. Latitude and longitude coordinates were collected for each passive badge using a Garmin eTrek

GPS device. After 14 days in-field, samplers were collected and sent to Assay Technology laboratories in Ohio for analysis of n-pentane (CAS 109-66-0), n-hexane (CAS 110-54-3), benzene (CAS 71-43-2), and 2-butoxyethanol (CAS 111-76-2). Passive badges were processed using a modified OSHA 7 method which included desorption in carbon disulfide with co-solvent and analysis by gas chromatography with flame ionization detector (GC/FID). Data was blank corrected and provided as average concentrations for the period of time monitored.

3.4 Results

Descriptive Statistics

Of the 15 TraceAir samples collected, one was damaged and, therefore, excluded from the analysis. Precision of duplicates was ≤10%, and the remaining field samples were blank corrected. Mean two-week time weighted average concentrations for benzene, n-hexane, and n-pentane were 0.51, 0.43, and 1.13 ppb, respectively; 2-butoxyethanol was found under the sample limit of detection for all deployed badges. Concentrations of benzene and n-pentane at the control location were within the range of the samples included in the transect; the n-hexane concentration measured at the control site was lower than the range of the samples included in transect. Non-significant relationships were found between n-pentane and n-hexane ($r^2 = 0.63$, $p = 0.04$) and n-pentane and benzene ($r^2 = 0.45$, p-value = 0.17). Descriptive statistics and correlations can be viewed in Table 3.1 and Table 3.2, respectively.

Distance Decay Gradient

Passive TraceAir badges were deployed at increasing distances along the prevailing eastern and western wind transects (Figure 3.2). Wind data from MesoWest (Station ID: KCQT) was plotted in a 40-degree panel wind rose diagram for the two-week deployment timeframe (Figure 3.1) revealing prevailing wind patterns from the western and eastern directions. Wind originating from the east and west contributed to 25% and 35% of the total mean wind patterns, respectively. Wind speeds in both directions ranged from 2 – 10.36 meters/second with an average wind speed of 1.21 and 0% calm. All other wind directions contributed to ~10% or less of the total mean wind patterns for the sampling timeframe. With an exception of the control location, all sensors were placed along the two prevailing (eastern and western) wind transects.

Two-week time weighted concentrations for all VOC species were standardized using the maximum value of the respective VOC from the full transect in the denominator and presented as a percent of the maximum. Standardized results were plotted against distance (in meters) from the center of the targeted ONG facility in both directions. Figure 3.2 represents a plot of the transect through the well pad and shows a decline in concentrations from the samples collected at the eastern fence line, closest to the ONG facility, compared to the second sampling location 70 meters in the eastern direction for all compounds over the sample limit of detection (LOD). Along the eastern transect, concentrations of benzene and n-hexane showed similar diffusion as distance from the targeted facility increased; however, n-pentane concentrations decayed until approximately 190 meters from the center of the targeted facility when concentrations increased. Along the western transect, n-pentane remained at a consistent level while both n-hexane and benzene levels increased as distance from the targeted facility increased.

3.5 Discussion

Passive samplers are inexpensive air quality sensors capable of measuring time weighted average concentrations of a variety of VOCs in ambient conditions. The proven utility of passive samplers has been demonstrated in several ONG monitoring studies[18,36,63], but these samplers have yet to be used around ONG facilities in dense, urban environments. Our results show that mean two-week time-weighted average concentrations of benzene and n-hexane from all transect samples exceeded those found in 28 cities[62] and in recent Multiple Air Toxics Exposure Study (MATES) IV reports on air quality within the Los Angeles area[155]. Overall, however, concentrations were comparable to levels measured at the control site, located several meters north of the facility and out of the path of the developed transect.

In urban environments, VOCs such as benzene, n-pentane, and n-hexane are predominately emitted from anthropogenic sources such as evaporating, unburned fuel. In Los Angeles, benzene, and to a lesser extent, n-pentane and n-hexane, are correlated with carbon monoxide, emitted via incomplete combustion, suggesting these VOCs share a common vehicle source[62]. Therefore, it may be difficult to characterize ONG emissions in urban environments where competing emission sources are difficult to isolate. Further complicating these efforts is the distribution of existing architectural structures within this dense urban neighborhood that may distribute particles and other air toxics unequally throughout the community.

While we identify gradient behavior on the eastern transect, the western transect is likely influenced by a source upwind of the sampling locations. This probable upwind source is combustion emissions from the highly utilized four-lane road (S Normandie Ave) one block west of the furthest passive badge, as evident in the diffusion of benzene and n-hexane concentrations from the prevailing westerly winds and the relatively consistent level of n-pentane. The difference between passive badge concentrations deployed at the eastern and western fence lines are likely the added air pollution burden emitted from the Jefferson drill site. From our analysis, the additional air pollution burden increases approximately 10%, 15%, and 20% for benzene, n-pentane, and n-hexane, respectively.

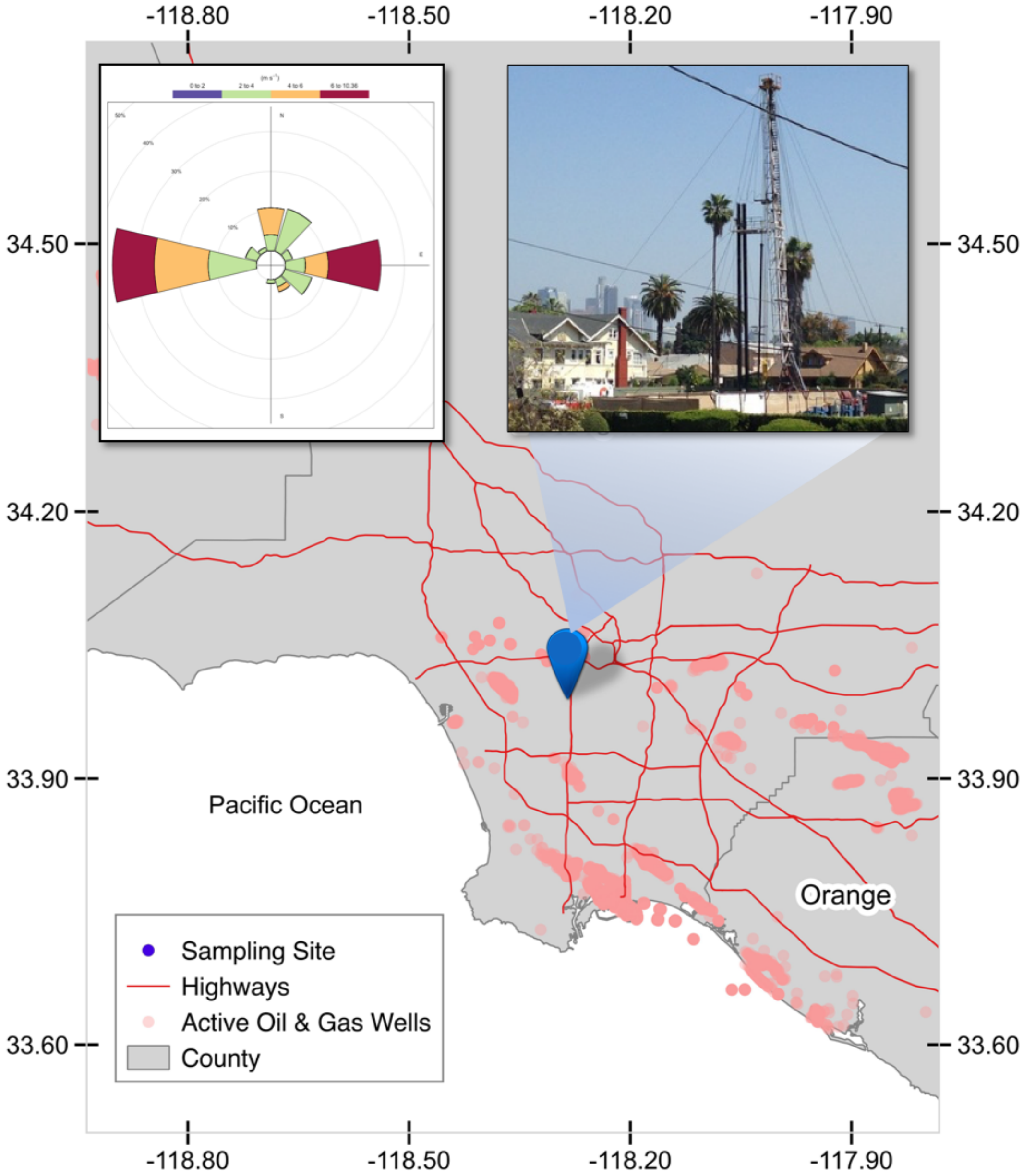
Using a distance-decay gradient, a previous study in the semi-rural region of the Barnett Shale, Texas found that measured VOCs decayed to background concentration within 100 meters of ONG facilities[36], and our previous work the Northern Front Range of Colorado found measured VOCs decayed to background ~200 meters from active ONG facilities[156]. Along the eastern transect of our current study, n-hexane concentrations decayed to control levels at 200 meters from the center of the Jefferson drill site (150 meters from the eastern fence line). Benzene concentrations decayed to control levels 160 meters from the center of the Jefferson drill site (125 meters from eastern the fence line). The last two sampling sites on the eastern transect were located in residential yards, further from the street, and thus may explain why concentrations were lower than those measured at the control location.

Concentrations of n-pentane follow the expected decay patterns better along the eastern transect compared to the western transect, where the major contribution to measured VOCs is likely from vehicle emissions. On the eastern transect, n-pentane decays similar to n-hexane and benzene until the final sampler (220 meters) where concentrations return back to levels closer to the facility. This rise in concentration levels further from the Jefferson drill site may be attributed to an additional local n-pentane source.

Despite the presence of multiple competing sources and the difficulties associated with deployment in dense urban environments, we were able to identify gradient behavior along the transect downwind of the target ONG facility; correlate target VOCs with the natural gas tracer compound, n-pentane; and identify added air quality exposure burden from the targeted ONG facility. We recommend the current gradient methodology for future ONG-related emission characterization, especially in environmental justice communities that lack access to exposure data.

3.6 Tables and Figures

Figure 3.1: Location of the Jefferson drill site in downtown Los Angeles with wind rose diagram for meteorological data collected February 17 – March 2, 2016.



Geographic shapefiles are from the California Department of Transportation and the Division of Oil, Gas, and Geothermal Resources. Image is borrowed from www.redeemercp.org.

Figure 3.2: Transect through the Jefferson drill site and results of the distance decay gradient for data collected between February 17 – March 2, 2016.

Table 3.1: Summary statistics for all passive TraceAir badges along the Jefferson drill site transect.

	Range	Median	Mean	Control	Baker[1]	MATES IV[2]
Benzene	0.47 – 0.55	0.51	0.51	0.51	0.48	0.40
2-Butoxyethanol	NA	< 1.00	< 1.00	< 1.00	NA	NA
n-Hexane	0.40 – 0.50	0.42	0.43	0.39	0.39	NA
n-Pentane	0.97 – 1.30	1.10	1.13	1.10	1.20	NA

Data provided in ppbv. Non-detects are denoted by the "less than" sign, followed by the sample limit of detection.

[1] Baker, A. K. *et al.* Measurements of nonmethane hydrocarbons in 28 United States cities. *Atmos. Environ.* 42, 170–182 (2008).

[2] MATES IV. Available at: http://www.aqmd.gov/home/air-quality/air-quality-studies/health-studies/mates-iv. (Accessed: 27th June 2018)

Table 3.2: Correlation analysis for all passive TraceAir badges within the transect.

	Benzene	n-Pentane	n-Hexane
Benzene	1	0.45	0.79**
n-Pentane	0.45	1	0.63*
n-Hexane	0.79**	0.63*	1

*p-value < 0.05

**p-value < 0.01

Chapter 4: An Investigation of the Association Between Particle Matter (PM), Hazardous Air Pollutants, and Methane Emissions from the Aliso Canyon Natural Gas Storage Facility During the 2015 Natural Gas Blowout

Authors:

Diane A. Garcia-Gonzales[1]

Michael Jerrett[1-3]

Affiliations:

[1] Environmental Health Sciences Division, 50 University Hall, School of Public Health, University of California, Berkeley, Berkeley, CA 94720. dgonzales98@gmail.com

[2]Department of Environmental Health Sciences, Fielding School of Public Health University of California, Los Angeles

[3]Center for Occupational and Environmental Health, Fielding School of Public Health University of California, Los Angeles

A similar version of this chapter will be submitted for publication to the journal of Environmental Health.

4.1 Abstract

In October of 2015, a storage well at the Aliso Canyon natural gas storage facility experienced a massive methane (CH_4) leak, which resulted in the largest anthropogenic release of CH_4 from a point source within the United States. Additional sampling conducted during the event revealed higher and more variable concentrations of particulate matter (PM) in the outdoor air at locations close to the leak site compared to those farther away, particularly for fine particles. Sampling of indoor environments, found a characteristic "fingerprint" of metals in the indoor dust samples similar to samples taken at the blowout site. With this pool of evidence, we investigate the association between the Aliso Canyon natural gas storage site and PM concentrations by: (a) conducting additional sourcing efforts using meteorological data and correlations between PM, CH_4, and other air toxins collected during the natural gas blowout, and (b) identifying characteristics unique to the homes that tested positive for air pollutants using data collected from extensive indoor environmental assessment surveys.

4.2 Introduction

Chemicals and equipment associated with upstream natural gas development (drilling and extraction) pose threats to human and ecosystem health[16,116,118], and a growing body of evidence suggests an association between proximity to site and potential health risks[14,42,99–105,112]; however, a paucity of peer-reviewed studies that investigate the potential for exposure to individuals residing near underground natural gas storage fields impedes efforts to protect public health around these facilities. The Aliso Canyon Natural Gas Storage field, located in Los Angeles County's Santa Susana Mountains, is the second-largest natural gas storage facility in the western United States with a total working storage capacity of 86 billion cubic feet (Bcf). Many of the natural gas storage wells were converted from abandoned and depleted oil wells and have been in continuous use over the past 40 years for injection, storage, and extraction of hydrocarbon reserves. On October 23, 2015, Southern California (SoCal) Gas operators at the Aliso Canyon facility reported an uncontrolled, non-routine methane (CH_4) leak at well site SS25, located less than one mile upwind from the Porter Ranch community. This event resulted in one of the largest anthropogenic releases of natural gas from a point source ever recorded in the United States[55].

For the first weeks of the event, elevated levels of hazardous air pollutants (HAPs), mercaptans (natural gas odorants including tert-butyl mercaptan and tetrahydrothiophene), and sulfides were measured in ambient air, and a visible "oily" residue was reported at multiple locations across the Porter Ranch community[157–160]. Emissions of HAP compounds are of particular concern as they are known or suspected to cause cancer or other serious health problems, including neurological and respiratory effects. A random survey of area residents found 61% experienced headaches or migraines; 40% experienced nausea, vomiting, stomachaches, GI issues, or diarrhea; 32% experienced bloody noses; and 27% experienced and respiratory/breathing symptoms[161]. On February 18, 2016, state officials announced that the leak was permanently plugged, but not before approximately 97,100 metric tons of methane were released into the atmosphere[55].

A Community Assessment for Public Health Emergency Response (CASPER) health survey conducted post-leak found nearly 63% of surveyed households experienced symptoms that persisted post-remediation[162]. A subsequent Public Health Assessment conducted in 114 indoor environments adjacent to the storage facility revealed several air toxins that were found above EPA health-based standards and a characteristic “fingerprint” of metals that provided biologically plausible explanations for health symptoms noted by area residents[163]. Furthermore, the metal cluster, consisting of barium, manganese, vanadium, and aluminum, was similar to the metal composition found in soil samples collected near well SS25, suggesting a related source.

A formal spatial clustering analysis was conducted on the locations positively identified by the metal fingerprint, using the Ripley-K statistics for a marked non-homogenous Poisson point process, but results did not provide evidence of clustering in the locations with higher levels of metals[164]. The complex topography of the Aliso Canyon hillside distributes particles and other air toxics unequally through the neighborhoods and the diversity of architectural elements influences air exchange rates into indoor environments where, on average, Americans spends more than 90% of their time[165]. This complex environment creates a setting where simple distance decay gradients are unable to predict potential exposures, thus complicating initial efforts to understand the geographical distribution of metal deposition. Recognizing the geographical and architectural heterogeneity and intricacies of the local landscape, the Los Angeles Department of Public Health (LADPH) complemented the indoor air and dust sampling with a household survey to identify characteristics unique to the homes that tested positive for the characteristic fingerprint of metals.

The current research aims to expand on the earlier investigations through supplementary sourcing efforts of criteria air pollutants, PM, and HAPs of biological importance. With these additional investigations, we aim to understand the deposition of the metal fingerprint into the indoor environments of proximate communities and further characterize air quality during the active blowout event. Such information can be useful for understanding potential exposures during the active blowout event and as evacuated residents returned to their homes. More broadly, the research will elucidate possible risks associated with potential leaks from the 328 natural gas storage fields within the United States that use depleted oil wells[166].

4.3 Methods

The community of Porter Ranch is located at the base of the Santa Susana Mountains, south of the Aliso Canyon natural gas storage field, and north of Northridge, in Los Angeles County. The Los Angeles Department of City Planning estimates a 2008 population of 30,571 individuals within the 5.59 square mile area of Porter Ranch. On November 19, 2015, during the ongoing natural gas blowout event, the LADPH issued a Resident Relocation Directive resulting in the relocation of an estimated 2,200 families[167], followed by an additional directive for students and staff of local area schools[168]. Both directives cited health and sulfur-type odor complaints consistent with inhalational exposure to mercaptans; however, neither etiological agent nor exposure pathway could be confirmed. Conversant with the broad range of air pollutants associated with oil and natural (ONG) gas development[142], and the need to understand the full range of potential exposures, we initiated the following analysis.

Site Selection

Air quality monitoring and sampling sites were selected based on accessibility, community and host interest, and ability to saturate the sampling area without significant influence from confounding emissions sources. Locations included residential yards, a public school, and a community pool area. Distance ranged from approximately 1.2 to 4.5 kilometers from the blowout site, well SS25; the furthest location was selected to collect background air quality within a residential neighborhood of northern Northridge, 7.3 kilometers southeast of well SS25. Monitor hosts were educated in proper maintenance to minimize exposure from competing HAP sources. A map of all primary dataset sampling locations can be found in Figure 4.1.

Data Collection

Active Sampling

Sensor Networks for Air Quality (SNAQ) monitors used for the air quality monitoring in this study were developed in Dr. Rod Jone's laboratory, Chemistry Department, University of Cambridge, UK[169]. These monitors are capable of measuring carbon monoxide (CO), nitrogen oxide (NO), ozone (O_3), sulfur dioxide (SO_2), and nitrogen dioxide (NO_2) gas phase species using electrochemical sensors from Alphasense (www.alphasense.com). In addition, SNAQ monitors measure carbon dioxide (CO_2) and total volatile organic compounds (tVOC) via optical sensors. A compact optical particle counter, designed and built at the Center for Atmospheric and Instrumentation Research at the University of Hertfordshire, also incorporated into the unit, measures aerosol concentrations every 20 seconds in the form of 16-bin histograms covering size ranges between 0.38 – 17.4 µm. Meteorological data including temperature, relative humidity, wind speed, and direction are also gathered by each node. Monitors contain a geographic positioning system (GPS) receiver and data were collected and stored via an onboard universal serial bus (USB) drive and manually downloaded. Six SNAQ monitors were deployed between January 13 – February 20, 2016, and data were post-processed at the University of Cambridge in preparation for analysis.

Passive Sampling

Passive samplers are commonly used in occupational settings but have also been used successfully in ambient environments with longer exposure timeframes. The proven utility of commercially available passive samplers has been demonstrated across several upstream oil and natural gas monitoring studies[18,31,36,41,63], but has yet to be used to characterize the ambient environment around an underground natural gas storage facility during either routine or non-routine operations. Passive TraceAir badges, from Assay Technology (www.assaytech.us), are capable of collecting a panel of organic air pollutants through passive diffusion in a time-integrated manner. We deployed two rounds of passive badges across 22 different locations south of the natural gas storage facility. The first and second rounds of passive badges were deployed January 13 and 28, 2016 respectively, and remained in the field for two weeks. This period corresponded to the last month before well SS25 was plugged. Upon collection, passive badges were sealed and promptly returned to Assay Technology's laboratory for analysis of 25 different volatile organic compounds (VOCs).

Radiello Cartridge Adsorbents, from Sigma Aldrich (www.sigmaaldrich.com), measure hydrogen sulfide (H_2S) on a microporous polyethylene matrix impregnated with zinc acetate. Radiello Cartridge Adsorbents for H_2S were deployed at 11 different locations south of the natural gas storage facility on February 4, 2016 for one-week. A second round of samplers was deployed on February 12 which coincided with the well plug and, thus, represents air quality sampling post-remediation. One-week post-deployment, Radiello Cartridge Adsorbents were sealed and shipped to Inter-Mountain Labs in Sheridan, Wyoming, for analysis. To protect the samplers from the elements, all passive samplers were placed within a non-treated AllCan West (http://allstatecan.com/) tin and affixed to a metal fence post or existing structure at each site.

Secondary Data Sources

On December 16, 2015, the South Coast Air Quality Management District (SCAQMD) deployed an air monitoring trailer in the private community of Highlands, a subdivision in Porter Ranch, located in the northern most part of the community downwind of the blowout at well SS25. Monitors within the trailer collected and reported 1-hour average concentrations for CH_4. This publicly available dataset is available for download on CARB's Air Quality and Meteorological Information (AQMIS2) clearinghouse (ww2.arb.ca.gov). In addition, 5-minute and 24-hour time-integrated canister samples were collected at the trailer and several additional locations within the Porter Ranch community. The 5-minute samples were collected when continuous CH_4 monitors reflected elevated concentrations. Time-integrated 24-hour samples commenced on December 21, 2015, collecting samples every 3 days, on average. Canister were analyzed for 55 VOCs using Gas Chromatography (GC) and Flame Ionization Detection (FID), CH_4 using method 25.1 (TCA FID), and mercaptans by SCAQMD Method 307-91. All samples were analyzed by an in-house SCAQMD laboratory in Diamond Bar, CA, and PDF copies of the lab reports were made available through the SCAQMD website (http://www.aqmd.gov/).

Data was downloaded, and hand digitized in preparation for analysis. Due to SCAQMD's extensive sampling of VOCs, we limited the current analysis to include only HAPs, as they are the pollutants suspected to cause cancer or other serious health effects. There are currently 187 HAPs listed for regulation under the Clean Air Act[19], some which have been associated with upstream oil and natural gas (ONG) activities, but little research exists on their role in natural gas storage. Hydrogen sulfide (H_2S) was removed from the official list in 1991 but was included in our analysis due to its high toxicity at lower concentrations and key role in natural gas composition. Passive and canister sampling efforts included the collection and analysis of 18 HAP compounds.

On January 14, 2016, CARB deployed an additional continuous CH_4 monitor within the subdivision known as Porter Ranch Estates, located several meters south of the Highlands community. A continuous benzene monitor was co-located at the site and provided 1-hour average concentrations starting February 1, 2016. These publicly available datasets are available for download on CARB's Air Quality and Meteorological Information (AQMIS2) clearinghouse (ww2.arb.ca.gov).

Argos Scientific installed an air-monitoring Fenceline system designed to measure real-time CH_4 concentrations and report the information to the community via a public access website (www.fenceline.org/porter). The Fenceline system utilizes light beams to detect and quantify the gases and then reports the data in five-minute average concentrations. The Fenceline system has been continuously running since January 27, 2016 at a residential home in the Highlands community, approximately 345 meters east of the SCAQMD trailer. To understand the relationship between CH_4 and criteria air pollutants, we co-located a SNAQ monitor next to the Fenceline system. Data from the Fenceline system was provided in Excel format from Argos Scientific (permission granted).

Public Health Assessment Household Survey

LADPH developed an indoor environmental assessment survey that was conducted during the Public Health Assessment of 114 indoor environments directly after the natural gas storage blowout. The survey consisted of 35 questions, including open ended, dichotomous, and multiple-choice questions. These questions covered several topics including: (1) household attributes, (2) relocation history, (3) post-remediation cleaning behavior, (4) use of portable and in-duct air purifiers during the blowout, (5) identification of either an oily residue or "gas-like" odor, (6) indoor home environment, (7) pet health, and (8) indoor chemical usage. The population of interest included all residential homes within a five-mile radius from well SS25. LADPH oversampled in environments where residents were symptomatic to ensure air and dust samples were able to identify rapidly deteriorating pollutants post-blowout. Survey data was digitized and coded by "House IDs" by LADPH to ensure privacy for all survey participants. The data does not contain personal or location identifiers. Human health data was collected but not included in the current analysis.

Data Analyses

All datasets were collected and saved as comma separated value (csv) files and imported into the R programming environment for processing, visualization, and analysis. Within R, air quality data was analyzed using the open-source tools for air pollution data analysis, OpenAir[131], a Natural Environment Research Council (NERC) knowledge exchange project for the analysis of air pollution data (www.openair-project.org). The indoor environmental assessment survey conducted during the Public Health Assessment was analyzed using the CCA package[170], also within the R environment.

Source Attribution

To elucidate potential emission sources, we first investigated pollutant concentrations using bivariate polar plots with meteorological variates to visualize concentration levels by geographic source direction. Peak emission concentrations during anomalous meteorological conditions may shift polar plot outputs when based on simple mean concentrations. Thus, to identify conditions that dominate overall concentrations amid the intricate topography of the Aliso Canyon hillside, a weighted mean was used to estimate source direction. Data was further analyzed by filtering for VOCs measured during CH_4, the main constituent of natural gas[171], enhancements from co-located monitors. In California, background CH_4 concentrations range from 1.7 to 2.0 ppm[172]; concentrations above background may indicate a local source. To further distinguish on-road traffic from ONG emissions, we investigated the relationship between measured VOCs with tracer compounds. Strong correlations with CH_4, in the absence of a correlation with acetylene, a pollutant commonly found in vehicle emissions[173], can help differentiate attributions from competing VOC sources.

Tracer compound ratios of pentane isomers provide additional source indicators to distinguish contributions of ONG sources from traffic emissions. Isomers of *i*-pentane and *n*-pentane have similar reaction rate constants and, thus, degrade at a similar rate. In areas dense with ONG infrastructure, an *i/n*-pentane ratio close to 1:1 is expected. Previous studies near upstream ONG development in Colorado and Pennsylvania found ranges of *i/n*-pentane ratios between 0.86 and 1.2 ppbv/ppbv[17,34,40,42,48,65]. Larger ratios are associated with emissions from urban centers and traffic-related sources. Los Angeles area *i/n*-pentane ratios have been reported in previous studies ranging between 1.9 and 2.3 ppbv/ppbv[62,174,175], near the ratios found in tunnel studies (2.2 – 3.8 ppbv/ppbv) where traffic dominates VOC emissions[176,177]. In California, aerial samples over the Inglewood Oil Field found significantly lower ratios (1.91 ppbv/ppbv) than in Los Angeles area samples (2.38 ppbv/ppbv) without ONG activities[178]. Additional sampling in Riverside County found ratios between 1.41 and 1.97 ppbv/ppbv indicating leakages along oil and natural gas pipelines.

Canonical Correlation Analysis

Data from the Public Health Assessment Household Survey was analyzed using a Canonical Correlation Analysis (CCA), a multivariate technique, to investigate correlations between metal "signatures" and survey variables. By employing CCA, a latent variable is computed to allow for a combined analysis of the metal signature instead of single outcome analyses. Compounds of the metal fingerprint include: barium, manganese, vanadium, iron, strontium, and aluminum[163], which were used to build the first latent variable in the CCA analysis. Previous research indicates that five to 10 observations should be available for each variable included in the analysis[179]. Using this guideline, a second latent variable using groups of less than 10 survey variables was created to correlate the latent variable for metals. Due to the constraints of latent variable size, results are provided in groups constructed from the eight survey topics previously listed.

4.4 Results

Hazardous Air Pollutants

Passive Samplers

Two-week time integrated passive sampling concentrations were very low for most the HAPs tested, below normal background levels in the Los Angeles area, and below state and national health-based standards (Table 4.1). Several passive samplers reported values well under the reporting limits of detection. For HAPs found above the sample limit of detection, concentrations were slightly lower than values obtained by SCAQMD 5-min and 24-hour canister samples for a similar period. Furthermore, these concentrations were below what was measured at a background control site located about 5.5 miles away in Northridge, which had more influences from common urban sources such as traffic.

24-Hour Canister Samples

SCAQMD sampled and reported results on eight HAPs from 132 individual canisters collected across several Porter Ranch locations between December 16, 2015 and February 11, 2016 (Table 4.1). In the 24-hour integrated canister samples, a strong correlation was identified between levels of CH_4 and several organic molecules: n-hexane ($r = 0.86$), toluene ($r = 0.72$), styrene ($r = 0.68$), benzene ($r = 0.65$); and moderately strong correlation was identified between CH_4 and o-xylene ($r = 0.54$). In contrast, weak ($r < 0.20$) or negative correlations were found among levels of acetylene and several VOCs including: n-hexane, o-xylene, toluene, and styrene. Acetylene was, however, found to have a relatively strong correlation with benzene ($r = 0.67$). In a two-variable linear regression model ($n = 29$), CH_4 explains 40% ($p < 0.001$) of the variability of benzene concentrations; the coefficient of determination increases to 74% ($p < 0.0001$) when acetylene is added to the model.

5-Minute Canister Samples

Results from SCAQMD's 5-min "trigger" samples (Table 4.2), collected during peak CH_4 concentrations, revealed a strong correlation between levels of CH_4 and n-hexane ($r = 0.95$), benzene ($r = 0.92$), 2,2,4-trimethypentane ($r = 0.86$), m/p-xylene ($r = 0.80$), and ethylbenzene ($r = 0.62$); a moderately strong correlation was identified between CH_4 and both toluene ($r = 0.51$) and o-xylene ($r = 0.49$) levels. In contrast, very weak ($r < 0.20$), weak ($r < 0.40$), or negative correlations were found between acetylene and benzene, n-hexane, toluene, o-xylene, ethylbenzene, m/p-xylene, 2,2,4-trimethylpentane, and styrene levels. Regression analyses between levels of CH_4 and individual HAP compounds during these peak CH_4 emission events found a significant ($p < 0.0001$) coefficient of determination between CH_4 and n-hexane ($r^2 = 0.91$), benzene ($r^2 = 0.85$), 2,2,4-trimethypentane ($r^2 = 0.73$), m/p-xylene ($r^2 = 0.64$), ethylbenzene ($r^2 = 0.37$), toluene ($r^2 = 0.25$), and o-xylene ($r^2 = 0.24$) levels.

Continuous 1-Hr Benzene Samples

During the active blowout event, CARB co-located a continuous sampling benzene and CH_4 monitor within the private community of Porter Ranch Estates. Similar to the results from the 5-min canister sampling, benzene concentrations was found to have a strong correlation with CH_4 concentrations ($r = 0.93$) in all samples collected prior to February 12, 2016; in the weeks post-remediation, a weak correlation ($r = 0.30$) was present. A regression analysis was conducted on all samples collected between February 1 – 11, 2016, and results indicate that during this time, benzene concentration was expected to increase 15.45 ppt ($r^2 = 0.86$, p-value < 0.001) when CH_4 concentration increased by 1 ppm.

i/n-Pentane Ratios

Mean *i/n*-pentane ratios for all Porter Ranch area 5-min canister samples were 1.03 during the active leak and 5.02 post-remediation. An enhancement ratio of 0.12 ppbv/ppbv was calculated for all 5-minute canister samples measured during the active blowout event (Figure 4.2). Plots of pentane isomer and tracer compound ratios reflects larger methane/acetylene ratios at the lower *i/n*-pentane scale (Figure 4.3). Using these values as a guide, we find stronger coefficients of determination between HAPs and CH_4 when the 5-minute canister data is filtered for *i/n*-pentane ratios between 0.24 and 1.40 ppbv/ppbv (Figure 4.4).

Particulate Matter

Polar plots of weighted mean CH_4 concentrations in Figure 4.5 show divergent geographic source directions when CH_4 is filtered at 2.24 ppm. This finding suggests that the lower "background" levels of methane (=< 2.24 ppm) originated from the south, or in the direction of the city of Los Angeles (Figure 4.5, first row, Column A); and the enhanced CH_4 concentrations (> 2.24 ppm) originated from the northwest, or the direction of well SS25 (Figure 4.5, first row, Column B). To further distinguish urban background concentrations from natural gas blowout enhancements, we created polar plots for carbon monoxide (CO), a common tracer for urban emissions[15,48]. Using a conservative CH_4 concentration threshold of 2.3 ppm, we filtered CO data by co-measured CH_4 concentrations. Results revealed that when CH_4 concentrations were below 2.3 ppm (Figure 4.5, second row, Column A), two potential sources emerge: (1) a local source at the monitor location (identified by minimal wind speed), and (2) a source originating from the south, or from the direction of the city of Los Angeles. Samples filtered to include only CH_4 concentrations greater than 2.3 ppm (Figure 4.5, second row, Column B) did not identify a southern origin of CO, indicating minimal impact from the greater Los Angeles area when CH_4 concentrations were above 2.3 ppm.

Using the identified CH_4 background threshold of 2.3 ppm, additional bivariate polar plots were created for PM_1, $PM_{2.5}$, and PM_{10} (Figure 4.6). All plots indicate both a local source at the monitor site and another close source from the northwest, the direction of well SS25. The northwestern source for all particle datasets is similar to source direction of elevated CH_4 concentrations, suggesting a similar geographical origin. A correlation analysis of the data provides additional insights into the relationship between particles and elevated CH_4 concentrations. Using a 6-hour rolling correlation analysis (Figure 4.7), the strongest correlations were identified during the last few days prior to the leak control on February 12, 2016. Another bivariate polar plot was created to elucidate the particle source direction for these two timeframes (Figure 4.8).

Public Health Assessment Household Survey

Preliminary observations of the SNAQ dataset revealed marked differences in the temporal patterns of particles at locations near the leak site compared to those farther away. In March 2016, we conducted a small hypothesis-driven investigation into the indoor environments of seven Porter Ranch households and found HAPs within the collected dust samples tested at two unoccupied homes. The combination of these preliminary findings and the influx of adverse health symptoms reported by individuals re-entering their previously unoccupied residences post-remediation prompted the LADPH to conduct a series of rapid surveys and additional dust sampling of indoor environments. These investigations were conducted to understand the possible exposures associated with the blowout event, particularly of chemically stable particles capable of penetrating into indoor environments. Results identified a characteristic fingerprint of metals that matched the soil samples collected on-site, near well SS25, and provided plausible explanations for persisting health symptoms. An indoor household survey was conducted at the time of the air and dust sampling to help investigators identify characteristics unique to the homes that tested positive for the characteristic fingerprint of metals.

A CCA analysis of the two latent variables was conducted for each of the eight questionnaire topics (Figure 4.9). Results revealed a correlation between the metal fingerprint and several variables from the "household attributes" and "indoor home environment" survey categories. Since each of these categories were analyzed using their own latent variables, they are not directly comparable. Therefore, questions that were most strongly correlated with the latent variable for metals were regrouped into the same latent "survey" variable and reanalyzed, resulting in a similar outcome. This analysis yielded a canonical correlation coefficient of 0.71 (p-value < 0.0001) with the following attributes in the latent "survey" variable: (1) the year the house was built; (2) if any member of the household, or any visitors ever smoked cigarettes or cigars, or used any smokeless tobacco products inside the home; (3) whether SoCal Gas installed weather-proofing materials in the homes to seal windows, doors, or other gaps that allow air to enter the home during and as a result of the blowout event; (4) presence of any gas appliances in the home; and (5) if the home is a detached single-family unit. The first two variables were positively correlated with the latent "metal" variable, indicating that the metals were associated with older homes where smokers were present. The last three variables were negatively correlated with the latent metal variable, indicating that the metals were less associated with single family (detached) homes, professionally sealed by SoCal Gas during the blowout events, and that had gas appliances.

A sensitivity analysis was conducted using a second latent variable that included only the metals that overlapped with the results of the soil samples: vanadium, aluminum, manganese, and barium. These results yielded a similar outcome to the larger fingerprint, with a slightly decreased canonical correlation coefficient of 0.58 (p < 0.0001), and similar cross canonical variate direction among the individual survey variables. Descriptive statistics revealed a low total number of respondents indicating a smoker in the home (5.62%) or indicating the home did not have any gas appliances (4.44%); thus, the outcome of these results must be interpreted accordingly. No other correlations were found in the CCA analysis.

4.5 Discussion

Hazardous Air Pollutants

Results from SCAQMD canister samples revealed that during the 24-hour sampling timeframe, several HAP compounds were highly influenced by emissions from well SS25 including n-hexane, styrene, toluene, and o-xylene. During peak CH_4 emissions events, 5-

minute canister samples found a broader range of HAPs were influenced by well SS25 including BTEX compounds, n-hexane, toluene, and 2,2,4-trimethylpentane. HAP concentrations exceeded the 8-hour and chronic Reference Exposure Levels (REL) set by the California Office of Environmental Health Hazard Assessment (OEHHA)[86]. When extrapolated to fit these longer timeframes, these HAP concentrations can elicit an adverse human health response; however, no samples collected during the active blowout event exceeded acute (1-hr) RELs. While encouraging, it is important to note that ambient BTEX concentrations, below health benchmarks, have been associated with adverse health outcomes in numerous epidemiological studies, and the WHO has declared no safe threshold for benzene inhalation[67–80]. Furthermore, evidence suggests that a broad range of HAPs co-emitted during peak CH_4 emissions may increase original estimates of health risks of exposure if those co-emitted compounds are biologically additive or synergistic.

A regression analysis was conducted on all continuous 1-hr benzene samples collected between February 1 – 11, 2016, and results indicate that during this time, benzene concentration was expected to increase 15.45 ppt ($r^2 = 0.86$, p-value < 0.001) when CH_4 concentration increased by 1 ppm. Based on estimates from this data, and using OEHHA's 8-hr health-based standard of 1 ppb, methane would have to be over 64 ppm for a timeframe of over 8 hours to elicit a non-cancer benzene-related health response[82]. In-situ monitors deployed in the Highland community reported 1-hour time integrated average concentrations of CH_4 exceeding 65 ppm during the final days of the blowout. It is unclear if these peak concentrations are restricted to this timeframe; flyover measurements show peak concentrations occurred during the first few weeks of the event[55], but ground-level CH_4 data during this time is not available for analysis and modeling potential emissions or estimates of exposure are beyond the scope of the current work.

i/n-Pentane Ratios

Enhancement ratio of the 5-minute canister samples during the active blowout event (0.12 ppbv/ppbv) was well below those measured in rural ONG development regions (0.86 - 1.2 ppbv/ppbv) and near a Los Angeles area ONG field (1.91 ppbv/ppbv). This observation suggests that either the 5-minute canister samples collected air pollutants from a variety of sources, that the emitted natural gas did not contain hydrocarbons with expected enhancement ratios, or some combination of the above. To understand the distribution of the broad range of *i/n*-pentane ratios measured during peak CH_4 concentrations, a plot of tracer compound ratios was created. The resulting scatterplot showed larger methane/acetylene tracer ratios at the lower *i/n*-pentane scale, where the natural gas storage well blowout dominated emission contributions over emissions from traffic-related sources. These results suggest an optimal pentane isomer ratio range between 0.24 and 1.40 ppbv/ppbv. Filtered 5-minute canister samples based on these estimates found stronger coefficients of determination between measured HAPs and CH_4; 94% of these samples routinely occurred between the hours of 1:00 – 8:00 am and 3:00 – 9:00 pm. These two pieces of evidence suggest that this unique *i/n*-pentane ratio signature was associated with emissions from the blowout event, which may be used to aid in the characterization of future blowout constituents.

Particulate Matter

Results from the bivariate polar plots and correlation analyses suggest activities that occurred during the final attempt to control the flow of gas out of the leaking well were a likely source of various size particles measured in the atmosphere. During this timeframe, operators drilled to the base of well SS25 and used "heavy fluids" pumped into the relief well to control the flow of gas[180]. Considering the evidence that overlaps with this timeframe, and the lack of correlation between PM and CH_4 prior to these events, this evidence suggests that the final attempts to control the flow of gas out of the leaking well were a likely source of various size particles measured in the atmosphere. While we have an adequate understating about particles near roadways, a dearth of scientific literature exists investigating the constituents of particles from natural gas storage wells and their impact to human health.

Public Health Assessment Household Survey

Indoor dust sampling post-remediation revealed a characteristic metal fingerprint within the homes, but without baseline sampling, we cannot make temporally explicit conclusions about when the deposition occurred. Two pieces of evidence, however, imply these depositions are related to emissions from well SS25. First, as noted in the earlier report, identified metal constituents matched those found in soil samples collected near well SS25[161]. Second, as discovered from the CCA analysis, the latent variable describing the metal fingerprint was negatively correlated with homes that were provided weather-proofing materials by SoCal Gas to seal windows, doors, or other gaps that allow air to enter the home. Depositions that occurred prior to the blowout are not expected to correlate with any remediation efforts during the active event; and thus, the presence of a correlation suggests depositions occurred after homes were weather-proofed. Older homes were found to correlate with the metal fingerprint suggesting that aged windows, doors, and other materials prone to larger gaps that allow increased amounts of air to enter the home, compared to newer construction, affected the impact of exposure to area residents. In combination with the previous findings of the protective properties of weather proofing materials, these results provide additional evidence that the metal fingerprint deposition occurred during the active blowout event from activities associated with well SS25.

Limitations

Several limitations to the current work merit mention. First, despite extensive sampling efforts conducted by multiple organizations, we are still not aware of the full suite of chemicals that may have been emitted during the blowout and, thus, may not have captured the full range of HAPs associated with this event. Second, samples included in the current analysis are limited to the final month of the blow out, when CH_4 concentrations were approximately half of those measured during the first few weeks of the of the blowout event, thus underestimating the impact on air quality[55]. Finally, while conducting the Public Health Assessment*,* LADPH oversampled in environments where residents were symptomatic to ensure air and dust samples were able to identify rapidly deteriorating pollutants post blowout. Thus, the indoor household survey was conducted amongst a potentially biased population, which may have led to recall bias in the answers to the surveys.

4.6 Conclusions

Although a complete reconstruction of the likely exposures cannot be achieved with the available monitoring data, we found compelling evidence that ambient levels of several HAPs were elevated in the surrounding communities of Porter Ranch during the blowout event. We also found evidence that the final attempts to plug the well were associated with particle emissions likely from the SS25 well site. Whether these were liquid aerosols directly from the site or emissions from heavy equipment used to plug the well remains unknown. Taken together, however, with the findings of metal concentrations that match the composition of the soils at the site, and the CCA analyses which showed that newer homes and homes with professionally installed weather proofing materials had lower concentrations of these metals, our results suggest that the blowout and attempts to plug the well had a discernable effect on the indoor air environments of sampled homes. Thus, the principal finding of this investigation is that accidents at natural gas storage facilities have the potential to release harmful pollutants into proximate community settings and indoor environments.

Approximately 20% of active, underground natural gas storage wells, are vulnerable to leaks due to obsolete well designs[181], leaving surrounding communities at risk for exposure to particles and elevated levels of various HAP compounds. The California Council on Science and Technology (CCST) estimates that, among California's underground natural gas storage fields, an incidence of severity significant of reporting will occur, on average, 4.1 times per year[182]. In the absence of policies and regulations designed to protect communities located near underground natural gas storage facilities, it is imperative that future research aims to understand the risks associated with exposures stemming from these activities. Therefore, and in line with recommendations set forth by the CCST, we recommend facility-specific meteorological data-collection equipment installed at all natural gas storage facilities to ensure (a) data collection for baseline concentrations against which to compare in the event of an accidental release and (b) to monitor whether routine emissions have the potential to harm public health.

4.7 Tables and Figures

Figure 4.1: Map of sampling locations within Porter Ranch, California.

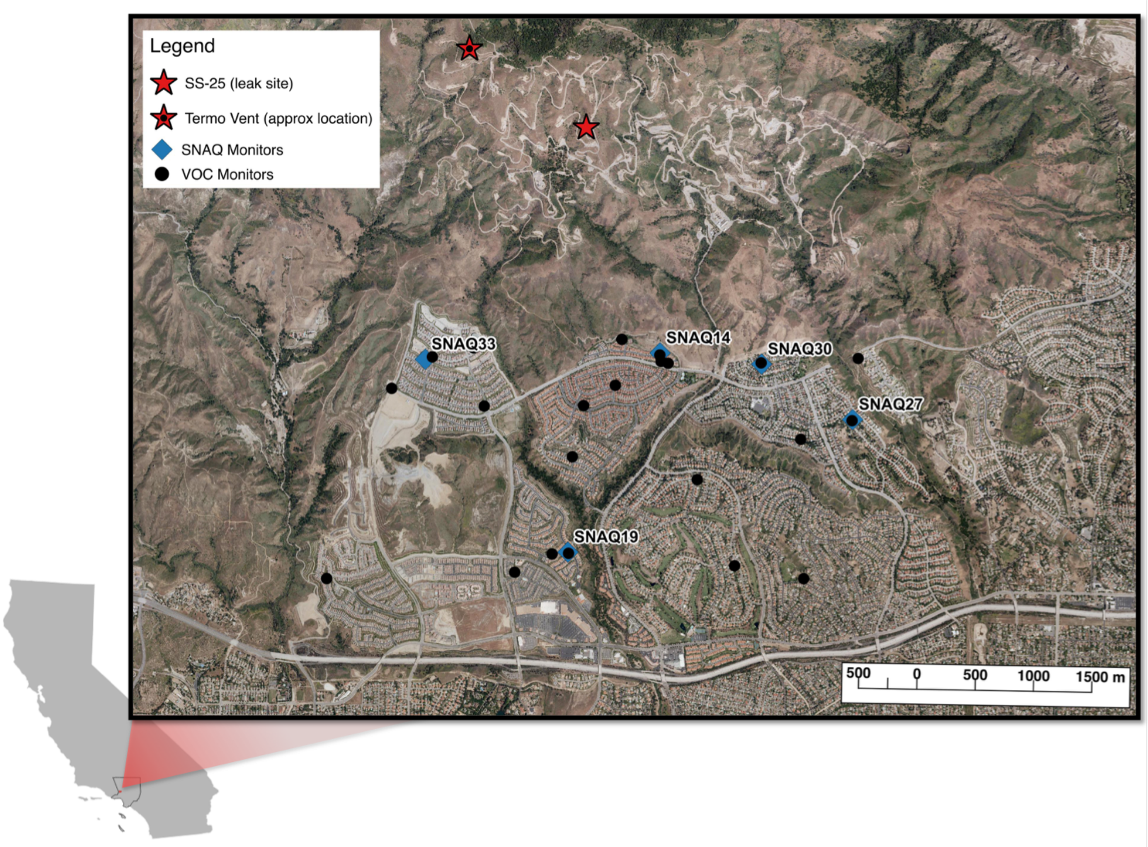
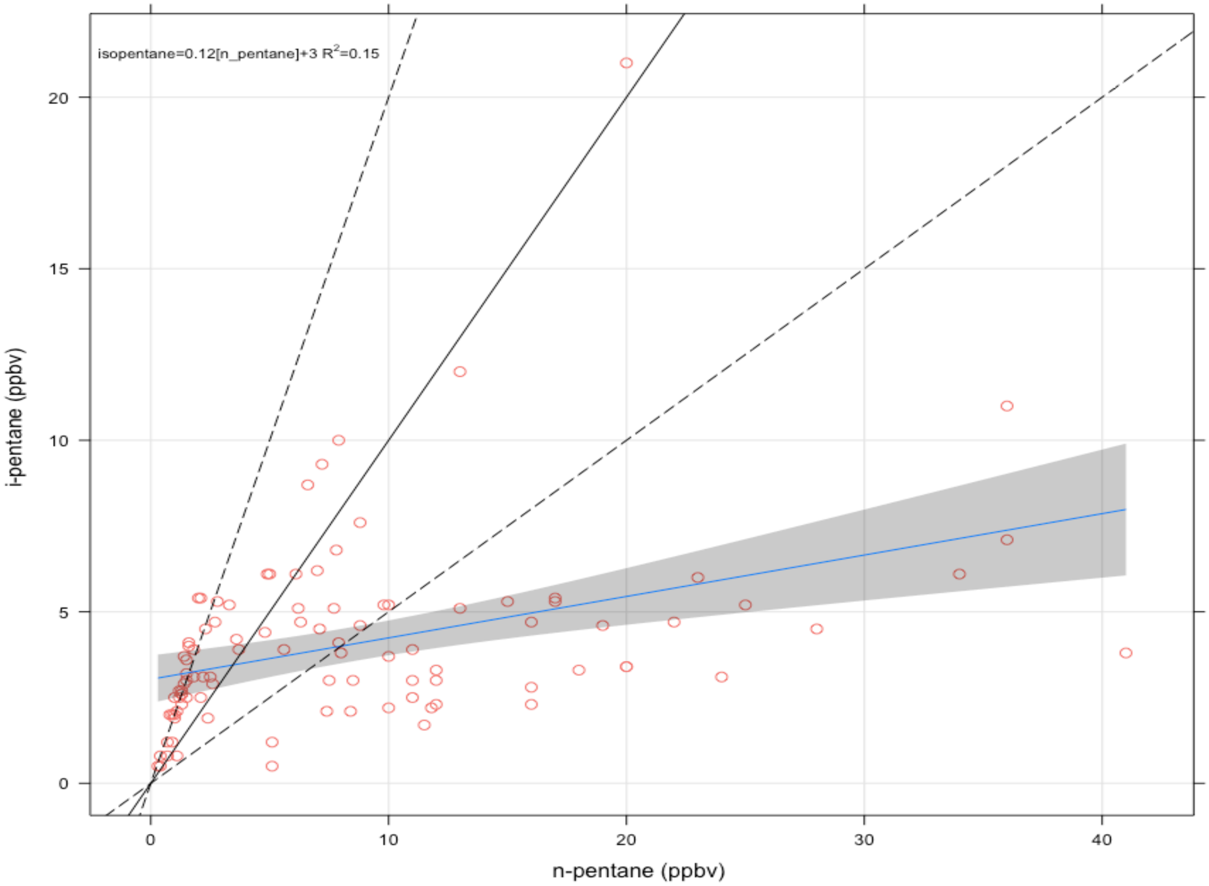
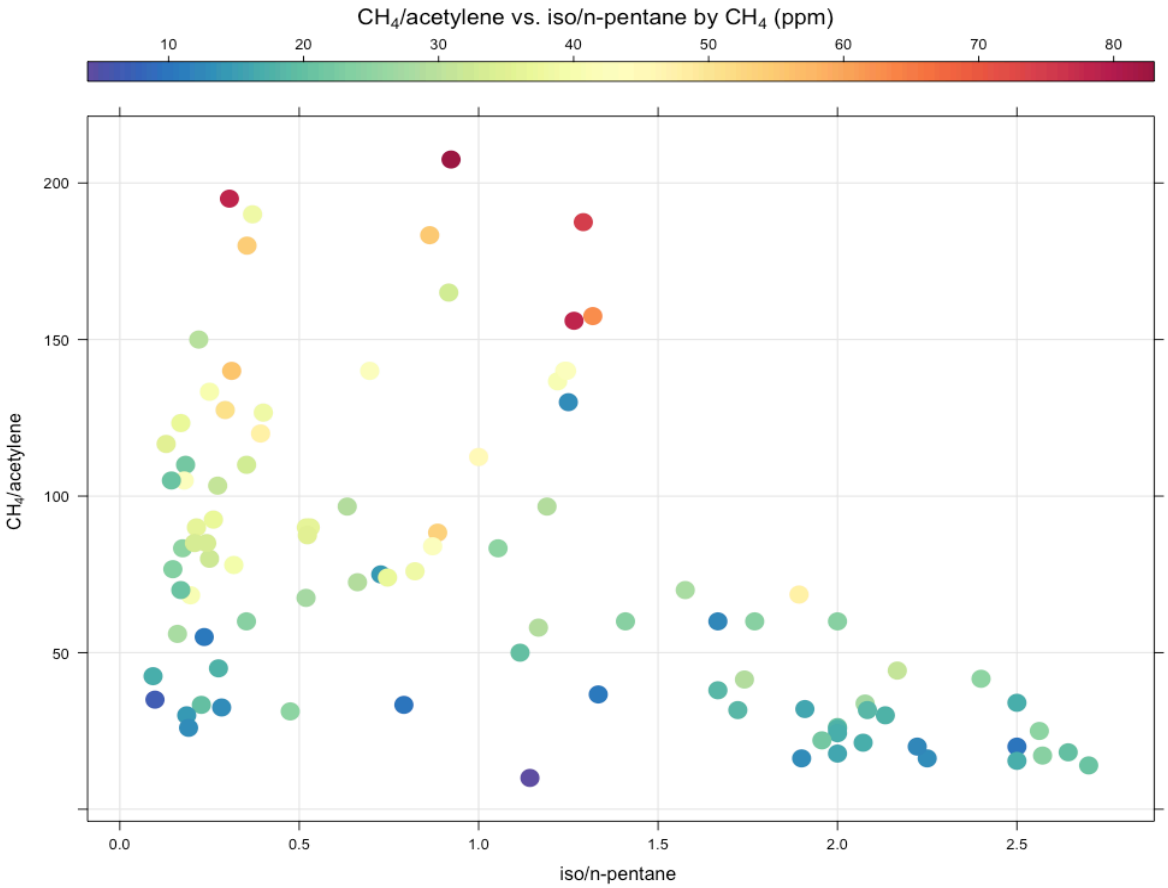


Figure 4.2: Correlation plot of iso-pentane versus n-pentane collected from 5-min canister samples between December 16, 2015 - February 10, 2016 near the Aliso Canyon natural gas storage facility.



Data from the current analysis is fitted with a blue line. The added black lines are added to help inform model evaluation. The solid black line shows a 1:1 relationship, and the upper and lower dotted lines show a 2:1 and 1:2 relationship, respectively, between the two-tracer species.

Figure 4.3: Scatterplot of pentane isomer (i/n pentane) and tracer compound (CH_4/acetylene) ratios.



Concentrations of CH_4 are denoted on the graduated color bar. Larger CH_4 ratios are most prominent at the lower i/n-pentane ratio scale, between 0.24 and 1.4 ppbv/ppbv.

Figure 4.4: Regression plots of several compounds versus CH_4 measured in the 5-min "trigger" canisters collected between December 16, 2015 - February 11, 2016 for data collected when *i/n*-pentane ratio measured between 0.24 and 1.4.

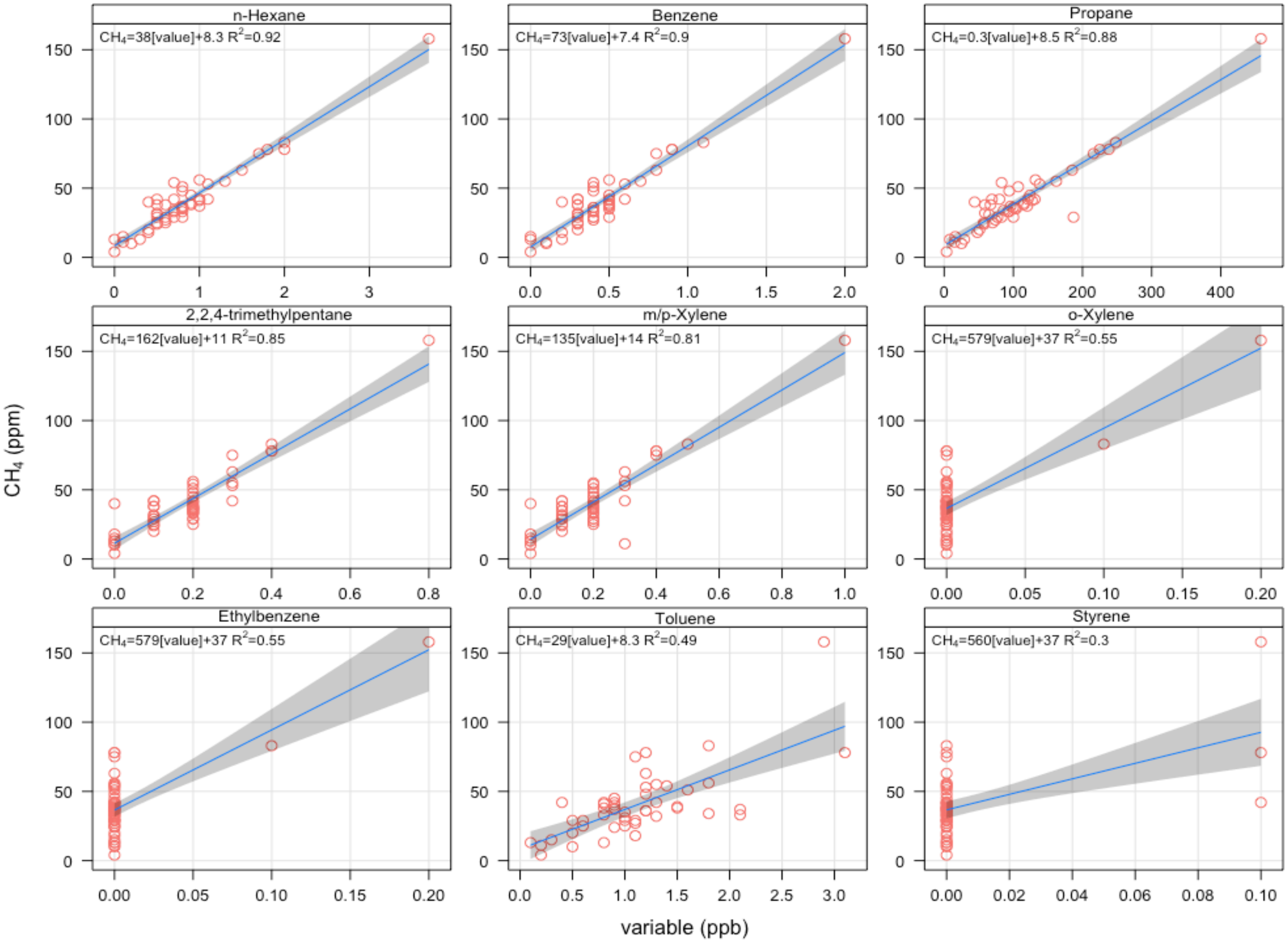
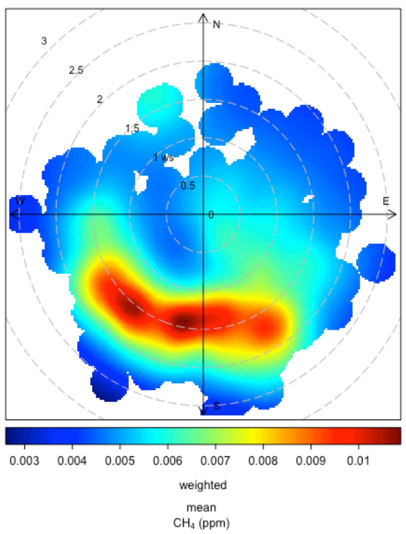
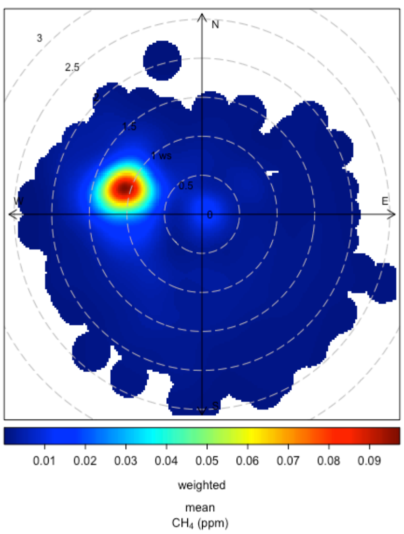
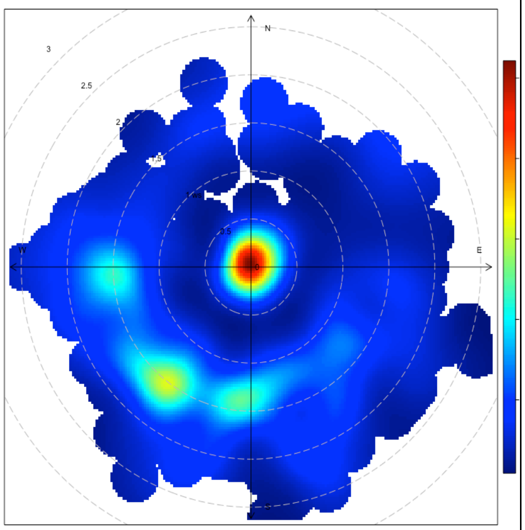
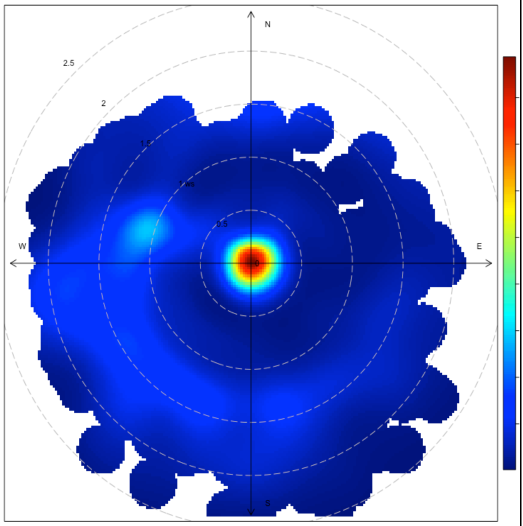
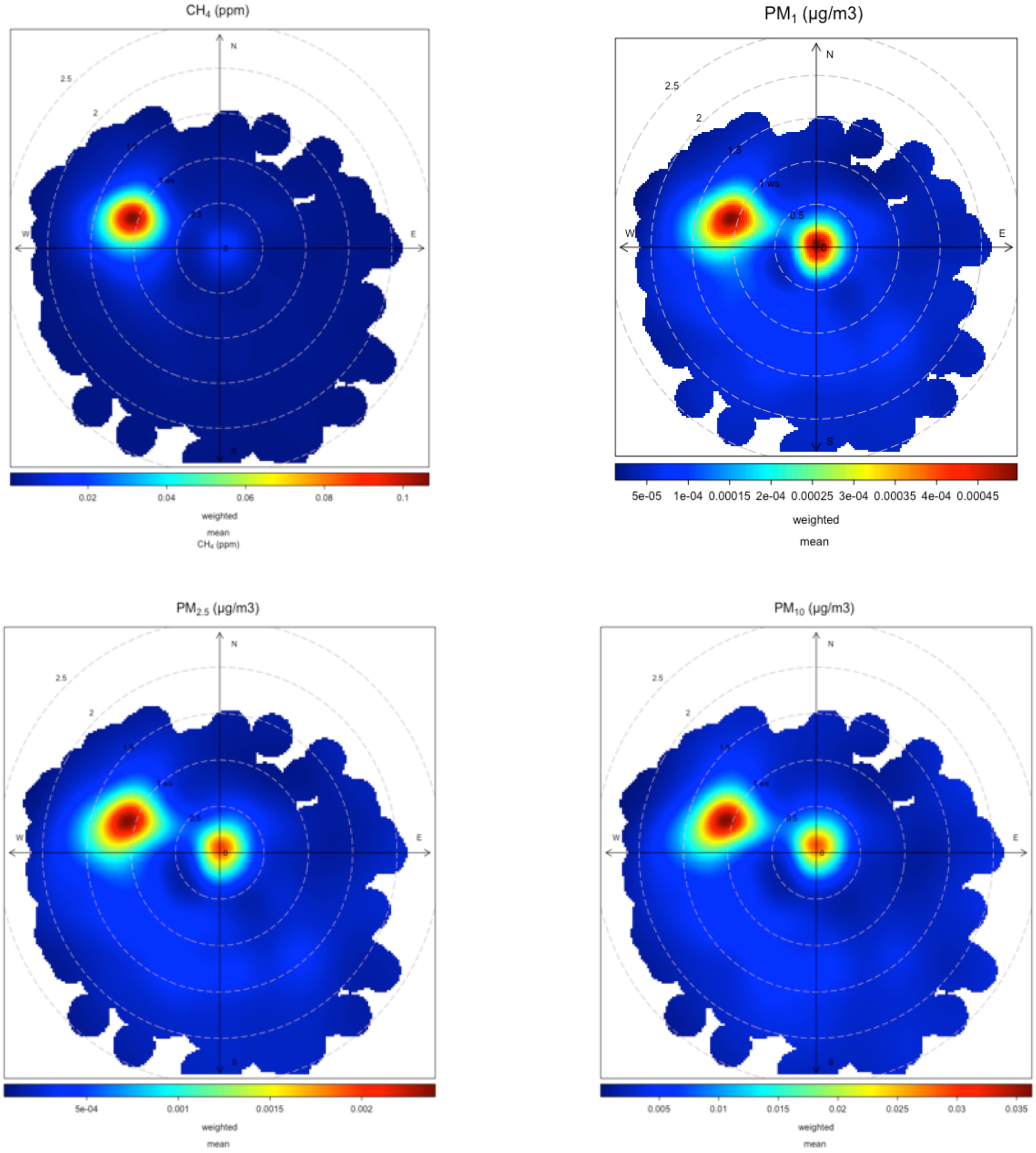


Figure 4.5: Weighted mean polar plot of CH₄ concentrations below 2.24 ppm (Column A) and above or equal to 2.24 ppm (Column B).

	Column A	**Column B**
CH₄ (ppm)	CH$_4$ (ppm) =< 2.24 ppm  	CH$_4$ (ppm) > 2.24 ppm 
CO (ppb)	 	

Column A represents all data and Column B represents only the data collected with CH₄ was greater than 2.3 ppm.
Row 1 represents CO (ppb) from values collected when CH₄ was below 2.3 ppm (column A), and when CH₄ was above 2.3 ppm (column B).
Row 2 represents PM1 (µg/m3) from values collected when CH₄ was below 2.3 ppm (Column A), and when CH₄ was above 2.3 ppm (Column B).

Figure 4.6: Bivariate polar plots using weighted means of all values collected while CH_4 was over 2.3 ppm. Plots are for CH_4, PM_1, $PM_{2.5}$, and PM_{10}.



CH_4 (ppm)

PM_1 (µg/m3)

$PM_{2.5}$ (µg/m3)

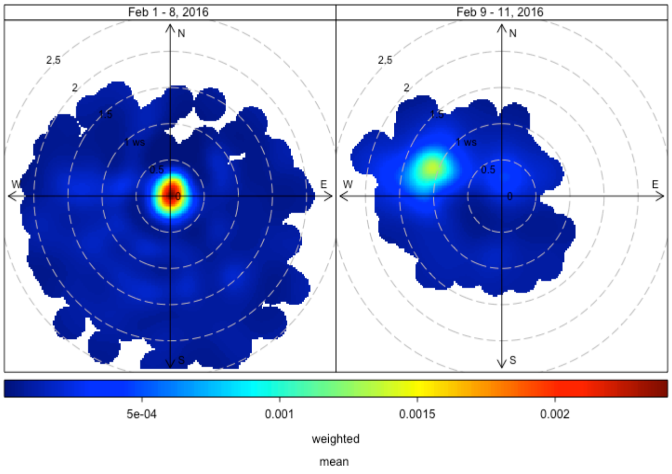
PM_{10} (µg/m3)

Figure 4.7: Timeseries analysis for correlations between PM$_1$, PM$_{2.5}$, PM$_{10}$, and CH$_4$ using a six-hour rolling correlation for all values collected while CH$_4$ was above 2.3 ppm.

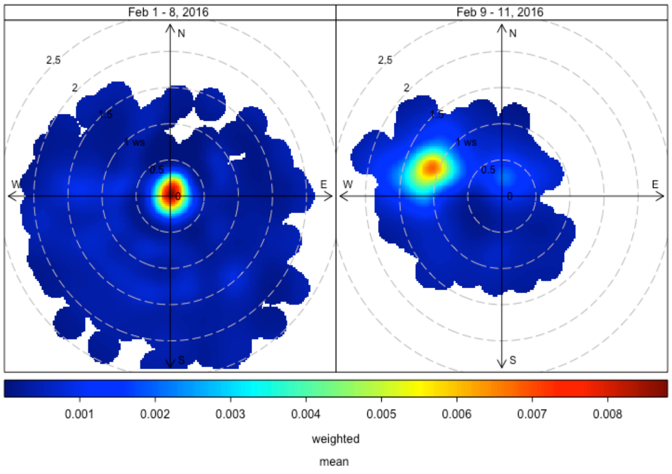
Grey area on the plot indicates no correlations/very weak correlations. Dotted horizontal line indicates (approximate) timeframe for well kill.

Figure 4.8: Polarplots of weighed means for PM_1, $PM_{2.5}$, and PM_{10} for two time periods.

PM_1 (μg/m3)



$PM_{2.5}$ (μg/m3)



PM_{10} (μg/m3)

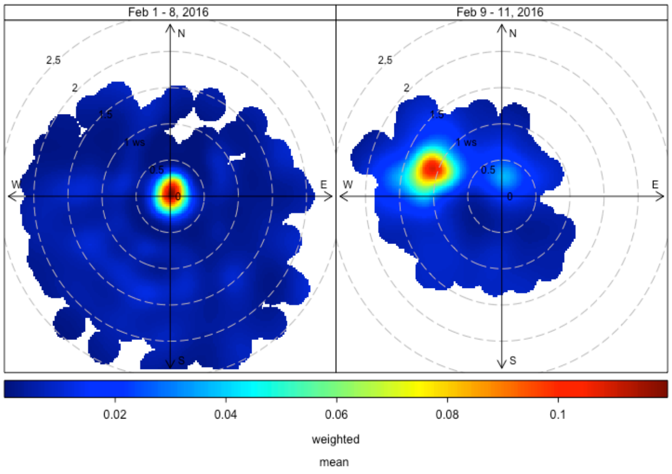
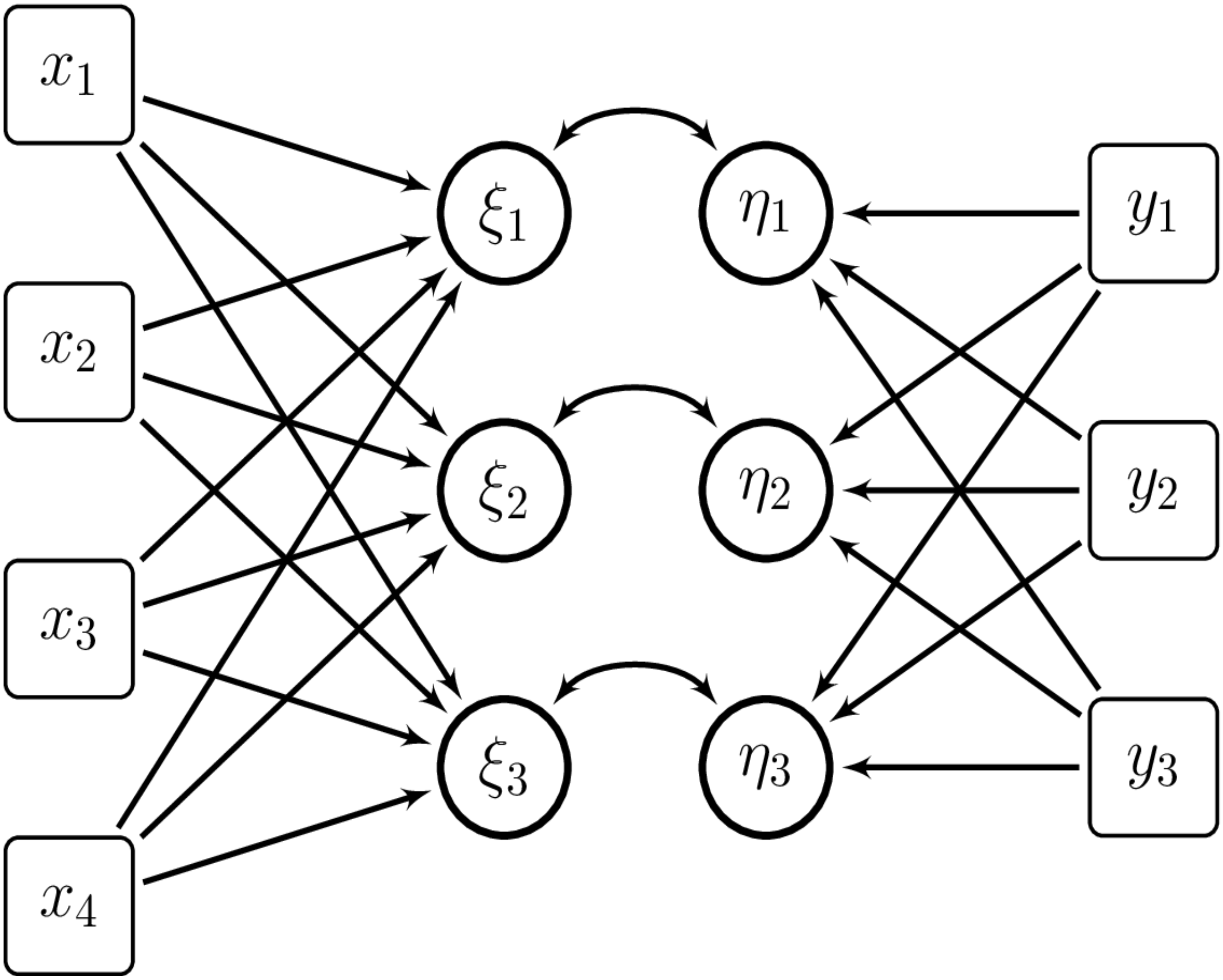


Figure 4.9: Example of a CCA variable design.



The x variables are the inputs (questions) from the survey and the ξ represents the latent variable built from each survey input. The y variables are inputs from the metal fingerprint and provided as a binary variable: detected (1) or not detected (0). The η represents the latent variable built from each metal fingerprint input. The relationship between each ξ and η canonical pair (represented by an arched arrow) describes the canonical correlation. Image borrowed from: http://my.ilstu.edu/~wjschne/444/CanonicalCorrelation.html#(1).

Table 4.1: Mean concentrations of all HAPs analyzed using passive and canister sampling in the Porter Ranch community prior to February 12, 2016.

HAP Names	CAS ID	MATES[a] (ppb)	Mean (ppb)		
			5-Min (canister)	24-Hr (canister)	7-14 Day (passive)
Benzene	71432	0.4	0.39	0.16	0.13
Chloroform	67663	0.04	NA	NA	< 0.46
Ethylbenzene	100414	0.72	0.13	< 0.1	< 0.1
Hexane	110543	NA	0.66	0.28	0.15
Hydrogen sulfide	7783064	NA	NA	NA	< 10*
Methyl chloroform (1,1,1-trichloroethane)	71556	NA	NA	NA	< 0.51
Methyl isobutyl ketone (hexone)	108101	NA	NA	NA	< 0.14
Methyl methacrylate	80626	NA	NA	NA	< 0.21
Methylene chloride (Dichloromethane)	75092	0.32	NA	NA	0.40
Naphthalene	91203	NA	NA	NA	< 1.17
Styrene	100425	0.03	0.13	0.7	< 0.11
Tetrachloroethylene (perchloroethylene)	127184	0.03	NA	NA	0.23
Toluene	108883	1.15	1.04	2.53	0.40
Trichloroethylene	79016	0.02	NA	NA	< 0.29
2,2,4-trimethylpentane	540841	NA	0.13	0.04	NA
m/p-Xylene	108383/106423	2.50	0.20	0.18	NA
o-Xylene	95476	0.52	0.12	0.1	NA
Xylenes (isomers and mixtures)	1330207	NA	NA	NA	< 0.21

[a] The column titled "MATES" is the ambient concentrations of the pollutant at AQMD's Multiple Air Toxics Exposure Study (MATES) fixed site for the 2015 reporting period.

*reported as µg/filter; Non-detects were labeled with a "<" followed by the mean reporting limit concentration; Mean values is inclusive of concentrations over the reporting limit; HAPs not included in the sampling method are marked with "NA"

Table 4.2: Summary statistics and Pearson correlation analyses for 5-min, 1-hr, and 24-hour samples in within the Porter Ranch community collected between December 16, 2015 – February 11, 2016.

	% above LOD	**Mean⁺ (ppb)**	**Pearson's r**	
			CH_4	**Acetylene**
24-Hr Canister Sampling (n = 29)				
Acetylene	100	0.62	0.13	1**
Benzene	79.31	0.16	0.65**	0.67**
Ethylbenzene	0	-	-	-
Ethylene	100	0.51	0.25	0.96**
n-Hexane	44.83	0.28	0.86**	0.02
Styrene	17.24	0.7	0.68*	-0.25
Toluene	51.72	2.53	0.72**	-0.23
2,2,4-trimethylpentane	31.03	0.04	0.32	0.85**
m/p-Xylene	31.03	0.18	0.48	0.68**
o-Xylene	6.9	0.1	0.54*	-0.02
1-Hr Continuous Data (n = 421)				
Benzene	100	0.14	0.93**	NA
5-min "Trigger" Canister Sampling (n = 105)				
Acetylene	96.12	0.47	-0.15	1**
Benzene	89.32	0.39	0.92**	0.1
Ethylbenzene	2.91	0.13	0.62**	-0.01
Ethylene	86.41	0.518	-0.12	0.60**
n-Hexane	92.23	0.66	0.95**	-0.02
Styrene	8.74	0.13	0.17	0.07
Toluene	94.17	1.04	0.51**	-0.19
2,2,4-trimethylpentane	66.02	0.13	0.86**	0.03
m/p-Xylene	74.76	0.20	0.80**	0.29*
o-Xylene	4.85	0.12	0.49**	0.14

⁺ Mean concentrations includes all data found above the sample limit of detection

* p-value less than 0.01; ** p-value less than 0.001

Chapter 5: Conclusions

Results from this work have identified exposure impact zones near oil and natural gas development in both urban and semi-rural environments. Spatial distance investigations suggest measured HAP compounds are discernable from background concentrations less than 220 meters from targeted oil and natural gas facilities during upstream production-phase activities. Additional measurements of various sized particles suggest PM can be measured in ambient air at distances as far as 560 meters from the facility fence line. Similar results from the 2015 Aliso Canyon natural gas storage blowout revealed an impact zone larger than those measured in chapters 2-3. Through indoor dust samples and investigations into the deposition timeline, we found compelling evidence that several HAPs were elevated in the surrounding communities of Porter Ranch during the blowout event, and final attempts to plug the well were associated with emission of particles. Taken together, our results suggest that upstream oil and natural gas development and storage events are associated with emissions of multiple HAP compounds and particles capable of deposition into proximate communities and indoor environments with the potential to increase health risks from exposure.

While we found concentrations of HAP compounds indiscernible from background over 220 meters from upstream oil and natural gas development facilities, concentrations remained elevated at levels higher than in most cities. Correlations between n-pentane and measured HAP compounds suggest that a broad range of pollutants are co-emitted during upstream oil and natural gas development and activities. These co-emissions may increase health risks of exposure if compounds are biologically additive or synergistic, especially in environments with an already high pollutant burden. Single pollutant health-based standards may fail to provide accurate risk estimates, especially for sensitive subpopulations exposure to chronic, low-concentrations of HAP compounds. Furthermore, while we have an adequate understating about constituents of particles near roadways, there is a dearth of scientific literature investigating the constituents of particles from upstream oil and natural gas development and their impact on human health.

Several limitations to the current work merit mention. First, we are still not aware of the full suite of chemicals that may be associated with upstream oil and gas development and storage, thus, our conclusions may underestimate actual impacts; however, the review of the current literature detailed in chapter 1 provides insights into a larger range of possible co-emitted HAP compounds. Second, samples included in the current analysis were measured during a narrow timeframe which may limit interpretability of our conclusions. Third, while we found compelling evidence that several HAPs were elevated in the surrounding communities of Porter Ranch during the blowout event, a complete reconstruction of the likely exposures cannot be achieved with the available data. Lastly, while we found evidence of metal deposition into indoor environments, it is not clear if the actual elevated particle concentrations measured were liquid aerosols directly from the site or emissions from heavy equipment used to plug the well. Hence, these limitations restrict our ability to extrapolate these results into other communities or similar events.

In review of the current results, we recommend several research priorities. First, we recommend additional research on upstream oil and natural gas development exposure impact zones to better understand the relationship between proximity and health impacts, including additional sampling of a broad range of HAP compounds to understand the full suite of chemicals that may be associated with these activities. Furthermore, we recommend facility-specific meteorological data-collection equipment installed at natural gas storage facilities to collect baseline concentrations against which to compare in the event of an accidental release and to monitor whether routine emissions have the potential to harm public health. Finally, we recommend additional research on health impacts from chronic, low-level ambient exposures to multiple HAP pollutants to better characterize exposure risks near upstream oil and natural gas development facilities.

Within the United States, an estimated 18 million people live within 1,600 meters from an active ONG well[5]; of which, 1.7 million individuals live within the Los Angeles Basin[150]. While the number of individuals living near these facilities is cause for concern during routine operations, these risks and zone of impact are potentially exponentiated in the event of an uncontrolled leak or blowout. Approximately 10% of upstream oil and natural gas development facilities are responsible for up to ~40% of the total CH_4 emissions[56] and approximately 20% of active, underground natural gas storage wells, are vulnerable to leaks due to obsolete well designs[181]. In the absence of policies and regulations designed to protect communities located near natural gas development and storage facilities, it is imperative that future research aims to understand the risks associated with exposures stemming from these activities. We hope that the current analysis will help guide policy around developing necessary setback requirements and, thus, minimize potential health risks of populations residing near oil and natural gas operations during both routine and non-routine operations. Adoption of these research priorities will help guide future policy aimed at the implementation of appropriate control measures that will protect human and environmental health and decrease the impacts of the oil and natural gas industry.

References

(1) Doman, L.; Kahan, A. United States Remains the World's Top Producer of Petroleum and Natural Gas Hydrocarbons. *U.S. Energy Information Administration*. May 21, 2018.

(2) U.S. Energy Information Administration. *Short-Term Energy Outlook (STEO), February 2018*; 2018.

(3) Banan, Z.; Gernand, J. M. Evaluation of Gas Well Setback Policy in the Marcellus Shale Region of Pennsylvania in Relation to Emissions of Fine Particulate Matter. *J. Air Waste Manag. Assoc.* **2018**, 1–13.

(4) Haley, M.; McCawley, M.; Epstein, A. C.; Arrington, B.; Bjerke, E. F. Adequacy of Current State Setbacks for Directional High-Volume Hydraulic Fracturing in the Marcellus, Barnett, and Niobrara Shale Plays. *Environ. Health Perspect.* **2016**, *124* (9).

(5) Czolowski, E. D.; Santoro, R. L.; Srebotnjak, T.; Shonkoff, S. B. C. Toward Consistent Methodology to Quantify Populations in Proximity to Oil and Gas Development: A National Spatial Analysis and Review. *Environ. Health Perspect.* **2017**, *125* (8).

(6) United States House of Representatives Committee on Energy and Commerce Minority Staff. *Chemicals Used in Hydraulic Fracturing*; 2011.

(7) US EPA. *Assessment of the Potential Impacts of Hydraulic Fracturing for Oil and Gas on Drinking Water Resources - External Review Draft*; EPA/600/R-15/047a; Office of Research and Development, U.S. Environmental Protection Agency: Washington, D.C., 2015.

(8) NYSDEC. *Final Supplemental Generic Environmental Impact Statement on the Oil, Gas, and Solution Mining Regulatory Program*; New York State Department of Environmental Conservation, 2015.

(9) Colborn, T.; Kwiatkowski, C.; Schultz, K.; Bachran, M. Natural Gas Operations from a Public Health Perspective. *Hum. Ecol. Risk Assess. Int. J.* **2011**, *17* (5), 1039–1056.

(10) Elliott, E. G.; Trinh, P.; Ma, X.; Leaderer, B. P.; Ward, M. H.; Deziel, N. C. Unconventional Oil and Gas Development and Risk of Childhood Leukemia: Assessing the Evidence. *Sci. Total Environ.* **2017**, *576*, 138–147.

(11) Bunch, A.; Perry, C. S.; Abraham, L.; Wikoff, D. S.; Tachovsky, J. A.; Hixon, J. G.; Urban, J. D.; Harris, M. A.; Haws, L. C. Evaluation of Impact of Shale Gas Operations in the Barnett Shale Region on Volatile Organic Compounds in Air and Potential Human Health Risks. *Sci. Total Environ.* **2014**, *468–469*, 832–842.

(12) Helmig, D.; Thompson, C. R.; Evans, J.; Boylan, P.; Hueber, J.; Park, J.-H. Highly Elevated Atmospheric Levels of Volatile Organic Compounds in the Uintah Basin, Utah. *Environ. Sci. Technol.* **2014**, *48* (9), 4707–4715.

(13) Litovitz, A.; Curtright, A.; Abramzon, S.; Burger, N.; Samaras, C. Estimation of Regional Air-Quality Damages from Marcellus Shale Natural Gas Extraction in Pennsylvania. *Environ. Res. Lett.* **2013**, *8* (1), 014017.

(14) McKenzie, L. M.; Witter, R. Z.; Newman, L. S.; Adgate, J. L. Human Health Risk Assessment of Air Emissions from Development of Unconventional Natural Gas Resources. *Sci. Total Environ.* **2012**, *424*, 79–87.

(15) Pétron, G.; Frost, G.; Miller, B. R.; Hirsch, A. I.; Montzka, S. A.; Karion, A.; Trainer, M.; Sweeney, C.; Andrews, A. E.; Miller, L.; et al. Hydrocarbon Emissions Characterization in the Colorado Front Range: A Pilot Study. *J. Geophys. Res. Atmospheres* **2012**, *117* (D4), D04304.

(16) Colborn, T.; Schultz, K.; Herrick, L.; Kwiatkowski, C. An Exploratory Study of Air Quality near Natural Gas Operations. *Hum. Ecol. Risk Assess. Int. J.* **2014**, *20* (1), 86–105.

(17) Gilman, J.; Lerner, B.; Kuster, W.; de Gouw, J. Source Signature of Volatile Organic Compounds from Oil and Natural Gas Operations in Northeastern Colorado. *Environ. Sci. Technol.* **2013**, *47* (3), 1297–1305.

(18) Macey, G.; Breech, R.; Chernaik, M.; Cox, C.; Larson, D.; Thomas, D.; Carpenter, D. O. Air Concentrations of Volatile Compounds near Oil and Gas Production: A Community-Based Exploratory Study. *Environ. Health* **2014**, *13* (1), 82.

(19) US EPA. The Clean Air Act Amendments of 1990 List of Hazardous Air Pollutants http://www.epa.gov/ttn/atw/orig189.html (accessed Aug 22, 2015).

(20) The Endocrine Disruption Exchange. Chemicals in Oil and Gas Operations https://endocrinedisruption.org/audio-and-video/chemical-health-effects-spreadsheets (accessed Feb 11, 2017).

(21) Basu, N.; Bradley, M.; McFeely, C.; Perkins, M. *Hydraulic Fracturing in the State of Michigan - Public Health Technical Report*; 5; University of Michigan, 2013.

(22) Brown, D.; Weinberger, B.; Lewis, C.; Bonaparte, H. Understanding Exposure from Natural Gas Drilling Puts Current Air Standards to the Test. *Rev. Environ. Health* **2014**, *29* (4), 277–292.

(23) Field, R. A.; Soltis, J.; Murphy, S. Air Quality Concerns of Unconventional Oil and Natural Gas Production. *Environ. Sci. Process. Impacts* **2014**, *16* (5), 954–969.

(24) Goetz, J. D.; Floerchinger, C.; Fortner, E. C.; Wormhoudt, J.; Massoli, P.; Knighton, W. B.; Herndon, S. C.; Kolb, C. E.; Knipping, E.; Shaw, S. L.; et al. Atmospheric Emission Characterization of Marcellus Shale Natural Gas Development Sites. *Environ. Sci. Technol.* **2015**, *49* (11), 7012–7020.

(25) Moore, C. W.; Zielinska, B.; Pétron, G.; Jackson, R. B. Air Impacts of Increased Natural Gas Acquisition, Processing, and Use: A Critical Review. *Environ. Sci. Technol.* **2014**, *48* (15), 8349–8359.

(26) Srebotnjak, T.; Rotkin-Ellman, M. *Fracking Fumes: Air Pollution from Hydraulic Fracturing Threatens Public Health and Communities*; Natural Resources Defense Council, 2014.

(27) Webb, E.; Bushkin-Bedient, S.; Cheng, A.; Kassotis, C. D.; Balise, V.; Nagel, S. C. Developmental and Reproductive Effects of Chemicals Associated with Unconventional Oil and Natural Gas Operations. *Rev. Environ. Health* **2014**, *29* (4), 307–318.

(28) PSE Healthy Energy. Repository for Oil and Gas Energy Research (ROGER) https://www.psehealthyenergy.org/our-work/shale-gas-research-library/.

(29) Annevelink, M. P. J. A.; Meesters, J. A. J.; Hendriks, A. J. Environmental Contamination Due to Shale Gas Development. *Sci. Total Environ.* **2016**, *550*, 431–438.

(30) Brantley, H. L.; Thoma, E. D.; Eisele, A. P. Assessment of Volatile Organic Compound and Hazardous Air Pollutant Emissions from Oil and Natural Gas Well Pads Using Mobile Remote and On-Site Direct Measurements. *J. Air Waste Manag. Assoc.* **2015**, *65* (9), 1072–1082.

(31) Esswein, E.; Snawder, J.; King, B.; Breitenstein, M.; Alexander-Scott, M.; Kiefer, M. Evaluation of Some Potential Chemical Exposure Risks during Flowback Operations in Unconventional Oil and Gas Extraction: Preliminary Results. *J. Occup. Environ. Hyg.* **2014**, *11* (10), D174-184.

(32) Hildenbrand, Z. L.; Carlton, D. D.; Fontenot, B. E.; Meik, J. M.; Walton, J. L.; Taylor, J. T.; Thacker, J. B.; Korlie, S.; Shelor, C. P.; Henderson, D.; et al. A Comprehensive Analysis of Groundwater Quality in The Barnett Shale Region. *Environ. Sci. Technol.* **2015**, *49* (13), 8254–8262.

(33) Rich, A.; Grover, J. P.; Sattler, M. L. An Exploratory Study of Air Emissions Associated with Shale Gas Development and Production in the Barnett Shale. *J. Air Waste Manag. Assoc.* **2014**, *64* (1), 61–72.

(34) Abeleira, A.; Pollack, I. B.; Sive, B.; Zhou, Y.; Fischer, E. V.; Farmer, D. K. Source Characterization of Volatile Organic Compounds in the Colorado Northern Front Range Metropolitan Area during Spring and Summer 2015. *J. Geophys. Res.-Atmospheres* **2017**, *122* (6), 3595–3613.

(35) Field, R.; Soltis, J.; McCarthy, M.; Murphy, S.; Montague, D. Influence of Oil and Gas Field Operations on Spatial and Temporal Distributions of Atmospheric Non-Methane Hydrocarbons and Their Effect on Ozone Formation in Winter. *Atmospheric Chem. Phys.* **2015**, *15* (6), 3527–3542.

(36) Zielinska, B.; Campbell, D.; Samburova, V. Impact of Emissions from Natural Gas Production Facilities on Ambient Air Quality in the Barnett Shale Area: A Pilot Study. *J. Air Waste Manag. Assoc.* **2014**, *64* (12), 1369–1383.

(37) Field, R. A.; Soltis, J. J.; Perez-Ballesta, P.; Grandesso, E.; Montague, D. C. Distributions of Air Pollutants Associated with Oil and Natural Gas Development Measured in the Upper Green River Basin of Wyoming. *Elem.-Sci. Anthr.* **2015**, *3*, 1–14.

(38) Ghosh, B. Impact of Changes in Oil and Gas Production Activities on Air Quality in Northeastern Oklahoma: Ambient Air Studies in 2015-2017. *Environ. Sci. Technol.* **2018**, *52* (5), 3285–3294.

(39) Goetz, J. D.; Avery, A.; Werden, B.; Floerchinger, C.; Fortner, E. C.; Wormhoudt, J.; Massoli, P.; Herndon, S. C.; Kolb, C. E.; Knighton, W. B.; et al. Analysis of Local-Scale Background Concentrations of Methane and Other Gas-Phase Species in the Marcellus Shale. *Elem.-Sci. Anthr.* **2017**, *5*, 1–20.

(40) Halliday, H. S.; Thompson, A. M.; Wisthaler, A.; Blake, D. R.; Hornbrook, R. S.; Mikoviny, T.; Mueller, M.; Eichler, P.; Apel, E. C.; Hills, A. J. Atmospheric Benzene Observations from Oil and Gas Production in the Denver-Julesburg Basin in July and August 2014. *J. Geophys. Res.-Atmospheres* **2016**, *121* (18), 11055–11074.

(41) Paulik, L. B.; Donald, C. E.; Smith, B. W.; Tidwell, L. G.; Hobbie, K. A.; Kincl, L.; Haynes, E. N.; Anderson, K. A. Emissions of Polycyclic Aromatic Hydrocarbons from Natural Gas Extraction into Air. *Environ. Sci. Technol.* **2016**, *50* (14), 7921–7929.

(42) Swarthout, R. F.; Russo, R. S.; Zhou, Y.; Miller, B. M.; Mitchell, B.; Horsman, E.; Lipsky, E.; McCabe, D. C.; Baum, E.; Sive, B. C. Impact of Marcellus Shale Natural Gas Development in Southwest Pennsylvania on Volatile Organic Compound Emissions and Regional Air Quality. *Environ. Sci. Technol.* **2015**, *49* (5), 3175–3184.

(43) Caulton, D. R.; Shepson, P. B.; Santoro, R. L.; Sparks, J. P.; Howarth, R. W.; Ingraffea, A. R.; Cambaliza, M. O. L.; Sweeney, C.; Karion, A.; Davis, K. J.; et al. Toward a Better Understanding and Quantification of Methane Emissions from Shale Gas Development. *Proc. Natl. Acad. Sci.* **2014**, *111* (17), 6237–6242.

(44) Brown, D.; Lewis, C.; Weinberger, B. Human Exposure to Unconventional Natural Gas Development: A Public Health Demonstration of Periodic High Exposure to Chemical Mixtures in Ambient Air. *J. Environ. Sci. Health Part A* **2015**, *50* (5), 460–472.

(45) Bloomdahl, R.; Abualfaraj, N.; Olson, M.; Gurian, P. L. Assessing Worker Exposure to Inhaled Volatile Organic Compounds from Marcellus Shale Flowback Pits. *J. Nat. Gas Sci. Eng.* **2014**, *21*, 348–356.

(46) Maskrey, J. R.; Insley, A. L.; Hynds, E. S.; Panko, J. M. Air Monitoring of Volatile Organic Compounds at Relevant Receptors during Hydraulic Fracturing Operations in Washington County, Pennsylvania. *Environ. Monit. Assess.* **2016**, *188* (7).

(47) Ho, K. F.; Lee, S. C.; Ho, W. K.; Blake, D. R.; Cheng, Y.; Li, Y. S.; Ho, S. S. H.; Fung, K.; Louie, P. K. K.; Park, D. Vehicular Emission of Volatile Organic Compounds (VOCs) from a Tunnel Study in Hong Kong. *Atmospheric Chem. Phys.* **2009**, *9* (19), 7491–7504.

(48) Swarthout, R. F.; Russo, R. S.; Zhou, Y.; Hart, A. H.; Sive, B. C. Volatile Organic Compound Distributions during the NACHTT Campaign at the Boulder Atmospheric Observatory: Influence of Urban and Natural Gas Sources. *J. Geophys. Res. Atmospheres* **2013**, *118* (18), 10,614-10,637.

(49) Warneke, C.; Geiger, F.; Edwards, P. M.; Dube, W.; Pétron, G.; Kofler, J.; Zahn, A.; Brown, S. S.; Graus, M.; Gilman, J.; et al. Volatile Organic Compound Emissions from the Oil and Natural Gas Industry in the Uinta Basin, Utah: Point Sources Compared to Ambient Air Composition. *Atmos Chem Phys Discuss* **2014**, *14* (8), 11895–11927.

(50) Eapi, G. R.; Sabnis, M. S.; Sattler, M. L. Mobile Measurement of Methane and Hydrogen Sulfide at Natural Gas Production Site Fence Lines in the Texas Barnett Shale. *J. Air Waste Manag. Assoc.* **2014**, *64* (8), 927–944.

(51) Lan, X.; Talbot, R.; Laine, P.; Torres, A.; Lefer, B.; Flynn, J. Atmospheric Mercury in the Barnett Shale Area, Texas: Implications for Emissions from Oil and Gas Processing. *Environ. Sci. Technol.* **2015**, *49* (17), 10692–10700.

(52) Marrero, J. E.; Townsend-Small, A.; Lyon, D. R.; Tsai, T. R.; Meinardi, S.; Blake, D. R. Estimating Emissions of Toxic Hydrocarbons from Natural Gas Production Sites in the Barnett Shale Region of Northern Texas. *Environ. Sci. Technol.* **2016**, *50* (19), 10756–10764.

(53) Zavala-Araiza, D.; Alvarez, R. A.; Lyon, D. R.; Allen, D. T.; Marchese, A. J.; Zimmerle, D. J.; Hamburg, S. P. Super-Emitters in Natural Gas Infrastructure Are Caused by Abnormal Process Conditions. *Nat. Commun.* **2017**, *8*, 14012.

(54) Hildenbrand, Z. L.; Mach, P. M.; McBride, E. M.; Dorreyatim, M. N.; Taylor, J. T.; Carlton, D. D.; Meik, J. M.; Fontenot, B. E.; Wright, K. C.; Schug, K. A.; et al. Point Source Attribution of Ambient Contamination Events near Unconventional Oil and Gas Development. *Sci. Total Environ.* **2016**, *573*, 382–388.

(55) Conley, S.; Franco, G.; Faloona, I.; Blake, D. R.; Peischl, J.; Ryerson, T. B. Methane Emissions from the 2015 Aliso Canyon Blowout in Los Angeles, CA. *Science* **2016**, *351* (6279), 1317–1320.

(56) Yuan, B.; Kaser, L.; Karl, T.; Graus, M.; Peischl, J.; Campos, T. L.; Shertz, S.; Apel, E. C.; Hornbrook, R. S.; Hills, A.; et al. Airborne Flux Measurements of Methane and Volatile Organic Compounds over the Haynesville and Marcellus Shale Gas Production Regions. *J. Geophys. Res.-Atmospheres* **2015**, *120* (12), 6271–6289.

(57) Ethridge, S.; Bredfeldt, T.; Sheedy, K.; Shirley, S.; Lopez, G.; Honeycutt, M. The Barnett Shale: From Problem Formulation to Risk Management. *J. Unconv. Oil Gas Resour.* **2015**, *11*, 95–110.

(58) Li, R.; Warneke, C.; Graus, M.; Field, R.; Geiger, F.; Veres, P. R.; Soltis, J.; Li, S.-M.; Murphy, S. M.; Sweeney, C.; et al. Measurements of Hydrogen Sulfide (H2S) Using PTR-MS: Calibration, Humidity Dependence, Inter-Comparison and Results from Field Studies in an Oil and Gas Production Region. *Atmospheric Meas. Tech.* **2014**, *7* (10), 3597–3610.

(59) Harrison, R. J.; Retzer, K.; Kosnett, M. J.; Hodgson, M.; Jordan, T.; Ridl, S.; Kiefer, M. Sudden Deaths among Oil and Gas Extraction Workers Resulting from Oxygen Deficiency and Inhalation of Hydrocarbon Gases and Vapors — United States, January 2010–March 2015. *MMWR Morb. Mortal. Wkly. Rep.* **2016**, *65* (1), 6–9.

(60) Lyon, D. R.; Alvarez, R. A.; Zavala-Araiza, D.; Brandt, A. R.; Jackson, R. B.; Hamburg, S. P. Aerial Surveys of Elevated Hydrocarbon Emissions from Oil and Gas Production Sites. *Environ. Sci. Technol.* **2016**, *50* (9), 4877–4886.

(61) Wilbur, S.; Bosch, S. *Interaction Profile for Benzene, Toluene, Ethylbenzene, and Xylenes (BTEX)*; 2004.

(62) Baker, A. K.; Beyersdorf, A. J.; Doezema, L. A.; Katzenstein, A.; Meinardi, S.; Simpson, I. J.; Blake, D. R.; Sherwood Rowland, F. Measurements of Nonmethane Hydrocarbons in 28 United States Cities. *Atmos. Environ.* **2008**, *42* (1), 170–182.

(63) Eisele, A. P.; Mukerjee, S.; Smith, L. A.; Thoma, E. D.; Whitaker, D. A.; Oliver, K. D.; Wu, T.; Colon, M.; Alston, L.; Cousett, T. A.; et al. Volatile Organic Compounds at Two Oil and Natural Gas Production Well Pads in Colorado and Texas Using Passive Samplers. *J. Air Waste Manag. Assoc.* **2016**, *66* (4), 412–419.

(64) Rich, A. L.; Orimoloye, H. T. Elevated Atmospheric Levels of Benzene and Benzene-Related Compounds from Unconventional Shale Extraction and Processing: Human Health Concern for Residential Communities. *Environ. Health Insights* **2016**, *10*, 75–82.

(65) Thompson, C. R.; Hueber, J.; Helmig, D. Influence of Oil and Gas Emissions on Ambient Atmospheric Non-Methane Hydrocarbons in Residential Areas of Northeastern Colorado. *Elem. Sci. Anthr.* **2014**, *2*, 000035.

(66) Collins, J. F. *Benzene Reference Exposure Levels: Technical Support Document for the Derivation of Noncancer Reference Exposure Levels (Appendix D1)*; Office of Environmental Health Hazard Assessment, 2014.

(67) Lan, Q. Hematotoxicity in Workers Exposed to Low Levels of Benzene. *Science* **2004**, *306* (5702), 1774–1776.

(68) Xing, C.; Marchetti, F.; Li, G.; Weldon, R. H.; Kurtovich, E.; Young, S.; Schmid, T. E.; Zhang, L.; Rappaport, S.; Waidyanatha, S.; et al. Benzene Exposure near the U.S. Permissible Limit Is Associated with Sperm Aneuploidy. *Environ. Health Perspect.* **2010**, *118* (6), 833–839.

(69) Marchetti, F.; Eskenazi, B.; Weldon, R. H.; Li, G.; Zhang, L.; Rappaport, S. M.; Schmid, T. E.; Xing, C.; Kurtovich, E.; Wyrobek, A. J. Occupational Exposure to Benzene and Chromosomal Structural Aberrations in the Sperm of Chinese Men. *Environ. Health Perspect.* **2012**, *120* (2), 229–234.

(70) Koh, D.-H.; Jeon, H.-K.; Lee, S.-G.; Ryu, H.-W. The Relationship between Low-Level Benzene Exposure and Blood Cell Counts in Korean Workers. *Occup. Environ. Med.* **2015**, *72* (6), 421–427.

(71) Lupo, P. J.; Symanski, E.; Waller, D. K.; Chan, W.; Langlois, P. H.; Canfield, M. A.; Mitchell, L. E. Maternal Exposure to Ambient Levels of Benzene and Neural Tube Defects among Offspring: Texas, 1999–2004. *Environ. Health Perspect.* **2010**, *119* (3), 397–402.

(72) Llop, S.; Ballester, F.; Estarlich, M.; Esplugues, A.; Rebagliato, M.; Iñiguez, C. Preterm Birth and Exposure to Air Pollutants during Pregnancy. *Environ. Res.* **2010**, *110* (8), 778–785.

(73) Zahran, S.; Weiler, S.; Mielke, H. W.; Pena, A. A. Maternal Benzene Exposure and Low Birth Weight Risk in the United States: A Natural Experiment in Gasoline Reformulation. *Environ. Res.* **2012**, *112*, 139–146.

(74) Ghosh, J. K. C.; Wilhelm, M.; Su, J.; Goldberg, D.; Cockburn, M.; Jerrett, M.; Ritz, B. Assessing the Influence of Traffic-Related Air Pollution on Risk of Term Low Birth Weight on the Basis of Land-Use-Based Regression Models and Measures of Air Toxics. *Am. J. Epidemiol.* **2012**, *175* (12), 1262–1274.

(75) Aguilera, I.; Guxens, M.; Garcia-Esteban, R.; Corbella, T.; Nieuwenhuijsen, M. J.; Foradada, C. M.; Sunyer, J. Association between GIS-Based Exposure to Urban Air Pollution during Pregnancy and Birth Weight in the INMA Sabadell Cohort. *Environ. Health Perspect.* **2009**, *117* (8), 1322–7.

(76) Aguilera, I.; Garcia-Esteban, R.; Iñiguez, C.; Nieuwenhuijsen, M. J.; Rodríguez, À.; Paez, M.; Ballester, F.; Sunyer, J. Prenatal Exposure to Traffic-Related Air Pollution and Ultrasound Measures of Fetal Growth in the INMA Sabadell Cohort. *Environ. Health Perspect.* **2010**, *118* (5), 705–711.

(77) Zhou, C.; Baïz, N.; Banerjee, S.; Charpin, D. A.; Caillaud, D.; de Blay, F.; Raherison, C.; Lavaud, F.; Annesi-Maesano, I. The Relationships between Ambient Air Pollutants and Childhood Asthma and Eczema Are Modified by Emotion and Conduct Problems. *Ann. Epidemiol.* **2013**, *23* (12), 778-783.e3.

(78) Arif, A. A.; Shah, S. M. Association between Personal Exposure to Volatile Organic Compounds and Asthma among US Adult Population. *Int. Arch. Occup. Environ. Health* **2007**, *80* (8), 711–719.

(79) Delfino, R. J.; Gong, H.; Linn, W. S.; Pellizzari, E. D.; Hu, Y. Asthma Symptoms in Hispanic Children and Daily Ambient Exposures to Toxic and Criteria Air Pollutants. *Environ. Health Perspect.* **2002**, *111* (4), 647–656.

(80) Penard-Morand, C.; Raherison, C.; Charpin, D.; Kopferschmitt, C.; Lavaud, F.; Caillaud, D.; Annesi-maesano, I. Long-Term Exposure to Close-Proximity Air Pollution and Asthma and Allergies in Urban Children. *Eur. Respir. J.* **2010**, *36* (1), 33–40.

(81) World Health Organization. *Air Quality Guidelines for Europe*; World Health Organization, 2000.

(82) OEHHA. *Appendix D. Individual Acute, 8-Hour, and Chronic Reference Exposure Level Summaries*; The Office of Environmental Health Hazard Assessment, 2014.

(83) Agency for Toxic Substances and Disease Registry (ATSDR). *Toxicological Profile for Formaldehyde*; U.S. Department of Health and Human Services: Atlanta, GA, 1999.

(84) Chen, H.; Carter, K. E. Modeling Potential Occupational Inhalation Exposures and Associated Risks of Toxic Organics from Chemical Storage Tanks Used in Hydraulic Fracturing Using AERMOD. *Environ. Pollut.* **2017**, *224*, 300–309.

(85) Agency for Toxic Substances and Disease Registry (ATSDR). *Toxicological Profile for Hydrogen Sulfide and Carbonyl Sulfide*; U.S. Public Health Service, U.S. Department of Health and Human Services: Atlanta, GA, 2016.

(86) OEHHA. *Appendix D.3 Chronic RELs and Toxicity Summaries Using the Previous Version of the Hot Spots Risk Assessment Guidelines (OEHHA 1999)*; The Office of Environmental Health Hazard Assessment, 2000.

(87) Centers for Disease Control and Prevention. NIOSH pocket guide to chemical hazards https://www.cdc.gov/niosh/npg/npgd0337.html.

(88) Morello-Frosch, R. A.; Woodruff, T. J.; Axelrad, D. A.; Caldwell, J. C. Air Toxics and Health Risks in California: The Public Health Implications of Outdoor Concentrations. *Risk Anal.* **2000**, *20* (2), 273–292.

(89) McCarthy, M. C.; O'Brien, T. E.; Charrier, J. G.; Hafner, H. R. Characterization of the Chronic Risk and Hazard of Hazardous Air Pollutants in the United States Using Ambient Monitoring Data. *Environ. Health Perspect.* **2009**, *117* (5), 790–796.

(90) Woodruff, T.; Axelrod, D.; Cadwell, J.; Morello-Frosch, R.; Rosenbaum, A. Public Health Implications of 1990 Air Toxics Concentrations across the United States. *Environ. Health Perspect.* **1998**, *106* (5), 245–251.

(91) Tam, B. N.; Neumann, C. M. A Human Health Assessment of Hazardous Air Pollutants in Portland, OR. *J. Environ. Manage.* **2004**, *73* (2), 131–145.

(92) Air Resource Board. *Acrolein Research Project – Contract 00-721 Draft Report*; Planning and Technical Support Division, 2005.

(93) Goelen, E.; Lambrechts, M.; Geyskens, F. Sampling Intercomparisons for Aldehydes in Simulated Workplace Air. *Analyst* **1997**, *122* (5), 411–419.

(94) Ho, S. S. H.; Ho, K. F.; Liu, W. D.; Lee, S. C.; Dai, W. T.; Cao, J. J.; Ip, H. S. S. Unsuitability of Using the DNPH-Coated Solid Sorbent Cartridge for

Determination of Airborne Unsaturated Carbonyls. *Atmos. Environ.* **2011**, *45* (1), 261–265.

(95) Herrington, J. S.; Hays, M. D. Concerns Regarding 24-h Sampling for Formaldehyde, Acetaldehyde, and Acrolein Using 2,4-Dinitrophenylhydrazine (DNPH)-Coated Solid Sorbents. *Atmos. Environ.* **2012**, *55*, 179–184.

(96) Agency for Toxic Substances and Disease Registry (ATSDR). *Toxicological Profile for Acrolein*; U.S. Department of Health and Human Services: Atlanta, GA, 2007.

(97) Leighton Consulting. *Summary Report Time Critical Residential Indoor Environmental Sampling Aliso Canyon Natural Gas Incident Porter Ranch Community*; 603287.048; County of Los Angeles Department of Public and Environmental Health: Irvine, CA, 2016.

(98) Shonkoff, S.; Hill, L.; Czolowski, E.; Prasad, K.; Hammond, S.; McKone, T. *Human Health Hazards, Risks, and Impacts Associated with Underground Natural Gas Storage in California*; Long-Term Viability of Underground Gas Storage in California. California Council on Science and Technology; California Council on Science and Technology: Sacramento, CA, 2017.

(99) Casey, J. A.; Savitz, D. A.; Rasmussen, S. G.; Ogburn, E. L.; Pollak, J.; Mercer, D. G.; Schwartz, B. S. Unconventional Natural Gas Development and Birth Outcomes in Pennsylvania, USA. *Epidemiology* **2016**, *27* (2), 163–172.

(100) Currie, J.; Deutch, J.; Greenstone, M.; Meckel, K. The Impact of the Fracking Boom on Infant Health: Evidence from Detailed Location Data on Wells and Infants; 2014.

(101) Hill, E. Three Essays on the Impact of Unconventional Drilling on Early Life Health. PhD, Cornell University, Charles Dyson School Applied Economics and Management: Ithaca, NY, 2015.

(102) Stacy, S. L.; Brink, L. L.; Larkin, J. C.; Sadovsky, Y.; Goldstein, B. D.; Pitt, B. R.; Talbott, E. O. Perinatal Outcomes and Unconventional Natural Gas Operations in Southwest Pennsylvania. *PLoS ONE* **2015**, *10* (6), e0126425.

(103) Casey, J. A.; Ogburn, E. L.; Rasmussen, S. G.; Irving, J. K.; Pollak, J.; Locke, P. A.; Schwartz, B. S. Predictors of Indoor Radon Concentrations in Pennsylvania, 1989-2013. *Environ. Health Perspect.* **2015**, *123* (11), 1130–1137.

(104) Steinzor, N.; Subra, W.; Sumi, L. Investigating Links between Shale Gas Development and Health Impacts through a Community Survey Project in Pennsylvania. *New Solut. J. Environ. Occup. Health Policy NS* **2013**, *23* (1), 55–83.

(105) McKenzie, L. M.; Blair, B.; Hughes, J.; Allshouse, W. B.; Blake, N. J.; Helmig, D.; Milmoe, P.; Halliday, H.; Blake, D. R.; Adgate, J. L. Ambient Nonmethane Hydrocarbon Levels along Colorado's Northern Front Range: Acute and Chronic Health Risks. *Environ. Sci. Technol.* **2018**, *52* (8), 4514–4525.

(106) Pekney, N. J.; Veloski, G.; Reeder, M.; Tamilia, J.; Rupp, E.; Wetzel, A. Measurement of Atmospheric Pollutants Associated with Oil and Natural Gas Exploration and Production Activity in Pennsylvania's Allegheny National Forest. *J. Air Waste Manag. Assoc.* **2014**, *64* (9), 1062–1072.

(107) Schade, G. W.; Roest, G. Analysis of Non-Methane Hydrocarbon Data from a Monitoring Station Affected by Oil and Gas Development in the Eagle Ford Shale, Texas. *Elem. Sci. Anthr.* **2016**, *4*, 000096.

(108) Collier-Oxandale, A.; Hannigan, M. P.; Casey, J. G.; Piedrahita, R.; Ortega, J.; Halliday, H.; Johnston, J. Assessing a Low-Cost Methane Sensor Quantification System for Use in Complex Rural and Urban Environments. *Atmospheric Meas. Tech. Discuss.* **2018**, 1–35.

(109) Butler, K.; Tayour, C.; Batikian, C.; Bane, M.; Rhoades, E.; Masis, E.; Rangan, C.; Williams, T.; Blackwell, S.; De Rosa, C.; et al. *Public Health and Safety Risks of Oil and Gas Facilities in Los Angeles County*; Los Angeles County Department of Public Health: Los Angeles, CA, 2018.

(110) Bogacki, M.; Macuda, J. The Influence of Shale Rock Fracturing Equipment Operation on Atmospheric Air Quality. *Arch. Min. Sci.* **2014**, *59* (4), 897–912.

(111) COGCC. Colorado Oil and Gas Conservation Commission http://cogcc.state.co.us/data4.html#/production.

(112) Esswein, E.; Breitenstein, M.; Snawder, J.; Kiefer, M.; Sieber, W. K. Occupational Exposures to Respirable Crystalline Silica During Hydraulic Fracturing. *J. Occup. Environ. Hyg.* **2013**, *10* (7), 347–356.

(113) Jemielita, T.; Gerton, G. L.; Neidell, M.; Chillrud, S.; Yan, B.; Stute, M.; Howarth, M.; Saberi, P.; Fausti, N.; Penning, T. M.; et al. Unconventional Gas and Oil Drilling Is Associated with Increased Hospital Utilization Rates. *PLOS ONE* **2015**, *10* (7), e0131093.

(114) McKenzie, L. M.; Allshouse, W. B.; Byers, T. E.; Bedrick, E. J.; Serdar, B.; Adgate, J. L. Childhood Hematologic Cancer and Residential Proximity to Oil and Gas Development. *PLOS ONE* **2017**, *12* (2), e0170423.

(115) McKenzie, L. M.; Guo, R.; Witter, R. Z.; Savitz, D. A.; Newman, L. S.; Adgate, J. L. Birth Outcomes and Maternal Residential Proximity to Natural Gas Development in Rural Colorado. *Environ. Health Perspect.* **2014**.

(116) Osborn, S. G.; Vengosh, A.; Warner, N. R.; Jackson, R. B. Methane Contamination of Drinking Water Accompanying Gas-Well Drilling and Hydraulic Fracturing. *Proc. Natl. Acad. Sci.* **2011**, *108* (20), 8172–8176.

(117) Rabinowitz, P. M.; Slizovskiy, I. B.; Lamers, V.; Trufan, S. J.; Holford, T. R.; Dziura, J. D.; Peduzzi, P. N.; Kane, M. J.; Reif, J. S.; Weiss, T. R.; et al. Proximity to Natural Gas Wells and Reported Health Status: Results of a Household Survey in Washington County, Pennsylvania. *Environ. Health Perspect.* **2014**.

(118) Stringfellow, W. T.; Domen, J. K.; Camarillo, M. K.; Sandelin, W. L.; Borglin, S. Physical, Chemical, and Biological Characteristics of Compounds Used in Hydraulic Fracturing. *J. Hazard. Mater.* **2014**, *275*, 37–54.

(119) Tustin, A. W.; Hirsch, A. G.; Rasmussen, S. G.; Casey, J. A.; Bandeen-Roche, K.; Schwartz, B. S. Associations between Unconventional Natural Gas Development and Nasal and Sinus, Migraine Headache, and Fatigue Symptoms in Pennsylvania. *Environ. Health Perspect.* **2016**, *125* (2).

(120) Meng, Q.; Ashby, S. Distance: A Critical Aspect for Environmental Impact Assessment of Hydraulic Fracking. *Extr. Ind. Soc.* **2014**, *1* (2), 124–126.

(121) Beckerman, B.; Jerrett, M.; Brook, J. R.; Verma, D. K.; Arain, M. A.; Finkelstein, M. M. Correlation of Nitrogen Dioxide with Other Traffic Pollutants near a Major Expressway. *Atmos. Environ.* **2008**, *42* (2), 275–290.

(122) Barzyk, T. M.; George, B. J.; Vette, A. F.; Williams, R. W.; Croghan, C. W.; Stevens, C. D. Development of a Distance-to-Roadway Proximity Metric to Compare near-Road Pollutant Levels to a Central Site Monitor. *Atmos. Environ.* **2009**, *43* (4), 787–797.

(123) Baldauf, R.; Thoma, E.; Hays, M.; Shores, R.; Kinsey, J.; Gullett, B.; Kimbrough, S.; Isakov, V.; Long, T.; Snow, R.; et al. Traffic and Meteorological Impacts on Near-Road Air Quality: Summary of Methods and Trends from the Raleigh Near-Road Study. *J. Air Waste Manag. Assoc.* **2008**, *58* (7), 865–878.

(124) Hagler, G. S. W.; Baldauf, R. W.; Thoma, E. D.; Long, T. R.; Snow, R. F.; Kinsey, J. S.; Oudejans, L.; Gullett, B. K. Ultrafine Particles near a Major Roadway in Raleigh, North Carolina: Downwind Attenuation and Correlation with Traffic-Related Pollutants. *Atmos. Environ.* **2009**, *43* (6), 1229–1234.

(125) Hu, S.; Fruin, S.; Kozawa, K.; Mara, S.; Paulson, S. E.; Winer, A. M. A Wide Area of Air Pollutant Impact Downwind of a Freeway during Pre-Sunrise Hours. *Atmos. Environ.* **2009**, *43* (16), 2541–2549.

(126) Kittelson, D. B.; Watts, W. F.; Johnson, J. P. Nanoparticle Emissions on Minnesota Highways. *Atmos. Environ.* **2004**, *38* (1), 9–19.

(127) Zhou, Y.; Levy, J. I. Factors Influencing the Spatial Extent of Mobile Source Air Pollution Impacts: A Meta-Analysis. *BMC Public Health* **2007**, *7* (1).

(128) Zhu, Y.; Hinds, W. C.; Shen, S.; Sioutas, C. Seasonal Trends of Concentration and Size Distribution of Ultrafine Particles Near Major Highways in Los Angeles Special Issue of “Aerosol Science and Technology” on Findings from the Fine Particulate Matter Supersites Program. *Aerosol Sci. Technol.* **2004**, *38* (sup1), 5–13.

(129) Zhu, Y.; Kuhn, T.; Mayo, P.; Hinds, W. C. Comparison of Daytime and Nighttime Concentration Profiles and Size Distributions of Ultrafine Particles near a Major Highway. *Environ. Sci. Technol.* **2006**, *40* (8), 2531–2536.

(130) MesoWest, University of Utah. Meteorological data http://mesowest.utah.edu.

(131) Carslaw, D.; Ropkins, K. *Openair: Tools for the Analysis of Air Pollution Data*; 2018.

(132) Carslaw, D. C.; Beevers, S. D. Characterising and Understanding Emission Sources Using Bivariate Polar Plots and K-Means Clustering. *Environ. Model. Softw.* **2013**, *40*, 325–329.

(133) Elangasinghe, M. A.; Singhal, N.; Dirks, K. N.; Salmond, J. A.; Samarasinghe, S. Complex Time Series Analysis of PM10 and PM2.5 for a Coastal Site Using Artificial Neural Network Modelling and k-Means Clustering. *Atmos. Environ.* **2014**, *94*, 106–116.

(134) Fujita, E. M.; Croes, B. E.; Bennett, C. L.; Lawson, D. R.; Lurmann, F. W.; Main, H. H. Comparison of Emission Inventory and Ambient Concentration Ratios of CO, NMOG, and NOx in California’s South Coast Air Basin. *J. Air Waste Manag. Assoc.* **1992**, *42* (3), 264–276.

(135) Anderson, D. C.; Loughner, C. P.; Diskin, G.; Weinheimer, A.; Canty, T. P.; Salawitch, R. J.; Worden, H. M.; Fried, A.; Mikoviny, T.; Wisthaler, A.; et al.

Measured and Modeled CO and NOy in DISCOVER-AQ: An Evaluation of Emissions and Chemistry over the Eastern US. *Atmos. Environ.* **2014**, *96*, 78–87.

(136) Mellios, G.; Vanaalst, R.; Samaras, Z. Validation of Road Traffic Urban Emission Inventories by Means of Concentration Data Measured at Air Quality Monitoring Stations in Europe. *Atmos. Environ.* **2006**, *40* (38), 7362–7377.

(137) Guo, H.; Jiang, F.; Cheng, H. R.; Simpson, I. J.; Wang, X. M.; Ding, A. J.; Wang, T. J.; Saunders, S. M.; Wang, T.; Lam, S. H. M.; et al. Concurrent Observations of Air Pollutants at Two Sites in the Pearl River Delta and the Implication of Regional Transport. *Atmospheric Chem. Phys.* **2009**, *9* (19), 7343–7360.

(138) Petron, G.; Karion, A.; Sweeney, C.; Miller, B. R.; Montzka, S. A.; Frost, G. J.; Trainer, M.; Tans, P.; Andrews, A.; Kofler, J.; et al. A New Look at Methane and Nonmethane Hydrocarbon Emissions from Oil and Natural Gas Operations in the Colorado Denver-Julesburg Basin. *J. Geophys. Res.-Atmospheres* **2014**, *119* (11), 6836–6852.

(139) Agency for Toxic Substances and Disease Registry (ATSDR). *Toxicological Profile for Benzene*; U.S. Department of Health and Human Services: Atlanta, GA, 2007.

(140) Giles, L. V.; Koehle, M. S. The Health Effects of Exercising in Air Pollution. *Sports Med.* **2014**, *44* (2), 223–249.

(141) Bateson, T. F.; Schwartz, J. Children's Response to Air Pollutants. *J. Toxicol. Environ. Health A* **2007**, *71* (3), 238–243.

(142) Garcia-Gonzales, D.; Shonkoff, S.; Hays, J.; Jerrett, M. Hazardous Air Pollutants Associated with Upstream Oil and Natural Gas Development: An Examination of the Current Peer-Reviewed Literature (in Review). *Annu. Rev. Public Health* **2019**, *40.*

(143) Russo, P. N.; Carpenter, D. O. *Health Effects Associated with Stack Chemical Emissions from NYS Natural Gas Compressor Stations: 2008-2014*; Institute for Health and the Environment: University at Albany, 2017; p 305.

(144) CCST. *An Independent Scientific Assessment of Well Stimulation in California, Vol. 2*; 2015.

(145) Adgate, J. L.; Goldstein, B. D.; McKenzie, L. M. Potential Public Health Hazards, Exposures and Health Effects from Unconventional Natural Gas Development. *Environ. Sci. Technol.* **2014**, *48* (15), 8307–8320.

(146) McCawley, M. A. Does Increased Traffic Flow around Unconventional Resource Development Activities Represent the Major Respiratory Hazard to Neighboring Communities?: Knowns and Unknowns. *Curr. Opin. Pulm. Med.* **2017**, *23* (2), 161–166.

(147) Ezani, E.; Masey, N.; Gillespie, J.; Beattie, T. K.; Shipton, Z. K.; Beverland, I. J. Measurement of Diesel Combustion-Related Air Pollution Downwind of an Experimental Unconventional Natural Gas Operations Site. *Atmos. Environ.* **2018**, *189*, 30–40.

(148) Becker, K. H.; Lörzer; Kurtenbach, R.; Wiesen, P.; Jensen, T. E.; Wallington, T. J. Nitrous Oxide (N2O) Emissions from Vehicles. *Environ. Sci. Technol.* **1999**, *33* (22), 4134–4139.

(149) Herndon, S. C.; Jayne, J. T.; Lobo, P.; Onasch, T. B.; Fleming, G.; Hagen, D. E.; Whitefield, P. D.; Miake-Lye, R. C. Commercial Aircraft Engine Emissions

Characterization of In-Use Aircraft at Hartsfield-Jackson Atlanta International Airport. *Environ. Sci. Technol.* **2008**, *42* (6), 1877–1883.

(150) Shonkoff, S. B. C.; Gautier, D. A Case Study of the Petroleum Geological Potential and Potential Public Health Risks Associated with Hydraulic Fracturing and Oil and Gas Development in The Los Angeles Basin. 68.

(151) Jerrett, M.; Burnett, R. T.; Ma, R.; Pope, C. A.; Krewski, D.; Newbold, K. B.; Thurston, G.; Shi, Y.; Finkelstein, N.; Calle, E. E.; et al. Spatial Analysis of Air Pollution and Mortality in Los Angeles: *Epidemiology* **2005**, *16* (6), 727–736.

(152) Ghosh, J. K. C.; Heck, J. E.; Cockburn, M.; Su, J.; Jerrett, M.; Ritz, B. Prenatal Exposure to Traffic-Related Air Pollution and Risk of Early Childhood Cancers. *Am. J. Epidemiol.* **2013**, *178* (8), 1233–1239.

(153) Wilhelm, M.; Ghosh, J. K.; Su, J.; Cockburn, M.; Jerrett, M.; Ritz, B. Traffic-Related Air Toxics and Term Low Birth Weight in Los Angeles County, California. *Environ. Health Perspect.* **2011**, *120* (1), 132–138.

(154) EIA. *The Distribution of U.S. Oil and Natural Gas Wells by Production Rate*; U.S. Department of Energy: Washington, D.C., 2017.

(155) MATES IV http://www.aqmd.gov/home/air-quality/air-quality-studies/health-studies/mates-iv (accessed Jun 27, 2018).

(156) Garcia-Gonzales, D.; Jerrett, M. An Investigation of the Air Pollution Exposure Impact Zone around Oil and Natural Gas Operations in the Colorado Front Range (Pending Publication). **2018**.

(157) Walton, A. Porter Ranch Residents Face an Oily Problem as They Return Home. *Los Angeles Times*. March 10, 2016.

(158) SoCal Gas. Aliso Canyon Air Sample Results https://www.socalgas.com/newsroom/aliso-canyon-updates/aliso-canyon-air-sample-results (accessed Jun 28, 2018).

(159) Air Quality Management District. Aliso Canyon Ambient Air Analysis http://www.aqmd.gov/home/news-events/community-investigations/aliso-canyon-update/air-sampling (accessed Jun 28, 2018).

(160) Wilcox, G. Oily Mist Released at Site of Leaking Gas Well in Porter Ranch. *Daily News*. November 13, 2015.

(161) LAC DPH. *Aliso Canyon Gas Leak: Results of Air Monitoring and Assessments of Health*; Los Angeles County Department of Public Health, 2016.

(162) LAC DPH. *Aliso Canyon Gas Leak: Community Assessment for Public Health Emergency Response (CASPER)*; Los Angeles County Department of Public Health, 2016.

(163) LAC DPH. *Aliso Canyon Natural Gas Leak: Public Health Assessment*; Los Angeles County Department of Public Health, 2016.

(164) Beckerman, B.; Jerrett, M. *Interim Report: Cluster Analysis of Metals and Organics in Dust Samples: Porter Ranch Area*; GIS HEAL Labs, 2016.

(165) Klepeis, N. E.; Nelson, W. C.; Ott, W. R.; Robinson, J. P.; Tsang, A. M.; Switzer, P.; Behar, J. V.; Hern, S. C.; Engelmann, W. H. The National Human Activity Pattern Survey (NHAPS): A Resource for Assessing Exposure to Environmental Pollutants. *J. Expo. Anal. Environ. Epidemiol.* **2001**, *11* (3), 231–252.

(166) EIA. Underground Natural Gas Storage Capacity https://www.eia.gov/dnav/ng/ng_stor_cap_dcu_nus_a.htm.

(167) Los Angeles Department of Public Health. Resident Relocation Directive, 2015.

(168) Los Angeles Department of Public Health. Student and Staff Relocation Directive, 2015.

(169) Mead, M. I.; Popoola, O. A. M.; Stewart, G. B.; Landshoff, P.; Calleja, M.; Hayes, M.; Baldovi, J. J.; McLeod, M. W.; Hodgson, T. F.; Dicks, J.; et al. The Use of Electrochemical Sensors for Monitoring Urban Air Quality in Low-Cost, High-Density Networks. *Atmos. Environ.* **2013**, *70*, 186–203.

(170) González, I.; Déjean, S. *CCA: Canonical Correlation Analysis*; 2012.

(171) Nelson, P. F.; Quigley, S. M. The Hydrocarbon Composition of Exhaust Emitted from Gasoline Fuelled Vehicles. *Atmospheric Environ. 1967* **1984**, *18* (1), 79–87.

(172) Tyler, S. C.; Rice, A. L.; Ajie, H. O. Stable Isotope Ratios in Atmospheric CH4: Implications for Seasonal Sources and Sinks. *J. Geophys. Res.* **2007**, *112* (D3).

(173) Broderick, B. M.; Marnane, I. S. A Comparison of the C2–C9 Hydrocarbon Compositions of Vehicle Fuels and Urban Air in Dublin, Ireland. *Atmos. Environ.* **2002**, *36* (6), 975–986.

(174) Harley, R. A.; Hannigan, M. P.; Cass, G. R. Respeciation of Organic Gas Emissions and the Detection of Excess Unburned Gasoline in the Atmosphere. *Environ. Sci. Technol.* **1992**, *26* (12), 2395–2408.

(175) Borbon, A.; Gilman, J. B.; Kuster, W. C.; Grand, N.; Chevaillier, S.; Colomb, A.; Dolgorouky, C.; Gros, V.; Lopez, M.; Sarda-Esteve, R.; et al. Emission Ratios of Anthropogenic Volatile Organic Compounds in Northern Mid-Latitude Megacities: Observations versus Emission Inventories in Los Angeles and Paris. *J. Geophys. Res. Atmospheres 118* (4), 2041–2057.

(176) Fraser, M. P.; Cass, G. R.; Simoneit, B. R. T. Gas-Phase and Particle-Phase Organic Compounds Emitted from Motor Vehicle Traffic in a Los Angeles Roadway Tunnel. *Environ. Sci. Technol.* **1998**, *32* (14), 2051–2060.

(177) McGaughey, G. R.; Desai, N. R.; Allen, D. T.; Seila, R. L.; Lonneman, W. A.; Fraser, M. P.; Harley, R. A.; Pollack, A. K.; Ivy, J. M.; Price, J. H. Analysis of Motor Vehicle Emissions in a Houston Tunnel during the Texas Air Quality Study 2000. *Atmos. Environ.* **2004**, *38* (20), 3363–3372.

(178) Shetter, C.; Marrero, J.; Blake, D. Using Iso to N-Pentane Ratios to Identify Oil and Natural Gas Industry Influence in the LA Basin, 2013.

(179) Tabachnick, B. G.; Fidell, L. S. *Using Multivariate Statistics (3rd Ed.)*; HarperCollins: New York, NY, 1996.

(180) SoCal Gas. *State Regulators Confirm Aliso Canyon Well Is Permanently Sealed*; Press Release; SoCal Gas: Los Angeles, CA, 2016.

(181) Michanowicz, D. R.; Buonocore, J. J.; Rowland, S. T.; Konschnik, K. E.; Goho, S. A.; Bernstein, A. S. A National Assessment of Underground Natural Gas Storage: Identifying Wells with Designs Likely Vulnerable to a Single-Point-of-Failure. *Environ. Res. Lett.* **2017**, *12* (6), 064004.

(182) Long, J. C. S.; Feinstein, L. F.; Birkholzer, J.; Jordan, P.; Houseworth, J.; Dobson, P. F.; Heberger, M.; Gautier, D. L. *Well Stimulation Technologies and Their Past, Present, and Potential Future Use in California*; Volume 1; California Council on Science and Technology & Lawrence Berkeley National Laboratory, 2015.