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# Hazardous Air Pollutants Associated with Upstream Oil and Natural Gas Development: A Critical Synthesis of Current Peer-Reviewed Literature

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## Keywords

hazardous air pollutants, volatile organic compounds, oil and natural gas, air quality, oil and gas development

## Abstract

Increased energy demands and innovations in upstream oil and natural gas (ONG) extraction technologies have enabled the United States to become one of the world's leading producers of petroleum and natural gas hydrocarbons. The US Environmental Protection Agency (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 (a) identify HAPs associated with upstream ONG development, (b) identify their specific sources in upstream processes, and (c) examine the potential for adverse health outcomes from HAPs emitted during these phases of hydrocarbon development.

## 1. INTRODUCTION

Over the past several decades, as energy demands have increased contemporaneously with innovations in upstream oil and natural gas (ONG) extraction technologies, the United States has become the world's top producer of petroleum and natural gas hydrocarbons (34). The US Energy Information Administration (104) reported that US petroleum and other liquid fuel production reached 9.3 million barrels per day, and dry natural gas production averaged 73.6 billion cubic feet per day in 2017, with increases projected for 2018 and 2019. In some areas, including Pennsylvania, Colorado, Texas, and California, ONG extraction and development have expanded closer to residential communities, increasing risks of population exposures to air, water, soil, noise, and light pollution. Research suggests that 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 (12, 53). A growing, yet still relatively small body of studies has investigated the relationship between the proximity of these facilities and human health impacts (21, 22, 31, 60, 78, 79, 96, 97, 99). With a dearth of scientific data characterizing exposure risks, it is difficult to offer scientific guidance on specific adequate setback requirements, despite the fact that an estimated 18 million people live within 1,600 m (~1 mile) from an active ONG well (32). Special disclosure exemptions from the federal Emergency Planning and Community Right-to-Know Act allow the ONG industry to withhold information regarding chemical constituents used, produced, and emitted, further compounding the difficulty in identifying chemical-related hazards and their associated exposure pathways (106).

The current body of scientific literature suggests that upstream ONG development processes emit numerous air pollutants, including methane, nonmethane-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 (18, 41, 89, 95, 111, 115, 122). 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. Upstream processes consist of four broad phases of operation: (a) exploration and well pad and infrastructure construction; (b) well drilling and construction of associated surface and subsurface equipment and facilities; (c) application of well stimulation or secondary oil and gas recovery techniques (e.g., water flooding and steam injection) and completion, or both; and (d) hydrocarbon production and processing. 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, some classified as HAP compounds with known carcinogenic and noncarcinogenic toxicological properties (26, 38, 82, 108). Current research on oil and gas development provides conflicting evidence over the concentrations of various pollutants in the air across geographic, regulatory, and corporate spaces; however, a consensus exists regarding the presence of air pollutants that can pose human health hazards around ONG sites (19, 27, 48, 56, 68, 73, 79, 88).

Emissions of hazardous air pollutants (HAPs) from ONG are of particular concern because they are known or suspected to cause cancer or other serious noncancer health effects. The US Clean Air Act currently lists 187 HAPs for regulation (107), some of which have been associated

with ONG activities. The Committee on Energy and Commerce and the Endocrine Disruption Exchange have identified more than 20 different HAPs, which have been associated with upstream ONG activities or processes (101, 109). 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 (18, 44, 80, 114).

The purpose of this review is to summarize the research conducted to date on the associations between HAPs and upstream ONG development. Specifically, this article aims to (a) identify HAP compounds that have been investigated near upstream operations within the peer-reviewed literature; (b) determine which of these compounds has been traced to a specific upstream phase, process, or source; and (c) examine the potential health hazards attributable to these HAPs. Our synthesis of the science is intended to inform future research priorities and to assist in public health protection. A list of ONG industry terms can be found in the sidebar titled Terms and Definitions.

## TERMS AND DEFINITIONS

**Anthropogenic:** originating from human activities. With air pollution, these activities include those related to transportation (or mobile), agriculture, or industry sources.

**BTEX:** the group of compounds, including benzene, toluene, ethylbenzene, and total xylenes. These compounds occur naturally in petroleum and are released primarily through motor vehicle emissions, but they are also emitted naturally via volcanoes and forest fires.

**Condensate:** broadly defined as a liquid formed by condensation. With oil and natural gas, condensate is a gas that condenses into a liquid hydrocarbon mixture after being liberated from the high-pressure environment within a well.

**Hazardous air pollutant (HAP):** the US EPA defines HAPs as pollutants that are known or suspected to cause cancer or other serious health effects, such as reproductive effects or birth defects, or adverse environmental effects.

**Oil and natural gas (ONG):** describing both liquid and gas fossil fuel products. Oil refers to crude oil hydrocarbon mixtures that exist in liquid form, whereas natural gas consists mainly of methane (CH<sub>4</sub>), a small amount of hydrocarbon gas liquids, and nonhydrocarbon gases. Oil, gas, and liquid gas hydrocarbons can be found in underground reservoirs, sedimentary rocks, or tar sands and can be recovered in the near absence of the other forms or simultaneously.

**Polycyclic aromatic compounds (PAHs):** a class of organic compounds composed of multiple aromatic rings that occur naturally in crude oil. More than 100 different PAHs exist, including benzo[a]pyrene, benz[a]anthracene, and chrysene, with varying degrees of toxicity.

**Petrogenic:** originating from hydrocarbons formed by the decomposition of organic matter. In regard to petrogenic air pollutants, these may be released when fuel oil and crude oil are exposed during upstream oil and natural gas operations.

**Polycyclic organic matter (POM):** defines a broad class of compounds that generally includes structures containing 2–7 fused aromatic rings and are present in the atmosphere mostly in particle form. PAHs are a subset of POMs.

**Proppant:** a material (often sand) used to prop open cracks within fractured shale rocks to harvest oil, natural gas, or other targeted materials. Proppant is often mixed with a chemical liquid mixture and forced into shale formations at high pressure.

**Reference effect level (REL):** 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. RELs have been developed for a limited number of compounds for acute, eight-hour, and chronic exposures.

**Repository for Oil and Gas Energy Research (ROGER) database:** PSE's nearly exhaustive database of peer-reviewed literature on shale gas development, which can be found on the PSE website (<http://www.psehealthyenergy.org>).

**Wet gas:** a natural gas that contains less than ~85% methane and increased amounts of ethane and other hydrocarbons, as opposed to dry gas, which occurs in the near absence of condensate or liquid hydrocarbons.

## 2. MATERIALS AND METHODS

### 2.1. Scope

We began with the inclusion of all 187 HAPs listed by the US Environmental Protection Agency (EPA). Hydrogen sulfide ( $\text{H}_2\text{S}$ ) was removed from the official US EPA list in 1991 but was included in our review owing to its toxic properties, detection at low concentrations (0.03–0.05 ppm), and prevalence in oil and gas development operations. From this point forward, when referring to HAPs, we include all 187 compounds listed by the US EPA, plus  $\text{H}_2\text{S}$  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. Many 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 emitted from ONG operations (27). Although they are central to the question of HAP formation and atmospheric concentrations, HAP precursors fall outside the scope of this review.

### 2.2. Keyword Search

We developed a list of keywords to assist in a comprehensive literature search of all upstream ONG processes and target pollutants. Owing 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 terms “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 keywords for transport media to ensure that search results encompassed airborne compounds. We erred on the side of being overly inclusive and integrated broad group names, including volatile organic compounds (VOCs), nonmethane hydrocarbons (NMHCs), and hazardous air pollutants (HAPs) during the search process. Keywords and search queries are provided in **Supplemental Table 1**.

### 2.3. Electronic Database Search

We searched peer-reviewed journal articles within three electronic search databases in March 2018. First, we searched the Clarivate Analytics 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 by 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 1,146 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 (<https://www.psehealthyenergy.org/our-work/shale-gas-research-library/>). Articles found in the ROGER database that were not included in searches from the electronic databases were added to the collection, for a final count of 1,833 journal articles. These articles were then collected, organized, and evaluated using the inclusion/exclusion criteria.

## 2.4. Inclusion and Exclusion Criteria

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**). We first scanned titles to remove papers from our review on the bases of whether a paper met the following criteria: (a) not written in English; (b) was a review, commentary, or response paper and not a primary study; and (c) 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, modeled, or estimated HAP emissions and concentrations or did not conduct other 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 source attribution of 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.

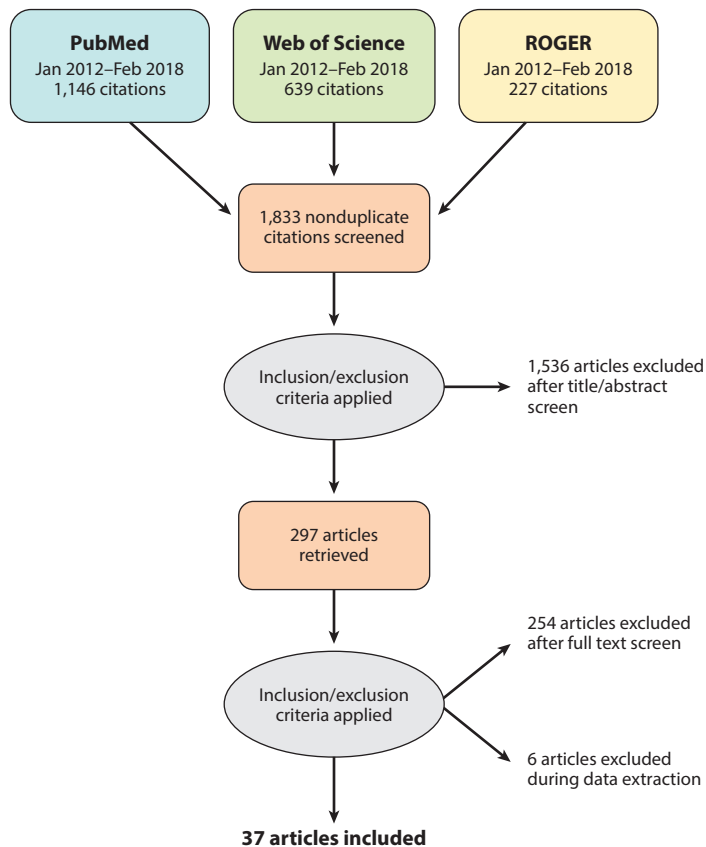
## 3. RESULTS

A total of 37 peer-reviewed journal articles, published between January 1, 2012, and February 28, 2018, met our inclusion/exclusion criteria (**Supplemental Table 2**). One peer-reviewed article focused on ONG operations in Poland, and the rest of the articles focused on operations 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. The remaining articles included primary data analyses from secondary data sources or publicly accessible data sets.

Supplemental Material >

### 3.1. HAPs Identified Within Review

To enable generalization of 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 in the atmosphere above the sample limit of detection (LOD) were labeled as "Not Detected" (for additional information on the metric of interest, see the sidebar titled Metric of Interest: Sample Limits of Detection versus Health-Based Comparison Values). 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



**Figure 1**

A Preferred Reporting Items for Systematic Reviews and Meta-Analyses (PRISMA) flow diagram for hazardous air pollutant (HAP) emissions near upstream oil and natural gas (ONG) development. Abbreviation: ROGER, PSE Healthy Energy's Repository for Oil and Gas Energy Research.

## Supplemental Material >

were collected and reported in more than one article as primary or in-situ data, of which 32 were found above the sample LOD. **Supplemental Figure 1** 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 **Supplemental Table 4**.

Many of the peer-reviewed studies investigated a broad range of target analytes in ambient air, several of which are ubiquitous in the environment and are sourced not only in upstream ONG operations. While some of the HAP compounds listed in **Supplemental Figure 1** and **Supplemental Table 4** may have a source in upstream ONG, without point source or source attribution methodologies, their association is speculative. Therefore, in the following sections, we have further assessed the 61 HAP compounds identified within the peer-reviewed literature to classify pollutants assessed for contributing sources and to determine their potential association with upstream ONG development.

## METRIC OF INTEREST: SAMPLE LIMITS OF DETECTION VERSUS HEALTH-BASED COMPARISON VALUES

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 (6). 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 (**Supplemental Table 3**). Finally, many health-based standards are derived from limited data sets and inadequate conversion factors that do not appropriately define the risk threshold of sensitive populations nor do they address the risks of exposure to multiple HAPs concurrently and, thus, may inappropriately imply the absence of health risks.

Despite these advantages, an LOD above health-based standards may erroneously imply low exposure risk when concentrations are not detected within the sample. To address these issues, we advise researchers to include LODs within the results to avoid misleading 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.

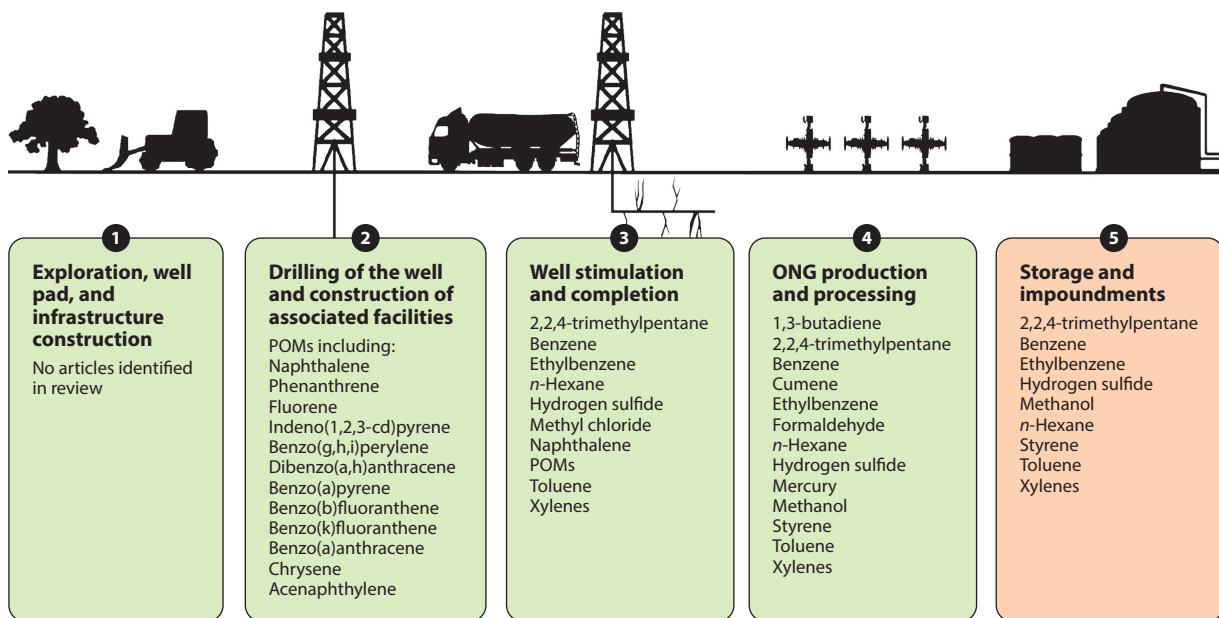
Supplemental Material >

### 3.2. Sources of HAP Emissions

The range of air pollutant emission sources identified in the reviewed literature includes equipment (e.g., dehydrators, condensate tanks), activities (e.g., flashings, gauging flowback tanks), development phases (e.g., drilling, well stimulation), and facilities (e.g., flowback and produced water treatment and recycling center, oil storage facility). To simplify these broadly categorized emission sources, we recategorized equipment, activities, and facilities into one of the four most appropriate upstream ONG phases: (a) exploration and well pad and infrastructure construction; (b) well drilling and construction of associated facilities; (c) well stimulation, enhanced oil recovery, and completion; and (d) ONG production and processing. For example, air quality measurements collected from flowback were recategorized into the third phase (well stimulation, enhanced oil recovery, and completion) because flowback is a fluid often recovered as a result of well stimulation (e.g., hydraulic fracturing). Storage tanks and impoundments can be present at the well pad through multiple phases or can be transported off-site via trucks or pipeline networks. Since the location of storage-related equipment and associated activities varies by location, HAP compounds identified from these sources have been recategorized into a separate storage and impoundment phase and described in Section 3.2.4.

Point source data are collected from stationary, identifiable locations and equipment that release pollutants into the atmosphere. Studies that included the collection of on-site primary point source air quality data, including Brantley et al. (15), Esswein et al. (39), and Hildenbrand et al. (58), provided detailed information about the equipment and activities that occurred during their sampling periods. On the basis of these detailed descriptions, we collected and recategorized the reported data into one of our five phases. In the absence of identifiable emission points, source attribution methods are important to estimate probable sources or categories of sources. Examples of source attribution methods employed in the reviewed literature include factor analyses (1, 43, 90), distance decay gradients (125), and sourcing ratios (45, 46, 50, 54, 85, 99), among others. Additional studies, including Macey et al. (73) and Colborn et al. (27), collected samples off-site and provided information about potential emission sources by detailing the most proximate upstream





**Figure 2**

Hazardous air pollutant (HAP) compounds collected through primary measurements and recategorized. Abbreviations: ONG, oil and natural gas; POMs, polycyclic organic matter.

ONG equipment or activities during the data collection timeframe but did not specifically apply commonly used source attribution techniques. Recognizing the limitations of off-site activity reporting in the absence of well-established source attribution analyses, we cautiously used these descriptions as a guide for recategorization but used our best discretion for inclusion.

A complete summary of recategorized HAP emissions from primary measurements within the reviewed literature is provided in **Figure 2**. We did not identify any HAPs that were sourced to emissions during the first phase of development (exploration and well pad and infrastructure construction).

### 3.2.1. HAP emissions from well drilling and construction of subsurface infrastructure.

After the site has been cleared and a well pad is established, a vertical well is drilled often using gas-powered rigs and other ancillary equipment to reach depths of several hundred meters below the surface. If necessary, operators will continue to drill directionally (e.g., horizontally) to increase the surface area of the target petroleum geologic zone (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 (23, 51). 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 during the drilling and well construction phase (17).

Colborn et al. (27) measured the most elevated chemical concentrations 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 twelve different polycyclic aromatic hydrocarbon (PAH) compounds, a subset of polycyclic organic matter (POM) compounds, during a timeframe dominated by drilling activities. Elevated carbonyl and VOC concentrations were also detected; however,



the individual VOC species were not detailed within the paper and, thus, are not included in this section. Source attribution using temporal patterns of PAH concentrations in the ambient environment without supplementary sourcing analyses is difficult to interpret, especially for PAHs that lack chemical disclosures or inventories as well as PAHs commonly formed from combustion or other anthropogenic sources. Yet, analyses of similar PAH compounds found evidence of petrogenic sources during a range of upstream ONG activities in Ohio (85); thus, we have included these within the current section. Additional mobile measurements in Pennsylvania detected acetaldehyde, acetonitrile, benzene, methanol, and toluene downwind from a drilling rig; however, concentrations were not elevated above background, suggesting that the rig was not operating at full capacity, the emissions from this activity in this particular geographic and geologic area did not have high emissions, or the activities and equipment associated with the drilling phase were not the source of these pollutants and thus were not included in our sourcing analyses (51).

**3.2.2. HAP emissions from well stimulation, secondary recovery, and completion.** The well completion phase encompasses all processes associated with preparing a newly drilled well for the production of oil and gas. This phase is relatively short in duration (3–15 days) but can include a variety of activities, including flowback collection, flaring, workovers, and completion venting. Once the well is drilled, cement and casing are installed to stabilize the wellbore and provide zonal isolation to minimize subsurface migration of liquid and gaseous fluids. This step is followed by the perforation of the casing in the target hydrocarbon reservoir to allow for the stimulation and other injected fluids to gain access to the petroleum reservoir and then subsequently for the flow of hydrocarbons into the well. In low-permeability reservoirs, where hydraulic fracturing and other stimulation are required to extract hydrocarbons, between 0.25 and 50 million gallons of water, chemicals, and proppant are injected down the well at a pressure high enough to increase the permeability of the target geology. The return of these stimulation fluids to the wellhead is referred to as “flowback.” Although chemical constituents from the geological formation are present in this flowback, these fluids are often opaquely distinguished from “produced” water, which surfaces shortly thereafter and often throughout the lifetime of active hydrocarbon production (13). Because flowback is limited mostly to the current phase, we include emissions associated with flowback, and not produced water, which is reviewed in subsequent sections. It should be noted, however, that scientific distinctions between the flowback and produced water phases of oil and gas development are not specific and vary considerably across geological and regulatory spaces (70).

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 completion activities and, with the exception of styrene, cumene, and 1,3-butadiene, median concentrations were higher than background in ONG area samples (79). 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 (76). Occupational and off-site measurements identified POMs (including naphthalene) and H<sub>2</sub>S near flowback and workover rigs (39, 73).

BTEX compounds and n-hexane are found in diesel combustion emissions from equipment and vehicles used in ONG, drilling fluids, and fracturing additives. BTEX compounds, in particular, occur naturally in oil and gas geological formations, and emissions of these compounds during oil and gas development are likely attributable to various processes, including those that provide an opportunity for gas compounds to migrate to the surface and volatilize into the ambient air. Therefore, many of the HAPs identified in ambient air near ONG operations during well stimulation and completion could be direct emissions from ancillary well pad equipment, loss of wellbore integrity, improper handling of flowback fluids, and volatilization from the chemical mixtures used

for stimulation fluids or completion activities (61, 101, 108, 109). With the current evidence, we cannot identify the specific source activity or equipment, although ONG development appears to be a likely source of these compounds identified at elevated concentrations in the ambient air.

**3.2.3. HAP emissions from oil and gas production and processing.** During the production phase, ONG 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 the upstream phases with the potential to emit maximum peak values that exceed the stimulation and completion phase (17), and it was linked to the most varied number of HAPs within our review. While a given shale well may be depleted within 1–5 years, migrated oil reservoirs may produce for decades. Hydrocarbon production in geological zones richer in oil and wet gas may be associated with HAPs and other larger-molecular-weight hydrocarbon emissions during the production and processing phase when target alkanes are separated from heavier compounds. Operational practices, the spud date, the petroleum geology, and production volumes can also heavily impact emissions from producing wells within the same shale play (51, 98). Therefore, without insight into reservoir composition and well pad operations, it is difficult to predict the geography and magnitude of HAP emissions or to extrapolate results to larger areas.

Wellheads, dehydrators, and separators are important sources of elevated HAP emissions during production and processing in regions rich in oil, wet gas, and condensate (43, 112). Dehydration units account for an estimated 40% of HAP emissions (36). 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 (15). Off-site measurements in Texas and Wyoming identified similar emissions with an addition of cumene and H<sub>2</sub>S near wellheads, separators, and produced water tanks and discharge canals (35, 73). Compressors used to maintain hydrocarbon flow were associated with emissions of BTEX compounds, 1,3-butadiene, methanol, formaldehyde, mercury, and n-hexane (35, 51, 65, 73, 75, 90). With the exception of mercury, these compounds are commonly emitted from continuously reciprocating natural gas-fired engines, and their presence within the collected samples was not unexpected. A report analyzing point source emissions data from 58 compressor stations found formaldehyde to be the fourth largest chemical released by compressors by total pounds, just after total VOCs (92). Mercury, a trace component in natural gas condensate, is removed from the compressor process; thus, its emission may actually be a result of ineffective mercury removal systems and therefore is included in this phase (65).

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 they may be responsible for a significant portion of ONG-related air pollution (16, 30, 59, 123). Flyover 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<sub>4</sub> emissions emitted from these operations (120). Although these measurements might not be representative of all associated HAP emissions, enhancement ratios and correlations between CH<sub>4</sub> and benzene suggest a similar source. Furthermore, mobile measurements in the Barnett Shale area found that only 4% of measured ONG facilities were responsible for a relatively large amount of the measured atmospheric mercury (65). Within the current review, few air quality samples were reported as collected during abnormal ONG development process conditions, yet it is possible that off-normal events occurred without operator knowledge or public disclosure. For example, samples collected near production phase equipment described as “rusty” recorded HAP concentrations up to 47 times higher than those described as being in “good” operating condition, yet neither were identified as abnormal processes (15). 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 detected on- and off-site and near residential homes (40).

**3.2.4. HAP emissions from storage tanks and impoundments.** Storage tanks and impoundments are often used to hold production and maintenance chemicals or condensate and recovered fluids collected and separated during various phases. Chemicals stored at upstream ONG sites include chemical additives and mixtures for well stimulation and various well and equipment maintenance needs. Condensate is different from stored chemicals, flowback, and produced water in that it 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<sub>2</sub>S, BTEX, n-hexane, styrene, methanol, and 2,2,4-trimethylpentane (15, 67, 112). 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 (55).

Such condensate tank emission events, even if brief, can be significant, which may have a substantial impact on local air quality (46), especially in oil-producing areas (72). Storage tanks can be housed at the well site that provide additional emissions source points during the associated phase; however, they can also be sited at different locations, far from the well pad, or piped off-site through transmission pipeline networks (45). Many of the listed HAPs in this section were found at well pads during production, but they were recategorized into the current separate group as the location of storage equipment and related activities varies by well site.

### 3.3. Summary of Health Impacts from HAP Compounds

HAP compounds are associated with multiple cancer and noncancer 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 because granular measurements of exposure have largely not been undertaken. 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 to be above sample LODs or above health benchmarks or that posed the highest risk from inhalation exposures. A summary of some of the key findings is provided in the following sections.

**3.3.1. HAPs of highest concern.** BTEX compounds are associated with several serious human health impacts, including neurological damage, birth defects, some cancers, and hearing loss (117). Ubiquitous in the environment, these compounds commonly exceed sample LODs in urban areas as a result of transportation and industrial processes (11); however, many of the reviewed samples were collected near ONG activities in rural regions, where urban emission sources are likely to have minimal impact on local and regional 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 health-based standards, with some concentrations over 2,900 ppb (parts per billion) (37, 43, 45, 46, 48, 51, 54, 73, 88, 91, 99, 102, 112). For reference, the Office of Environmental Health Hazard Assessment (OEHHA) acute reference effect level (REL)

in nonoccupational settings for benzene is 8 ppb, and the 8-hour and chronic RELs for benzene are 1.0 ppb (29). 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 (2, 3, 7, 33, 47, 63, 64, 69, 71, 74, 87, 119, 121, 124).

While health-based air quality standards provide a guide on which to base regulatory thresholds, many standards are extrapolated from in vivo or in vitro animal studies or human-based occupational studies that may not be appropriate for the protection of sensitive populations such as children and pregnant women (42, 110, 113). Recognizing the possible inadequacies of existing uncertainty factors for benzene, the OEHHA in California recently applied a stricter REL to include additional protections to sensitive populations (29), yet questions remain over whether these updated standards are protective enough. On the basis of the existing evidence of exposure risks from chronic, low-level concentrations, current noncancer health 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 states that “no level of exposure can be recommended,” implying that there is likely no safe lower threshold of exposure as implied by the RELs (116).

Formaldehyde and acetaldehyde were found to be the most abundant carbonyl species when sampling ambient air near ONG facilities. The chronic OEHHA nonoccupational RELs for acetaldehyde and formaldehyde are 80 ppb and 7 ppb, respectively (84). While many of the observed concentrations around ONG operations were below health standards, the International Agency for Research on Cancer has classified formaldehyde as a group 1 carcinogen, meaning it causes cancer in humans (8) and, generally, does not have a threshold below which there is a safe level of exposure. Furthermore, simplified health risk assessments and modeling estimates near ONG activities have suggested that formaldehyde and acetaldehyde are the dominant contributors to cancer risks (25, 99). The abundance of formaldehyde detection in ambient collected samples may actually indicate secondary atmospheric formation as the dominant source and not primary emissions released directly from an ONG point source. Mandated state inventories that focus on primary emissions may actually lead to underreporting if secondary atmospheric formation is the dominant pollutant source.

The natural gas and crude oil impurity  $\text{H}_2\text{S}$  is a colorless and flammable toxicant easily identifiable by its rotten egg odor.  $\text{H}_2\text{S}$  becomes detectable at concentrations as low as 0.5 ppb (10), becomes chronically toxic at 8 ppb (83), and has a National Institute for Occupational Safety and Health (NIOSH) immediately dangerous to life or health (IDLH) concentration of 100 ppm (24). Within the current review,  $\text{H}_2\text{S}$  has been measured in ambient air at various phases of upstream ONG development, including during separation, in storage tanks, and in discharge canals at concentrations exceeding those known to be safe (35, 39, 67, 73). Concentrations of  $\text{H}_2\text{S}$  above the odor threshold were measured just beyond the fence line in 8% of natural gas production sites in Texas during mobile measurements (35).

The simplest unsaturated aldehyde, acrolein, is fairly ubiquitous throughout the environment at concentrations above chronic noncancer benchmarks (77, 81, 100, 118). Used as a biocide additive and  $\text{H}_2\text{S}$  scavenger in ONG operations, acrolein is also emitted from more common sources, including incomplete combustion of petroleum products, tobacco smoke, and cooking activities. Owing to the current health burden of exposure in the ambient environment, the OEHHA identified acrolein as one of the top five most important pollutants of concern in California (4), 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 (49, 57, 62). Exposure to acrolein may cause adverse health effects, including eye, nose, and throat irritation, chest pain, and difficulty breathing (9). In California underground natural gas storage facilities, acrolein is reported as the eighth highest emitted air pollutant in California and was found at elevated levels in indoor environments near the site of the Aliso Canyon natural gas storage blowout (66, 94). Acrolein plays a substantial role in the upstream ONG process, and yet methodological constraints limit the availability of reliable industry-related emissions estimates and, consequently, obscure the understanding of the potential impact to human health.

**3.3.2. Gaps in 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 with further away (22, 31, 60, 96). Similarly, studies that utilize distance metrics as proxies of exposure reported increased health risks for individuals living near ONG activity compared with further away (21, 79, 99). These findings are corroborated by symptom surveys that found that the number of reported symptoms was higher among residents living closer to well pads compared with those living further away (97). Moreover, McKenzie et al. (78) paired in-situ air quality measurements with distance and cancer risk assessment. The study found that within 152 m (~500 feet) of active oil and gas development, the cancer risk estimate was 8.3 cases per 10,000 individuals, greatly exceeding the US EPA's upper threshold for acceptable risk (1 excess 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 the majority of 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 air pollutant concentration findings. First, in-situ measurements of emissions collected at a distance from well pad activities are prone to effects of atmospheric degradation, dispersion, and deposition (86), and yet they are commonly, and inappropriately, extrapolated to describe local exposures. Studies that utilize data from standard air monitoring networks, such as the Texas Commission on Environmental Quality (19, 40, 93), 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 capable of detailing only conditions at a particular—and short—moment in time and often fail to capture the episodic peaks commonly associated with many of the upstream ONG development processes (17). Similarly, integrated concentrations derived from longer sampling timeframes may dilute elevated concentrations during peak emission events and, thus, underestimate the full range of potentially recurring acute exposures (54). Recent evidence suggests that abnormal process conditions or uncontrolled emission events from a small proportion of wells or associated ancillary infrastructures may better explain the complex exposure environment from local to regional scales (123). Studies that estimate exposures on the basis of modeled emission masses and 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 intermittent sampling methods at select stages (28, 54).

Third, the current state of toxicological data and exposure science may not adequately address potential risks associated with long-term, chronic, lower levels of exposure, particularly when multiple air pollutants might be implicated (18, 20, 52). Thus, available health standards developed from inadequate uncertainty factors may not provide protection for human populations and especially for sensitive subpopulations, including infants, children, pregnant mothers, and people with preexisting medical conditions. Using OEHHA's conservative list of approved risk assessment health values as a guide to understand the current state of available health benchmarks (5), we found that fewer than 40% of all HAP compounds had inhalation cancer risks or noncancer health-based exposure levels. Several compounds that lack reference values were detected in air near, and are likely associated with, ONG sites. Other contaminants with health benchmarks, such as benzene, may still elicit health effects at concentrations lower than the REL. Furthermore, many HAP compounds are associated with cancer end points that, even at low atmospheric concentrations, generally do not have a threshold below which there is a safe level of exposure. Therefore, health studies that provide only comparisons to noncancer benchmarks may be misleading in their estimates of actual long-term health impacts.

Finally, health studies that use single pollutant health-based standards may fail to provide accurate risk estimates from concurrent or close-succession exposures to multiple pollutants that may act biologically antagonistic, synergistic, or additive (105). This situation of potential exposures to multiple air pollutants is particularly relevant for upstream ONG development where emission inventories and air quality monitoring have identified a wide range of pollutants that are often coemitted. Without knowledge of a specific etiological agent or exposure pathway, investigators may find that these studies fail to sample and analyze the full range of biologically relevant ONG pollutants or determine the most appropriate exposure pathways.

#### 4. DISCUSSION

We identified 37 peer-reviewed journal articles that met our inclusion/exclusion criteria, of which all but one focused on ONG operations within the United States. In our review, we found a lack of peer-reviewed literature from outside the United States, likely owing to the growing concerns about human health and environmental impacts, which may have slowed adoption of novel extraction methods in other countries. With the exception of Russia, the United States produced at least twice as much natural gas compared with all other regions in the world (103). In Europe, most exploratory shale gas extraction has occurred in Poland and the United Kingdom, but France and Norway have some of the most promising reserves that remain largely unexploited (44). Within the collected literature, we identified 61 HAPs, of which only 32 were collected during in-situ monitoring. Hydraulic fracturing has received the greatest attention for its potential impact to human and environmental health (14). In the context of HAPs, however, we did not find evidence to support the common assumption that the discrete hydraulic fracturing phase itself is associated with the highest risk of exposure. Instead, we found that the production phase—with its lengthy operation timeframe, episodic peak emission events, and largest number of HAPs sourced to the various equipment and operations—has the potential to emit the highest concentrations and the most varied mixture of HAPs over the longest time period, especially in regions rich in oil, wet gas, and condensate. Our review of the literature further suggests that exposure risks can be much higher if production equipment is colocated with condensate storage and wastewater impoundments. ONG development does not necessarily involve hydraulic fracturing but may include a myriad of different oil and gas development techniques, many that were not investigated within the collected literature.

In general, in-situ air pollutant measurements were found to be below health benchmarks, and yet multiple health-based studies found evidence of a spatial relationship between concentrations of HAPs and incidence of cancer and noncancer health end points in the context of proximity to oil and gas development operations. These findings suggest several possible explanations: (a) Spatial sampling methodologies fail to properly characterize exposures prior to atmospheric degradation, dispersion, and disposition of sampled pollutants; (b) ambient air sampling timeframes are inappropriate for capturing the episodic peak emission events characteristic of upstream ONG; and (c) prevailing health benchmarks are inadequate to identify 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 varying degrees of toxicity, of which some may have been overlooked during the inclusion/exclusion review. Second, some activities and equipment are used in both upstream and midstream (e.g., hydrocarbon transport) processes, and it was not always clear which was being measured when in-situ monitoring data was being collected. For example, compressors can be used to transport hydrocarbons and other compounds off the well pad during upstream activities, but the act of transportation would classify associated releases as midstream emissions. We used our best judgment when collecting and recategorizing HAP compounds; however, without clarification from the studies' authors, we may have 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 of summary findings. Although we attempted to recognize and address these inadequacies we may not have adjusted for all possible shortcomings in the reviewed literature. Fourth, we used sample LODs as the most appropriate metric of interest because the heterogeneity of sampling methodologies limited direct comparisons of measured or estimated concentrations across studies (for more information, see the sidebar titled Metric of Interest: Sample Limits of Detection versus Health-Based Comparison Values). While it would be helpful to consider sample LODs when evaluating nondetected HAPs, we identified a consistent failure to supply sample detection limits within the peer-reviewed literature in this review. Finally, our review was limited to constituents classified as HAPs; non-HAP compounds were beyond the scope of this article. Similarly, HAP compounds that were excluded from the collected literature were not extensively discussed here. By design, this review was limited to a select group of compounds that have been previously studied within the peer-reviewed literature. However, non-HAP compounds, HAP compounds not measured, and HAP compounds found under the sample LOD may still have a significant role in upstream ONG development and should be investigated in future studies.

Through our synthesis of the peer-reviewed literature, we have identified the following research priorities: (a) Increase research of 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; (b) undertake detailed source attribution investigations of emissions using spatially and temporally appropriate measurements; (c) conduct detailed health studies that focus on granular estimates of exposures near upstream ONG development via personalized and community-based monitoring; and (d) 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 to implement appropriate upstream ONG development emission control measures that will protect human and environmental health and decrease the adverse impacts of upstream oil and gas development.



## DISCLOSURE STATEMENT

The authors are not aware of any affiliations, memberships, funding, or financial holdings that might be perceived as affecting the objectivity of this review.

## LITERATURE CITED

1. Abeleira A, Pollack IB, Sive B, Zhou Y, Fischer EV, Farmer DK. 2017. Source characterization of volatile organic compounds in the Colorado Northern Front Range Metropolitan Area during spring and summer 2015. *J. Geophys. Res.-Atmos.* 122(6):3595–613
2. Aguilera I, Garcia-Esteban R, Iñiguez C, Nieuwenhuijsen MJ, Rodríguez À, et al. 2010. Prenatal exposure to traffic-related air pollution and ultrasound measures of fetal growth in the INMA Sabadell cohort. *Environ. Health Perspect.* 118(5):705–11
3. Aguilera I, Guxens M, Garcia-Esteban R, Corbella T, Nieuwenhuijsen MJ, et al. 2009. Association between GIS-based exposure to urban air pollution during pregnancy and birth weight in the INMA Sabadell Cohort. *Environ. Health Perspect.* 117(8):1322–27
4. Air Resour. Board. 2005. *Acrolein research project*. Contract 00–721 Draft Rep., Air Resour. Board, Plan. Tech. Support Div., Sacramento. [https://www.arb.ca.gov/ei/acrolein/acrolein\\_report.pdf](https://www.arb.ca.gov/ei/acrolein/acrolein_report.pdf)
5. Air Resour. Board. 2018. *OEHH/ARB approved risk assessment health values*. Consol. Table, Air Resour. Board, Sacramento. <https://www.arb.ca.gov/toxics/healthval/contable.pdf>
6. Annevelink MPJA, Meesters JAJ, Hendriks AJ. 2016. Environmental contamination due to shale gas development. *Sci. Total Environ.* 550:431–38
7. Arif AA, Shah SM. 2007. Association between personal exposure to volatile organic compounds and asthma among US adult population. *Int. Arch. Occup. Environ. Health* 80(8):711–19
8. ATSDR (Agency for Toxic Subst. Dis. Regist.). 1999. *Toxicological profile for formaldehyde*. Rep., US Dep. Health Hum. Serv., Atlanta. <https://www.atsdr.cdc.gov/toxprofiles/tp111.pdf>
9. ATSDR (Agency for Toxic Subst. Dis. Regist.). 2007. *Toxicological profile for acrolein*. Rep., US Dep. Health Hum. Serv., Atlanta. <https://www.atsdr.cdc.gov/toxprofiles/tp124.pdf>
10. ATSDR (Agency for Toxic Subst. Dis. Regist.). 2016. *Toxicological profile for hydrogen sulfide and carbonyl sulfide*. Rep., US Dep. Health Hum. Serv., Atlanta. <https://www.atsdr.cdc.gov/toxprofiles/tp114.pdf>
11. Baker AK, Beyersdorf AJ, Doeze LA, Katzenstein A, Meinardi S, et al. 2008. Measurements of non-methane hydrocarbons in 28 United States cities. *Atmos. Environ.* 42(1):170–82
12. Banan Z, Gernand JM. 2018. 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.* 68:988–1000
13. Bloomdahl R, Abualfaraj N, Olson M, Gurian PL. 2014. Assessing worker exposure to inhaled volatile organic compounds from Marcellus Shale flowback pits. *J. Nat. Gas Sci. Eng.* 21:348–56
14. Bogacki M, Macuda J. 2014. The influence of shale rock fracturing equipment operation on atmospheric air quality. *Arch. Min. Sci.* 59(4):897–912
15. Brantley HL, Thoma ED, Eisele AP. 2015. 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.* 65(9):1072–82
16. Brantley HL, Thoma ED, Squier WC, Guven BB, Lyon D. 2014. Assessment of methane emissions from oil and gas production pads using mobile measurements. *Environ. Sci. Technol.* 48(24):14508–15
17. Brown D, Lewis C, Weinberger BI. 2015. 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* 50(5):460–72
18. Brown D, Weinberger B, Lewis C, Bonaparte H. 2014. Understanding exposure from natural gas drilling puts current air standards to the test. *Rev. Environ. Health* 29(4):277–92
19. Bunch A, Perry CS, Abraham L, Wikoff DS, Tachovsky JA, et al. 2014. 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.* 468–469:832–42

20. Butler K, Tayour C, Batikian C, Contreras C, Bane M, et al. 2018. *Public health and safety risks of oil and gas facilities in Los Angeles County*. Rep., Los Angel. County Dep. Public Health, Los Angel. [http://publichealth.lacounty.gov/eh/docs/PH\\_OilGasFacilitiesPHSafetyRisks.pdf](http://publichealth.lacounty.gov/eh/docs/PH_OilGasFacilitiesPHSafetyRisks.pdf)
21. Casey JA, Ogburn EL, Rasmussen SG, Irving JK, Pollak J, et al. 2015. Predictors of indoor radon concentrations in Pennsylvania, 1989–2013. *Environ. Health Perspect.* 123(11):1130–37
22. Casey JA, Savitz DA, Rasmussen SG, Ogburn EL, Pollak J, et al. 2016. Unconventional natural gas development and birth outcomes in Pennsylvania, USA. *Epidemiology* 27(2):163–72
23. Caulton DR, Shepson PB, Santoro RL, Sparks JP, Howarth RW, et al. 2014. Toward a better understanding and quantification of methane emissions from shale gas development. *PNAS* 111(17):6237–42
24. CDC (Cent. Dis. Control Prev.). 2016. Hydrogen sulfide. *NIOSH pocket guide to chemical hazards*. <https://www.cdc.gov/niosh/npg/npgd0337.html>
25. Chen H, Carter KE. 2017. Modeling potential occupational inhalation exposures and associated risks of toxic organics from chemical storage tanks used in hydraulic fracturing using AERMOD. *Environ. Pollut.* 224:300–9
26. Colborn T, Kwiatkowski C, Schultz K, Bachran M. 2011. Natural gas operations from a public health perspective. *Hum. Ecol. Risk Assess. Int. J.* 17(5):1039–56
27. Colborn T, Schultz K, Herrick L, Kwiatkowski C. 2014. An exploratory study of air quality near natural gas operations. *Hum. Ecol. Risk Assess.* 20(1):86–105
28. Collier-Oxandale A, Casey JG, Piedrahita R, Ortega J, Halliday H, et al. 2018. Assessing a low-cost methane sensor quantification system for use in complex rural and urban environments. *Atmos. Meas. Tech. Discuss.* 11:3569–94
29. Collins JF. 2014. *Benzene reference exposure levels: technical support document for the derivation of noncancer reference exposure levels (appendix D1)*. Fin. Rep., Off. Environ. Health Hazard Assess., Calif. Environ. Prot. Agency, Sacramento. <https://oehha.ca.gov/media/downloads/crn/benzenerelsjune2014.pdf>
30. Conley S, Franco G, Faloona I, Blake DR, Peischl J, Ryerson TB. 2016. Methane emissions from the 2015 Aliso Canyon blowout in Los Angeles, CA. *Science* 351(6279):1317–20
31. Currie J, Deutch J, Greenstone M, Meckel K. 2014. *The impact of the fracking boom on infant health: evidence from detailed location data on wells and infants*. Abstract presented at the American Economic Association Annual Meeting, Philadelphia, PA, Jan. 3–5
32. Czolowski ED, Santoro RL, Srebotnjak T, Shonkoff SBC. 2017. Toward consistent methodology to quantify populations in proximity to oil and gas development: a national spatial analysis and review. *Environ. Health Perspect.* 125(8):086004
33. Delfino RJ, Gong H Jr., Linn WS, Pellizzari ED, Hu Y. 2002. Asthma symptoms in Hispanic children and daily ambient exposures to toxic and criteria air pollutants. *Environ. Health Perspect.* 111(4):647–56
34. Doman L, Kahan A. 2018. United States remains the world's top producer of petroleum and natural gas hydrocarbons. *U.S. Energy Information Administration*. <https://www.eia.gov/todayinenergy/detail.php?id=36292>
35. Eapi GR, Sabnis MS, Sattler ML. 2014. Mobile measurement of methane and hydrogen sulfide at natural gas production site fence lines in the Texas Barnett Shale. *J. Air Waste Manag. Assoc.* 64(8):927–44
36. East. Res. Group Inc. 2013. *Estimating nonpoint emissions from the oil and gas production sector*. EP-D-11–006, U.S. Environ. Prot. Agency, Washington, DC
37. Eisele AP, Mukerjee S, Smith LA, Thoma ED, Whitaker DA, et al. 2016. Volatile organic compounds at two oil and natural gas production well pads in Colorado and Texas using passive samplers. *J. Air Waste Manag. Assoc.* 66(4):412–19
38. Elliott EG, Trinh P, Ma X, Leaderer BP, Ward MH, Deziel NC. 2017. Unconventional oil and gas development and risk of childhood leukemia: assessing the evidence. *Sci. Total Environ.* 576:138–47
39. Esswein EJ, Snawder J, King B, Breitenstein M, Alexander-Scott M, Kiefer M. 2014. Evaluation of some potential chemical exposure risks during flowback operations in unconventional oil and gas extraction: preliminary results. *J. Occup. Environ. Hygiene* 11(10):D174–84
40. Ethridge S, Bredfeldt T, Sheedy K, Shirley S, Lopez G, Honeycutt M. 2015. The Barnett Shale: from problem formulation to risk management. *J. Unconv. Oil Gas Resour.* 11:95–110

41. Evanoski-Cole AR, Gebhart KA, Sive BC, Zhou Y, Capps SL, et al. 2017. Composition and sources of winter haze in the Bakken oil and gas extraction region. *Atmos. Environ.* 156:77–87
42. Ferguson A, Penney R, Solo-Gabriele H. 2017. A review of the field on children's exposure to environmental contaminants: a risk assessment approach. *Int. J. Environ. Res. Public Health* 14(3):265
43. Field RA, Soltis J, McCarthy MC, Murphy S, Montague DC. 2015. 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. *Atmos. Chem. Phys.* 15(6):3527–42
44. Field RA, Soltis J, Murphy S. 2014. Air quality concerns of unconventional oil and natural gas production. *Environ. Sci. Process Impacts* 16(5):954–69
45. Field RA, Soltis JJ, Perez-Ballesta P, Grandesso E, Montague DC. 2015. Distributions of air pollutants associated with oil and natural gas development measured in the Upper Green River Basin of Wyoming. *Elem.-Sci. Anthr.* 3:1–14
46. Ghosh B. 2018. Impact of changes in oil and gas production activities on air quality in Northeastern Oklahoma: ambient air studies in 2015–2017. *Environ. Sci. Technol.* 52(5):3285–94
47. Ghosh JKC, Wilhelm M, Su J, Goldberg D, Cockburn M, et al. 2012. 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.* 175(12):1262–74
48. Gilman JB, Lerner BM, Kuster WC, de Gouw JA. 2013. Source signature of volatile organic compounds from oil and natural gas operations in Northeastern Colorado. *Environ. Sci. Technol.* 47(3):1297–305
49. Goelen E, Lambrechts M, Geyskens F. 1997. Sampling intercomparisons for aldehydes in simulated workplace air. *Analyst* 122(5):411–19
50. Goetz JD, Avery A, Werden B, Floerchinger C, Fortner EC, et al. 2017. Analysis of local-scale background concentrations of methane and other gas-phase species in the Marcellus Shale. *Elem.-Sci. Anthr.* 5:1–20
51. Goetz JD, Floerchinger C, Fortner EC, Wormhoudt J, Massoli P, et al. 2015. Atmospheric emission characterization of Marcellus Shale natural gas development sites. *Environ. Sci. Technol.* 49(11):7012–20
52. Goldstein BD, Brooks BW, Cohen SD, Gates AE, Honeycutt ME, et al. 2014. The role of toxicological science in meeting the challenges and opportunities of hydraulic fracturing. *Toxicol. Sci.* 139(2):271–83
53. Haley M, McCawley M, Epstein AC, Arrington B, Bjerke EF. 2016. Adequacy of current state setbacks for directional high-volume hydraulic fracturing in the Marcellus, Barnett, and Niobrara Shale Plays. *Environ. Health Perspect.* 124(9):1323–33
54. Halliday HS, Thompson AM, Wisthaler A, Blake DR, Hornbrook RS, et al. 2016. Atmospheric benzene observations from oil and gas production in the Denver-Julesburg Basin in July and August 2014. *J. Geophys. Res.-Atmos.* 121(18):11055–74
55. Harrison RJ, Retzer K, Kosnett MJ, Hodgson M, Jordan T, et al. 2016. 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* 65(1):6–9
56. Helmig D, Thompson CR, Evans J, Boylan P, Hueber J, Park J-H. 2014. Highly elevated atmospheric levels of volatile organic compounds in the Uintah Basin, Utah. *Environ. Sci. Technol.* 48(9):4707–15
57. Herrington JS, Hays MD. 2012. Concerns regarding 24-h sampling for formaldehyde, acetaldehyde, and acrolein using 2,4-dinitrophenylhydrazine (DNPH)-coated solid sorbents. *Atmos. Environ.* 55:179–84
58. Hildenbrand ZL, Carlton DD Jr., Fontenot BE, Meik JM, Walton JL, et al. 2015. A comprehensive analysis of groundwater quality in the Barnett Shale region. *Environ. Sci. Technol.* 49(13):8254–62
59. Hildenbrand ZL, Mach PM, McBride EM, Dorreyatim MN, Taylor JT, et al. 2016. Point source attribution of ambient contamination events near unconventional oil and gas development. *Sci. Total Environ.* 573:382–88
60. Hill E. 2015. *Three essays on the impact of unconventional drilling on early life health*. PhD Thesis, Cornell Univ., Charles Dyson Sch. Appl. Econ. Manag.
61. Ho KF, Lee SC, Ho WK, Blake DR, Cheng Y, et al. 2009. Vehicular emission of volatile organic compounds (VOCs) from a tunnel study in Hong Kong. *Atmos. Chem. Phys.* 9(19):7491–504
62. Ho SSH, Ho KF, Liu WD, Lee SC, Dai WT, et al. 2011. Unsuitability of using the DNPH-coated solid sorbent cartridge for determination of airborne unsaturated carbonyls. *Atmos. Environ.* 45(1):261–65

63. Koh D-H, Jeon H-K, Lee S-G, Ryu H-W. 2015. The relationship between low-level benzene exposure and blood cell counts in Korean workers. *Occup. Environ. Med.* 72(6):421–27
64. Lan Q, Zhang L, Li G, Vermeulen R, Weinberg RS, et al. 2004. Hematotoxicity in workers exposed to low levels of benzene. *Science* 306(5702):1774–76
65. Lan X, Talbot R, Laine P, Torres A, Lefer B, Flynn J. 2015. Atmospheric mercury in the Barnett Shale area, Texas: implications for emissions from oil and gas processing. *Environ. Sci. Technol.* 49(17):10692–700
66. Leighton Consult. 2016. *Summary report: time critical residential indoor environmental sampling Aliso Canyon natural gas incident Porter Ranch community*. Summ. Rep. 603287.048, County Los Angel., Dep. Public Environ. Health, Irvine, CA
67. Li R, Warneke C, Graus M, Field R, Geiger F, et al. 2014. Measurements of hydrogen sulfide (H<sub>2</sub>S) using PTR-MS: calibration, humidity dependence, inter-comparison and results from field studies in an oil and gas production region. *Atmos. Meas. Tech.* 7(10):3597–610
68. Litovitz A, Curtright A, Abramzon S, Burger N, Samaras C. 2013. Estimation of regional air-quality damages from Marcellus Shale natural gas extraction in Pennsylvania. *Environ. Res. Lett.* 8(1):014017
69. Llop S, Ballester F, Estarlich M, Esplugues A, Rebagliato M, Iñiguez C. 2010. Preterm birth and exposure to air pollutants during pregnancy. *Environ. Res.* 110(8):778–85
70. Long JCS, Feinstein LF, Birkholzer J, Jordan P, Houseworth J, et al. 2015. *An independent scientific assessment of well stimulation in California*. Vol. 1. *Well stimulation technologies and their past, present, and potential future use in California*. Exec. Summ. Rep., Calif. Coun. Sci. Technol. Lawrence Berkeley Natl. Lab., Berkeley, CA. [https://sntr.senate.ca.gov/sites/sntr.senate.ca.gov/files/2\\_11\\_15\\_ccst\\_volume\\_1.pdf](https://sntr.senate.ca.gov/sites/sntr.senate.ca.gov/files/2_11_15_ccst_volume_1.pdf)
71. Lupo PJ, Symanski E, Waller DK, Chan W, Langlois PH, et al. 2011. Maternal exposure to ambient levels of benzene and neural tube defects among offspring: Texas, 1999–2004. *Environ. Health Perspect.* 119(3):397–402
72. Lyon DR, Alvarez RA, Zavala-Araiza D, Brandt AR, Jackson RB, Hamburg SP. 2016. Aerial surveys of elevated hydrocarbon emissions from oil and gas production sites. *Environ. Sci. Technol.* 50(9):4877–86
73. Macey GP, Breech R, Chernaik M, Cox C, Larson D, et al. 2014. Air concentrations of volatile compounds near oil and gas production: a community-based exploratory study. *Environ. Health* 13(1):82
74. Marchetti F, Eskenazi B, Weldon RH, Li G, Zhang L, et al. 2012. Occupational exposure to benzene and chromosomal structural aberrations in the sperm of Chinese men. *Environ. Health Perspect.* 120(2):229–34
75. Marrero JE, Townsend-Small A, Lyon DR, Tsai TR, Meinardi S, Blake DR. 2016. Estimating emissions of toxic hydrocarbons from natural gas production sites in the Barnett Shale region of Northern Texas. *Environ. Sci. Technol.* 50(19):10756–64
76. Maskrey JR, Insley AL, Hyndes ES, Panko JM. 2016. Air monitoring of volatile organic compounds at relevant receptors during hydraulic fracturing operations in Washington County, Pennsylvania. *Environ. Monit. Assess.* 188(7):410
77. McCarthy MC, O'Brien TE, Charrier JG, Hafner HR. 2009. Characterization of the chronic risk and hazard of hazardous air pollutants in the United States using ambient monitoring data. *Environ. Health Perspect.* 117(5):790–96
78. McKenzie LM, Blair B, Hughes J, Allshouse WB, Blake NJ, et al. 2018. Ambient nonmethane hydrocarbon levels along Colorado's Northern Front Range: acute and chronic health risks. *Environ. Sci. Technol.* 52(8):4514–25
79. McKenzie LM, Witter RZ, Newman LS, Adgate JL. 2012. Human health risk assessment of air emissions from development of unconventional natural gas resources. *Sci. Total Environ.* 424:79–87
80. Moore CW, Zielinska B, Pétron G, Jackson RB. 2014. Air impacts of increased natural gas acquisition, processing, and use: a critical review. *Environ. Sci. Technol.* 48(15):8349–59
81. Morello-Frosch RA, Woodruff TJ, Axelrad DA, Caldwell JC. 2000. Air toxics and health risks in California: the public health implications of outdoor concentrations. *Risk Anal.* 20(2):273–92

82. NYSDEC (NY State Dep. Environ. Conserv.). 2015. *Final supplemental generic environmental impact statement on the oil, gas, and solution mining regulatory program*. Rep., N.Y. State Dep. Environ. Conserv., Albany. [http://www.dec.ny.gov/docs/materials\\_minerals\\_pdf/fsgeis2015.pdf](http://www.dec.ny.gov/docs/materials_minerals_pdf/fsgeis2015.pdf)
83. OEHHA (Off. Environ. Health Hazard Assess.). 2000. *Appendix D.3 Chronic RELs and toxicity summaries using the previous version of the Hot Spots Risk Assessment guidelines (OEHHA 1999)*. Rep., OEHHA, Sacramento. <https://oehha.ca.gov/media/downloads/crn/appendixd3final.pdf>
84. OEHHA (Off. Environ. Health Hazard Assess.). 2014. *Appendix D. Individual acute, 8-hour, and chronic reference exposure level summaries*. Rep., OEHHA, Sacramento. <https://oehha.ca.gov/media/downloads/crn/appendixd1final.pdf>
85. Paulik LB, Donald CE, Smith BW, Tidwell LG, Hobbie KA, et al. 2016. Emissions of polycyclic aromatic hydrocarbons from natural gas extraction into air. *Environ. Sci. Technol.* 50(14):7921–29
86. Pekney NJ, Veloski G, Reeder M, Tamilia J, Rupp E, Wetzel A. 2014. 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.* 64(9):1062–72
87. Pénard-Morand C, Raheison C, Charpin D, Kopferschmitt C, Lavaud F, et al. 2010. Long-term exposure to close-proximity air pollution and asthma and allergies in urban children. *Eur. Respir. J.* 36(1):33–40
88. Pétron G, Frost G, Miller BR, Hirsch AI, Montzka SA, et al. 2012. Hydrocarbon emissions characterization in the Colorado Front Range: a pilot study. *J. Geophys. Res.-Atmos.* 117:D04304
89. Prenni AJ, Day DE, Evanowski-Cole AR, Sive BC, Hecobian A, et al. 2016. Oil and gas impacts on air quality in federal lands in the Bakken region: an overview of the Bakken Air Quality Study and first results. *Atmos. Chem. Phys.* 16(3):1401–16
90. Rich A, Grover JP, Sattler ML. 2014. An exploratory study of air emissions associated with shale gas development and production in the Barnett Shale. *J. Air Waste Manag. Assoc.* 64(1):61–72
91. Rich AL, Orimoloye HT. 2016. Elevated atmospheric levels of benzene and benzene-related compounds from unconventional shale extraction and processing: human health concern for residential communities. *Environ. Health Insights* 10:75–82
92. Russo PN, Carpenter DO. 2017. *Health effects associated with stack chemical emissions from NYS natural gas compressor stations: 2008–2014*. Rep., Inst. Health Environ., Univ. Albany, Rensselaer, NY. [https://www.albany.edu/about/assets/Complete\\_report.pdf](https://www.albany.edu/about/assets/Complete_report.pdf)
93. Schade GW, Roest G. 2016. 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.* 4:000096
94. Shonkoff SBC, Hill LAL, Czolowski ED, Prasad K, Hammond SK, McKone TE. 2018. Human health hazards, risks, and impacts associated with underground natural gas storage in California. In *Long-term viability of underground natural gas storage in California: an independent review of scientific and technical information*. Rep., Calif. Coun. Sci. Technol., Sacramento
95. Sommariva R, Blake RS, Cuss RJ, Cordell RL, Harrington JF, et al. 2014. Observations of the release of non-methane hydrocarbons from fractured shale. *Environ. Sci. Technol.* 48(15):8891–96
96. Stacy SL, Brink LL, Larkin JC, Sadovsky Y, Goldstein BD, et al. 2015. Perinatal outcomes and unconventional natural gas operations in Southwest Pennsylvania. *PLOS ONE* 10(6):e0126425
97. Steinzor N, Subra W, Sumi L. 2013. Investigating links between shale gas development and health impacts through a community survey project in Pennsylvania. *New Solut.* 23(1):55–83
98. Swarthout RF, Russo RS, Zhou Y, Hart AH, Sive B. 2013. Volatile organic compound distributions during the NACHTT campaign at the Boulder Atmospheric Observatory: influence of urban and natural gas sources. *J. Geophys. Res. Atmos.* 118(18):10614–37
99. Swarthout RF, Russo RS, Zhou Y, Miller BM, Mitchell B, et al. 2015. Impact of Marcellus Shale natural gas development in southwest Pennsylvania on volatile organic compound emissions and regional air quality. *Environ. Sci. Technol.* 49(5):3175–84
100. Tam BN, Neumann CM. 2004. A human health assessment of hazardous air pollutants in Portland, OR. *J. Environ. Manag.* 73(2):131–45
101. TEDX (Endocr. Disrupt. Exch.). 2017. Oil and gas spreadsheets. *Oil & Gas Program*. <https://endocrinedisruption.org/audio-and-video/chemical-health-effects-spreadsheets>

102. Thompson CR, Hueber J, Helmig D. 2014. Influence of oil and gas emissions on ambient atmospheric non-methane hydrocarbons in residential areas of Northeastern Colorado. *Elem.-Sci. Anthr.* 2:000035
103. US EIA (Energy Inf. Adm.). 2016. *International energy outlook 2016*. Rep., DOE/EIA-0484, U.S. Energy Inf. Adm., Washington, DC. [https://www.eia.gov/outlooks/ieo/pdf/0484\(2016\).pdf](https://www.eia.gov/outlooks/ieo/pdf/0484(2016).pdf)
104. US EIA (Energy Inf. Adm.). 2018. *Short-term energy outlook (STEO)*. News Release, Feb. 2018. <https://www.eia.gov/outlooks/steo/archives/feb18.pdf>
105. US EPA (Environ. Prot. Agency). 1986. *Guidelines for the health risk assessment of chemical mixtures*. EPA/630/R-98/002, US EPA, Washington, DC. [https://www.epa.gov/sites/production/files/2014-11/documents/chem\\_mix\\_1986.pdf](https://www.epa.gov/sites/production/files/2014-11/documents/chem_mix_1986.pdf)
106. US EPA (Environ. Prot. Agency). 1999. *EPCRA section 313 industry guidance*. 745-B-99-005, US EPA, Washington, DC. <https://www.epa.gov/sites/production/files/documents/1999chem.pdf>
107. US EPA (Environ. Prot. Agency). 2013. The Clean Air Act Amendments of 1990 list of hazardous air pollutants. *Technology Transfer Network—Air Toxics Web Site*. <http://www.epa.gov/ttn/atw/orig189.html>
108. US EPA (Environ. Prot. Agency). 2015. *Assessment of the potential impacts of hydraulic fracturing for oil and gas on drinking water resources—external review draft*. EPA/600/R-15/047a, Off. Res. Dev., US EPA, Washington, DC. [http://ofmpub.epa.gov/eims/eimscomm.getfile?p\\_download\\_id=523539](http://ofmpub.epa.gov/eims/eimscomm.getfile?p_download_id=523539)
109. US House Represent. Comm. Energy Commer. Minor. Staff. 2011. *Chemicals used in hydraulic fracturing*. Rep., US House Represent. Comm. Energy Commer. Minor. Staff, Washington, DC
110. Vesterinen HM, Morello-Frosch R, Sen S, Zeise L, Woodruff TJ. 2017. Cumulative effects of prenatal-exposure to exogenous chemicals and psychosocial stress on fetal growth: systematic-review of the human and animal evidence. *PLOS ONE* 12(7):e0176331
111. Warneke C, Geiger F, Edwards PM, Dube W, Pétron G, et al. 2014. 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. *Atmos. Chem. Phys.* 14(20):10977–88
112. Warneke C, Geiger F, Edwards PM, Dube W, Pétron G, et al. 2014. 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.* 14(8):11895–927
113. Webb E, Bushkin-Bedient S, Cheng A, Kassotis CD, Balise V, Nagel SC. 2014. Developmental and reproductive effects of chemicals associated with unconventional oil and natural gas operations. *Rev. Environ. Health* 29(4):307–18
114. Werner AK, Vink S, Watt K, Jagals P. 2015. Environmental health impacts of unconventional natural gas development: a review of the current strength of evidence. *Sci. Total Environ.* 505:1127–41
115. Weyant CL, Shepson PB, Subramanian R, Cambaliza MOL, Heimbürger A, et al. 2016. Black carbon emissions from associated natural gas flaring. *Environ. Sci. Technol.* 50(4):2075–81
116. WHO (World Health Organ.). 2000. *Air quality guidelines for Europe*. Rep., WHO Reg. Off. Eur., Copenhagen. [http://www.euro.who.int/\\_data/assets/pdf\\_file/0005/74732/E71922.pdf](http://www.euro.who.int/_data/assets/pdf_file/0005/74732/E71922.pdf)
117. Wilbur S, Bosch S. 2004. *Interaction profile for benzene, toluene, ethylbenzene, and xylenes (BTEX)*. Rep., Agency Toxic Subst. Dis. Regist., US Dep. Health Hum. Serv., Atlanta. <https://www.atsdr.cdc.gov/interactionprofiles/ip-btex/ip05.pdf>
118. Woodruff TJ, Axelrod DA, Cadwell J, Morello-Frosch R, Rosenbaum A. 1998. Public health implications of 1990 air toxics concentrations across the United States. *Environ. Health Perspect.* 106(5):245–51
119. Xing C, Marchetti F, Li G, Weldon RH, Kurtovich E, et al. 2010. Benzene exposure near the U.S. permissible limit is associated with sperm aneuploidy. *Environ. Health Perspect.* 118(6):833–39
120. Yuan B, Kaser L, Karl T, Graus M, Peischl J, et al. 2015. Airborne flux measurements of methane and volatile organic compounds over the Haynesville and Marcellus shale gas production regions. *J. Geophys. Res.-Atmos.* 120(12):6271–89
121. Zahran S, Weiler S, Mielke HW, Pena AA. 2012. Maternal benzene exposure and low birth weight risk in the United States: a natural experiment in gasoline reformulation. *Environ. Res.* 112:139–46
122. Zavala-Araiza D, Allen DT, Harrison M, George FC, Jersey GR. 2015. Allocating methane emissions to natural gas and oil production from shale formations. *ACS Sustain. Chem. Eng.* 3(3):492–98

123. Zavala-Araiza D, Alvarez RA, Lyon DR, Allen DT, Marchese AJ, et al. 2017. Super-emitters in natural gas infrastructure are caused by abnormal process conditions. *Nat. Commun.* 8:14012
124. Zhou C, Baiz N, Banerjee S, Charpin DA, Caillaud D, et al. 2013. The relationships between ambient air pollutants and childhood asthma and eczema are modified by emotion and conduct problems. *Ann. Epidemiol.* 23(12):778–83.e3
125. Zielinska B, Campbell D, Samburova V. 2014. 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.* 64(12):1369–83