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Environmental and individual PAH exposures near rural natural gas extraction☆

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ABSTRACT

Natural gas extraction (NGE) has expanded rapidly in the United States in recent years. Despite concerns, there is little information about the effects of NGE on air quality or personal exposures of people living or working nearby. Recent research suggests NGE emits polycyclic aromatic hydrocarbons (PAHs) into air. This study used low-density polyethylene passive samplers to measure concentrations of PAHs in air near active ($n = 3$) and proposed ($n = 2$) NGE sites. At each site, two concentric rings of air samplers were placed around the active or proposed well pad location. Silicone wristbands were used to assess personal PAH exposures of participants ($n = 19$) living or working near the sampling sites. All samples were analyzed for 62 PAHs using GC-MS/MS, and point sources were estimated using the fluoranthene/pyrene isomer ratio. $\sum$PAH was significantly higher in air at active NGE sites (Wilcoxon rank sum test, $p < 0.01$). PAHs in air were also more petrogenic (petroleum-derived) at active NGE sites. This suggests that PAH mixtures at active NGE sites may have been affected by direct emissions from petroleum sources at these sites. $\sum$PAH was also significantly higher in wristbands from participants who had active NGE wells on their properties than from participants who did not (Wilcoxon rank sum test, $p < 0.005$). There was a significant positive correlation between $\sum$PAH in participants' wristbands and $\sum$PAH in air measured closest to participants' homes or workplaces (simple linear regression, $p < 0.0001$). These findings suggest that living or working near an active NGE well may increase personal PAH exposure. This work also supports the utility of the silicone wristband to assess personal PAH exposure.

1. Introduction

Natural gas extraction (NGE) from shale has expanded rapidly in the United States in the last 15 years. This is largely due to technological improvements to hydraulic fracturing and horizontal drilling (colloquially known as "fracking"), which liberate previously inaccessible gas reserves from shale (EIA, 2011).

There is a need for data that directly assesses the environmental and public health impacts of NGE (Adgate et al., 2014; Goldstein et al., 2014; Penning et al., 2014). Some studies have acknowledged that reduced air quality may be the most significant risk to communities near NGE (McKenzie et al., 2012; Litovitz et al., 2013; Adgate et al., 2014; Bunch et al., 2014; Colborn et al., 2014; McKenzie et al., 2014; Roy et al., 2014; Shonkoff et al., 2014; Boyle et al., 2016; Fawole et al., 2016; Paulik et al., 2016a; Rasmussen et al., 2016). There is evidence that NGE emits methane (Brandt et al., 2014; Brantley et al., 2014), volatile organic compounds (VOCs) (McKenzie et al., 2012; Pétron et al., 2012; Macey et al., 2014; Roy et al., 2014; Marrero et al., 2016) and semi-volatile organic compounds (SVOCs) (Colborn et al., 2014; Paulik et al., 2016a). Recent studies have concluded that exposure to NGE emissions may pose health risks, and that many important data gaps remain (Shonkoff et al., 2014; Ward et al., 2016).

One class of SVOCs that has been measured in air near NGE is polycyclic aromatic hydrocarbons (PAHs) (Colborn et al., 2014; Paulik et al., 2016a; Elliott et al., 2017). PAHs are pervasive environmental pollutants that are commonly associated with fossil fuel production (Ana et al., 2012). PAHs are also commonly associated with and adverse health outcomes such as increased cancer risk

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(Menzie et al., 1992; Baird et al., 2005), respiratory distress (Miller et al., 2004; Padula et al., 2015), and developmental effects (Perera et al., 2009; Perera and Herbstman, 2011).

PAHs exist in two states in air: freely dissolved in the "gas phase" and bound to particles in the "particulate phase". The majority of research on health effects of inhaling PAHs has focused only on PAHs measured in the particulate phase. However, a growing body of evidence suggests that PAHs in the gas phase also contribute to the toxicity of inhaled PAH mixtures (Tsai et al., 2002; Liu et al., 2007; Samburova et al., 2017).

While carcinogenic potencies are typically higher for individual PAHs with higher molecular weights, lower molecular weight PAHs are often present at significantly higher concentrations in the gas phase; this can increase the contribution of gas phase PAHs to the total carcinogenic potency of a PAH mixture (Liu et al., 2007). In a recent review, Samburova et al. evaluated 13 studies and concluded that only measuring particulate phase PAHs significantly underrepresented the carcinogenic potency of PAH mixtures compared to measuring both the gas and particulate phases (Samburova et al., 2017). Samburova et al. made the recommendation that "gas-phase PAHs be included because of their strong contribution to the total [carcinogenic potency]" (Samburova et al., 2017). These findings provide rationale for measuring exposure to the fraction of PAHs in the gas phase, even if data for the particulate fraction is not available.

Increased understanding of the environmental fate of PAHs emitted from NGE would answer questions about the potential environmental health impacts of these emissions.

As air quality sampling moves toward more cost-effective and user-friendly techniques (Snyder et al., 2013), passive air sampling is becoming an increasingly more relevant tool. Low-density polyethylene (LDPE) passive samplers sequester freely dissolved lipophilic compounds through passive diffusion in a time-integrated manner (Huckins et al., 2006; Anderson et al., 2008; Lohmann, 2012; O'Connell et al., 2014; Paulik et al., 2016b; Tidwell et al., 2017). Since the development of LDPE as an air sampler in the 1990s, many studies have demonstrated its ability to measure gas phase PAHs in air (Petty et al., 1993; Prest et al., 1995; Bartkow et al., 2004; Khairy and Lohmann, 2012; Paulik et al., 2016a). In this study, stationary LDPE passive air samplers were used to perform spatial assessments of PAH concentrations in air at five NGE sites: three sites with active NGE wells and two proposed NGE sites. This sampling design allowed for assessment of emissions from the point sources and spatial assessment of PAHs in air at these sites.

In addition to questions surrounding the environmental fate of PAHs emitted from NGE, there is concern regarding human health and personal exposure to PAHs emitted from NGE (Penning et al., 2014; Werner et al., 2015). Some studies have used data from stationary monitors to estimate community-level health impacts (McKenzie et al., 2012; Bunch et al., 2014; Colborn et al., 2014; Marrero et al., 2016; Paulik et al., 2016a), while others have used health records or questionnaire responses to approximate individual health impacts of NGE (Brasier et al., 2011; Bamberger and Oswald, 2014; McKenzie et al., 2014; Rabinowitz et al., 2015; Rasmussen et al., 2016; Tustin et al., 2016). Still others have predicted exposures associated with NGE from emissions inventories or known toxicity information of chemicals reportedly used in NGE (Colborn et al., 2011; Roy et al., 2014; Boyle et al., 2016; Elliott et al., 2017). Personal monitoring is an effective tool for assessing individuals' contaminant exposures, as personal monitors yield more accurate exposure estimates than approximating exposure from questionnaires or extrapolating exposure from stationary monitoring data (Bohlin et al., 2007, Paulik and Anderson, 2018). To date, no study has directly measured personal PAH exposures of people living or working near active NGE wells.

Personal exposure to PAHs and other SVOCs has previously been assessed by active and passive personal monitors (Perera et al., 2003; Bohlin, Jones et al. 2007, 2010; Zhu et al., 2011; Herbstman et al., 2012). The silicone wristband (hereafter "wristband"), is a novel personal sampler that absorbs VOCs and SVOCs (O'Connell et al., 2014; Donald et al., 2016; Kile et al., 2016; Bergmann et al., 2017; Dixon et al., 2018). The wristband is lightweight, small, and easy to use, and it does not require a motor or batteries. In this study, 23 participants living or working near the five stationary air sampling sites wore wristbands to assess their personal PAH exposures.

This study combined stationary and personal passive sampling techniques to: a) compare PAH concentrations in air at active and proposed NGE sites, b) compare sources of PAHs at active and proposed NGE sites, and c) assess the contribution of active NGE wells to personal PAH exposure.

2. Materials and methods

2.1. Site description

This study was conducted in Carroll County and bordering counties of rural eastern Ohio, in the United States. This region has been heavily affected by the U.S. natural gas boom, as it sits atop natural gas and oil reserves in both the Utica and Marcelles shale formations. In 2014 Carroll County had the highest number of active wells in Ohio (Carlton et al., 2014). This historically rural region was expected to have limited pre-existing anthropogenic sources of pollution, relative to an industrial area or a city. The sampling was conducted on individual residential properties. The exact sampling locations are therefore not provided to protect the confidentiality of the participants. Landowners for stationary sampling and participants for personal sampling were identified through collaboration with a local community group. This study was approved by the Institutional Review Boards (IRB) at the University of Cincinnati (UC) and Oregon State University (OSU); UC was the IRB of record.

2.2. Sampling design

Stationary passive LDPE air samplers (hereafter referred to as LDPE) were deployed at five sites that were permitted for NGE activity. At the time of the study three of those sites had active NGE well pads, with NGE activity occurring on the well pads during the sampling period (hereafter referred to as "active" sites, labeled as sites A1-A3). These sites also had small service roads leading to the NGE well pads. The remaining two sites had neither well pads nor NGE activity occurring at the time of sampling (hereafter referred to as "proposed" sites, labeled as sites P1-P2). Sites were selected from a prior air sampling campaign (Paulik et al., 2016a) based on their NGE status. Landowners from each site agreed to have air samplers and communicate with study team regarding activity on the sites (e.g., farming activity, new NGE activity, planting/grazing needs). During sampler deployment, researchers trained landowners in protocols necessary to maintain sample integrity while retrieving and mailing LDPE to OSU for analysis.

At each site, six stationary air sampler cages were arranged in two concentric rings (each containing three LDPE samplers) around either the active NGE well pad or the proposed NGE well pad location (Fig. 1). This design yielded a total of 30 samplers. The inner and outer rings of samplers were 55–60 m and 112–122 m, respectively, from the edges of the active or proposed well pads at each site. Researchers worked with landowners to choose specific locations for sampling cages within each site. Care was taken to minimize both a) inputs from potentially confounding PAH sources