

Impact of Natural Gas Extraction on PAH Levels in Ambient Air

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S Supporting Information

ABSTRACT: Natural gas extraction, often referred to as “fracking,” has increased rapidly in the U.S. in recent years. To address potential health impacts, passive air samplers were deployed in a rural community heavily affected by the natural gas boom. Samplers were analyzed for 62 polycyclic aromatic hydrocarbons (PAHs). Results were grouped based on distance from each sampler to the nearest active well. PAH levels were highest when samplers were closest to active wells. Additionally, PAH levels closest to natural gas activity were an order of magnitude higher than levels previously reported in rural areas. Sourcing ratios indicate that PAHs were predominantly petrogenic, suggesting that elevated PAH levels were influenced by direct releases from the earth. Quantitative human health

risk assessment estimated the excess lifetime cancer risks associated with exposure to the measured PAHs. Closest to active wells, the risk estimated for maximum residential exposure was 2.9 in 10 000, which is above the U.S. EPA’s acceptable risk level. Overall, risk estimates decreased 30% when comparing results from samplers closest to active wells to those farthest. This work suggests that natural gas extraction may be contributing significantly to PAHs in air, at levels that are relevant to human health.



INTRODUCTION

Natural gas extraction from shale, colloquially known as “fracking,” has increased substantially in the United States in the past 15 years. U.S. shale gas production grew by 17% annually from 2000 to 2006, and then grew by 48% from 2006 to 2010.¹ This spike in activity has been driven predominantly by improvements to the technologies of horizontal drilling and hydraulic fracturing. Together, these processes enable companies to access gas reserves previously out of reach. As of 2011, the U.S. Energy Information Administration estimated that roughly 750 trillion cubic feet of natural gas were recoverable from shale reserves in the contiguous United States using these approaches.²

Despite this rapid expansion and implementation of technology, there has been relatively little research into the environmental and health impacts these processes may have. There has also been a lack of regulation, illustrated by the U.S. Energy Policy Act of 2005, which amended portions of the U.S. Safe Drinking Water Act and Clean Water Act to give gas-drilling companies more flexibility.³ Concerns have arisen about the impacts that natural gas extraction (hereafter NGE) may have on environmental and human health, due in part to this historic lack of regulation.^{4–7} In the past five years, studies have emerged assessing the impacts this activity may have on water quality, air quality, and human health.^{8–20}

Many studies have acknowledged that impact to air quality may be the most significant risk to communities living near NGE.^{8–15} Shonkoff et al. concluded that NGE has the potential to pose health risks through both air and water emissions, and urged that many important data gaps remain.⁹

Most of the air quality studies have focused on emissions of volatile organic compounds (VOCs). McKenzie et al. sampled air near NGE wells at different stages, measuring VOCs including BTEX (benzene, toluene, ethylbenzene and xylenes) and aliphatic hydrocarbons.¹⁰ They performed a public health risk assessment and found an increased risk of cancer and noncancer endpoints for people living within 0.5 miles of NGE well pads.¹⁰ In a subsequent study, McKenzie et al. assessed the correlation between decreased birth outcomes and NGE. They found an increase in congenital heart defects and neural tube defects as mothers’ residences got closer to NGE wells.¹¹ Roy et al. estimated emissions from NGE in the Marcellus Shale, and predicted that NGE contributes an average of 12% of all NO_x and VOC emissions to air in a given location.¹² Bunch et al. studied regional VOC levels in a part of Texas with NGE.¹⁴ Contrary to the majority of the scientific literature, this study

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concluded that NGE is not polluting the air at concerning levels. However, Bunch et al. considered any risk estimates less than 1 in 10 000 not to be concerning, which is the upper limit of risk that the EPA considers acceptable.²¹

Many studies have assessed the impacts of NGE on public health.^{7,9–11,14,16–20,22} Colborn et al. performed a hazard assessment of the chemicals that are used during NGE, and concluded that over 70% of these chemicals are potentially risky to humans.⁷ Other work has focused on the impacts of NGE on communities.^{18,19,22} NGE often takes place in rural areas, where it may present a larger change to ambient pollutant levels than it would in urban areas.

Other studies have reviewed the state of the science surrounding NGE, emphasizing the need for more concerted field sampling and data generation. In one such review, Goldstein et al. called for toxicological studies to help characterize the potential risks of NGE activity.¹⁷ Small et al. assessed the state of the science and regulation surrounding NGE in the U.S. They called for improved characterization of air pollutants emitted from NGE and their potential health impacts, and concluded that risks associated with NGE “remain under-analyzed”.⁶ Despite the recent surge of literature surrounding NGE, there are still many data gaps.

One data gap is the relationship between polycyclic aromatic hydrocarbons (PAHs) and NGE. PAHs are pervasive environmental pollutants of concern, known to be associated with both hydrocarbon extraction and negative health impacts.^{23,24} The main categories of health concerns associated with exposure to PAH mixtures are cancer risk and respiratory distress. PAH-related cancer risk has received a great deal of attention in relation to oil spills, traffic exhaust, wood smoke, and cooking. NGE involves extracting hydrocarbons from the earth, a process that is often associated with PAH emissions. NGE also brings large volumes of truck traffic into an area to move building materials, water, and product. Each of these stages could be sources of PAHs. Goldstein et al. and Adgate et al. both specifically include PAHs as a potential health concern at many or all stages of NGE.^{8,17} Colborn et al. sampled air near NGE well pads for 16 PAHs.¹⁵ However, they ceased sampling PAHs after the drilling phase ended. They later concluded that PAH levels during drilling were of concern to human health, citing that these levels ($\sum\text{PAH}_{16} \sim 15 \text{ ng/m}^3$) were comparable to those associated with small but significant decreases in IQ at 5 years of age in children exposed in utero.²⁵ Colborn et al. conclude that the relationship between NGE and PAH emissions “deserves further investigation.”¹⁵

Passive sampling could fill this data gap. Low-density polyethylene (LDPE) passive samplers sequester hydrophobic compounds through passive diffusion in a time-integrated manner, and are well-suited to passively sample vapor phase PAHs from air. Since this tool's development in the 1990s, many studies have demonstrated its ability to measure PAHs.^{26–29} The objective of this study was to use passive sampling to assess the impact of NGE on PAH levels in air in a rural community.

MATERIALS AND METHODS

Site Description and Sampling Design. This study took place predominantly in rural Carroll County, Ohio. As technology has made gas in the Utica shale more accessible in the last five years, NGE in eastern Ohio has increased. In 2011, Ohio had less than 50 horizontal natural gas drilling

leases.³⁰ As of June 2014, that number had jumped to 1386, with 421 in Carroll County.³¹

Passive air samplers were deployed on the properties of 23 volunteers in February 2014. Volunteer landowners were identified by advertisement through a community meeting and word of mouth. Volunteers were excluded from the study if their properties were within a city limit, near an airport, or otherwise could have presented results that were difficult to interpret due to substantial background PAH levels. Each sampling site was located between 0.04 and 3.2 miles from an active NGE well pad. Oregon State University (OSU) researchers deployed one sampler on each volunteer's land. Each sampler consisted of three LDPE strips in a metal cage. Sampling was replicated in triplicate at one site. The OSU research team has over 10 years of field sampling experience collectively. The team took care to place samplers as far as possible from potentially confounding PAH sources such as chimneys or roads. Samplers were deployed for 3–4 weeks, and then trained landowners mailed them to the Food Safety and Environmental Stewardship (FSES) lab at OSU in Corvallis, OR. Volunteer training is described further in the Supporting Information (SI). Samplers were transported in airtight polytetrafluoroethylene bags with Clip N Seal assemblies (Welch Fluorocarbon). Landowners were provided individual results from air sampling on their property. To put results in context, individual results were compared to a summary of results from all sampling sites.

Passive Sampler Preparation, Cleaning and Extraction. Details about chemicals and solvents are in the SI. Before deployment, LDPE was cleaned using hexanes as described previously.³² Each LDPE strip was infused with performance reference compounds (PRCs) to enable calculation of in situ sampling rates and time-integrated air concentrations.³³ PRCs used in this study were fluorene-d10, pyrene-d10 and benzo[b]fluoranthene-d12. PRCs were spiked into LDPE at 2–20 μg per strip. Samplers were cleaned after deployment in two isopropanol baths, stored in amber jars at -20°C , and extracted as described elsewhere.³² Briefly, extractions were performed using two dialyses with *n*-hexane. Prior to extraction, samples were spiked with deuterated PAHs to act as surrogate standards, allowing for quantification of extraction efficiency. Surrogate standards are specified in SI Table S1. Extracts were quantitatively concentrated to 1 mL using TurboVap closed cell evaporators, transferred to amber chromatography vials, and stored at -20°C .

Chemical Analysis. LDPE extracts were quantitatively analyzed for 62 PAHs using an Agilent 7890A gas chromatograph interfaced with an Agilent 7000 GC/MS-MS. An Agilent Select PAH column was used. Each PAH was calibrated with a curve of at least five points, with correlations ≥ 0.99 . Limits of detection (LODs) range from 0.24 to 1.7 ng/mL, and limits of quantitation (LOQs) range from 1.0 to 7.1 ng/mL, with the exception of two compounds that have higher LODs and LOQs. A list of PAHs, LODs and LOQs is included in SI Table S1.

Air Concentration Calculation. Air concentrations (ng/m^3) of PAHs were calculated from instrument concentrations (ng/mL) using PRCs. In situ sampling rates (R_s) were generated using calculations described by Huckins et al.³³ These calculations estimate the R_s of each PRC by incorporating deployment time, average temperature, initial amount and K_{OA} . An R_s is then calculated for each PAH, using

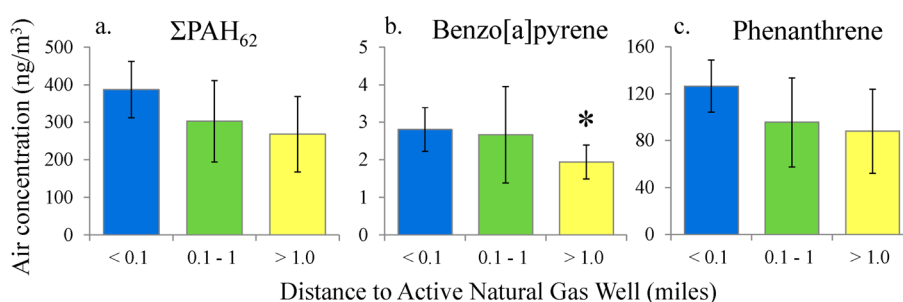


Figure 1. Average PAH concentrations grouped by distance to the closest active natural gas well. a. Sum of 62 PAHs, b. benzo[a]pyrene, and c. phenanthrene. The three distance groups are close ($n = 5$), middle ($n = 12$), and far ($n = 6$), defined in the text. Error bars represent one SD. The asterisk indicates a significant difference between the close and far groups for benzo[a]pyrene, $p < 0.05$.

the PAH's K_{OA} and the R_S of one of the PRCs. These calculations are included as SI eqs S1–S3.

Data Analysis. Data was grouped by distance from each sampling site to the closest active well pad. Three distance groups were created, with the “close” group <0.1 mile from an active well, the “middle” group from 0.1 to 1.0 mile from an active well, and the “far” group >1.0 mile from an active well. The close, middle and far groups had 5, 12, and 6 samples each. All results are presented in these three distance groups. Distances were determined using Google Earth version 7.1.2.2041, and well status information was taken from the Ohio Department of Natural Resource's Web site. A well was considered “active” if it was in the drilling, drilled, or producing stages at the time of sampling.

Parent PAH isomer ratios were used to determine sources of PAHs. Two PAH isomer pairs that are used to diagnose whether a PAH mixture is petrogenic or pyrogenic are phenanthrene and anthracene, and fluoranthene and pyrene.^{34–40} Phenanthrene/anthracene ratios ≤ 10 indicate pyrogenic sources, while ratios ≥ 15 indicate petrogenic sources.^{34,36–38} For this ratio, there is disagreement about interpretation of values between 10 and 15. Budzinski et al. state that values in this range suggest incomplete combustion of organic matter, and are thus pyrogenic.³⁴ Fluoranthene/pyrene ratios >1 indicate pyrogenic sources, while ratios <1 indicate petrogenic sources.^{34,37,38} Ratios of one isomer to the sum of both isomers are also used in PAH sourcing. Fluoranthene/(fluoranthene+pyrene) ratios ≥ 0.5 indicate pyrogenic sources, and ratios ≤ 0.4 indicate petrogenic sources.^{36,39} Yunker et al. suggests that ratios between 0.4 and 0.5 indicate liquid fossil fuel combustion.³⁵ Anthracene/(anthracene+phenanthrene) ratios <0.1 indicate petrogenic sources and ratios >0.1 indicate pyrogenic sources.^{35,39,40} A fifth ratio of two nonisomer parent PAHs, benzo[a]pyrene/benzo[g,h,i]perylene, was used to obtain sourcing information for the 5- and 6-ring PAHs measured in this study. For this ratio, values >0.6 are indicative of traffic emissions while values <0.6 indicate nontraffic emission sources.³⁹ There were samples in the middle and far groups for which benzo[a]pyrene, benzo[g,h,i]perylene, or both were below limits of detection (BLOD). So, the sample sizes for the close, middle, and far groups for this final ratio are 5, 9, and 4, respectively.

Risk Assessment. The carcinogenic potency of the PAH mixture at each site was calculated by multiplying the concentration of each PAH by the relative potency factor (RPF) it was given by the U.S. EPA.²³ A list of the RPFs is in SI Table S2. This estimate of carcinogenic potency is referred to as the benzo[a]pyrene equivalent concentration, or BaP_{eq}.

These values were used in quantitative risk assessments to estimate cancer risks of exposure to the measured PAHs through inhalation, using the EPA's framework.⁴¹ Exposure parameters were modeled after the “residential” and “outdoor worker” examples presented to Superfund risk assessors by the EPA in 2014.⁴² Specifically, the average lifetime was set at 70 years for all exposure scenarios. For the residential scenarios, exposure duration and exposure frequency were set at 26 years and 350 days/year, respectively. For the outdoor worker scenario, these parameters were set at 25 years and 225 days/year. The residential assessment was performed for a worst-case and best-case scenario, by adjusting the daily exposure time to 24 or 1 h, while the outdoor worker assessment was performed with daily exposure time set at 8 h. Risk assessment equations are included as SI equations S4–S5.

Statistical Analysis. Welch's two sample t tests were performed on the data for Σ PAH₆₂, benzo[a]pyrene, phenanthrene, pyrene, and carcinogenic potency, between each pairwise combination of distance groups, using R version 2.15.3. It was assumed that variance between each two groups was unequal. Results were deemed significantly different when $\alpha < 0.05$. Exploratory principle components analysis is included in SI Figure S1.

Quality Control. During passive sampler preparation, one LDPE strip was hung in the room to account for potential contamination during PRC infusion. In the field, sampling was replicated at one site, $n = 3$. A trip blank was taken to each sampling site to account for contamination during transport. One blank LDPE strip was included each day in the cleaning process after deployment, as a cleaning blank. This also doubled as a blank during sampler extraction. Perylene-d12 was spiked into all extracts at 500 ng/mL before instrumental analysis, to act as an internal standard. The analytical method was validated using its calibration, precision and accuracy, and detection limits prior to use. During instrument analysis, instrument blanks and continuing calibration verifications were run at the beginning and end of each set of samples. All laboratory and field procedures were performed according to FSES Standard Operating Procedures.

RESULTS AND DISCUSSION

PAH Levels and Trends. The data show a common trend: PAH levels decrease as samplers get farther from active NGE wells. Three distance groups were created, with the “close” group <0.1 mile from an active well, the “middle” group between 0.1 and 1.0 mile from an active well, and the “far” group >1.0 mile from an active well. This trend is consistent when comparing averages in the three distance groups for

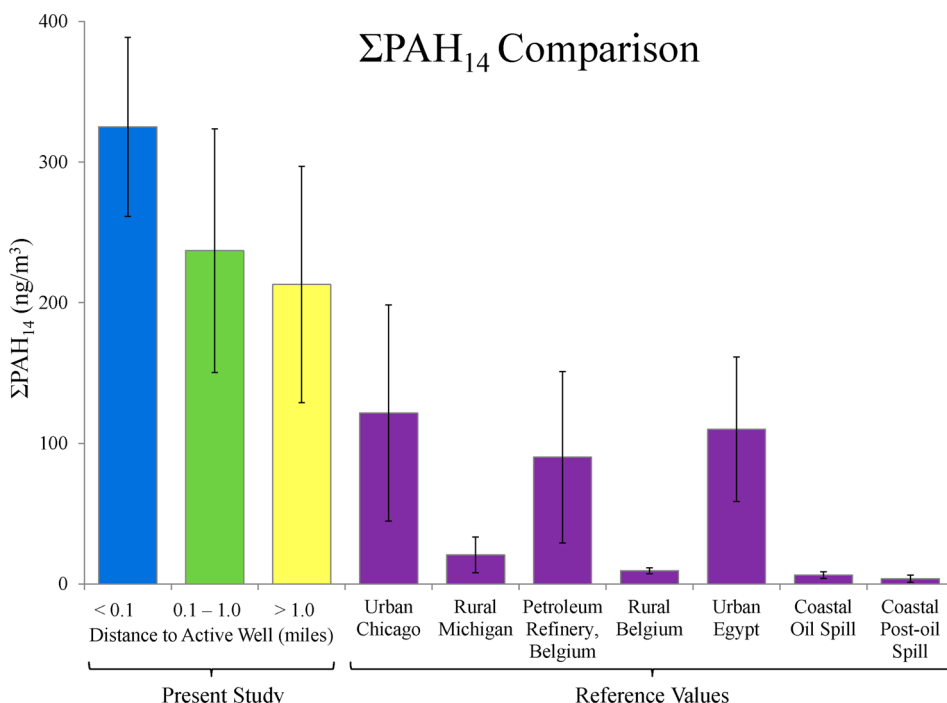


Figure 2. Average sum of 14 PAHs, grouped by distance to the closest active natural gas well, with comparisons to previous studies.^{29,44–46} All data are vapor phase PAHs. The three distance groups in the present study are close ($n = 5$), middle ($n = 12$), and far ($n = 6$), defined in the text. Error bars represent one SD.

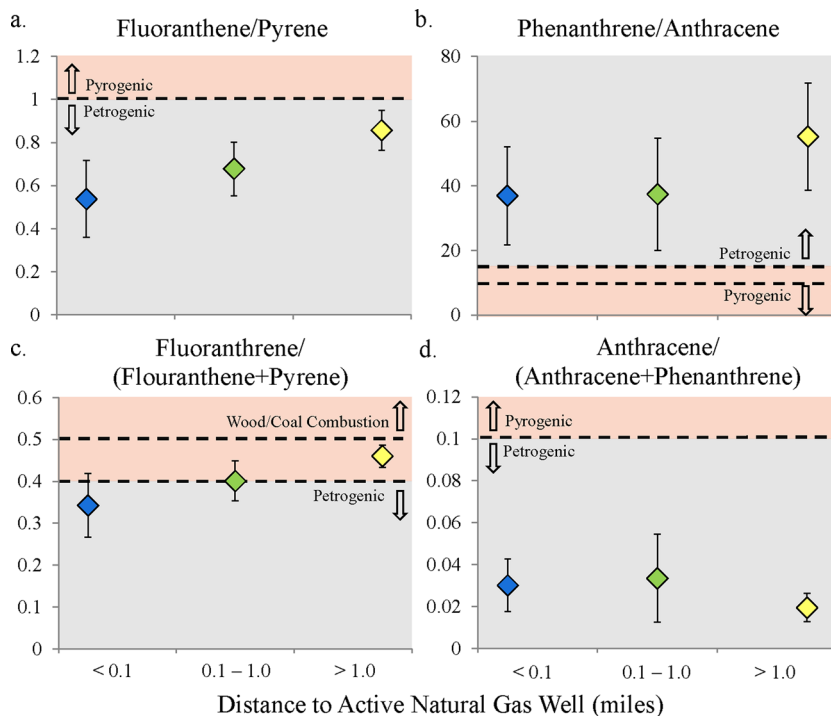


Figure 3. Petrogenic vs. pyrogenic sourcing ratios, grouped by distance to the closest active natural gas well. a. Fluoranthene/pyrene, b. phenanthrene/anthracene, c. fluoranthene/(fluoranthene+pyrene), and d. anthracene/(anthracene+phenanthrene) ratios. Pyrogenic and petrogenic thresholds are defined in text. The three distance groups are close ($n = 5$), middle ($n = 12$), and far ($n = 6$), defined in the text. Error bars represent one SD.

Σ PAH₆₂, benzo[a]pyrene, and phenanthrene (Figure 1a–c). Average Σ PAH₆₂ were 390, 300, and 270 ng/m³ for the close, middle, and far groups. Phenanthrene was the most abundant PAH in all samples, contributing over 30% to average Σ PAH₆₂ in all distance groups. The next most abundant PAHs were

fluorene, pyrene, and fluoranthene, collectively contributing more than an additional 35% to average Σ PAH₆₂ in all distance groups. The other 58 PAHs made up the remaining ~30%.

The predominant health concerns associated with exposure to PAH mixtures are cancer and respiratory distress, so

benzo[a]pyrene and phenanthrene were chosen as representative individual PAHs generally associated with each of these health endpoints. Benzo[a]pyrene has been extensively studied in relation to its carcinogenicity and phenanthrene has been associated with respiratory distress.^{23,43} Average benzo[a]pyrene levels were 2.8, 2.7, and 1.9 ng/m³ for the close, middle, and far groups. Average phenanthrene levels were 130, 96, and 88 ng/m³ for the close, middle, and far groups. The close and far distance groups for benzo[a]pyrene were significantly different (Welch's two sample *t* test, $p < 0.05$). The close and far distance groups for $\sum\text{PAH}_{62}$ and phenanthrene were just above the $\alpha = 0.05$ significance level (Welch's two sample *t* tests, $p = 0.053$, and $p = 0.061$, respectively). Close and middle groups for phenanthrene were also just above this significance level (Welch's two sample *t* test, $p = 0.058$).

Comparison to Literature Values. Results from the present study were directly compared to the sum of 14 PAHs in the air, reported in four previous studies (Figure 2). These 14 PAHs are listed in the SI. Average $\sum\text{PAH}_{14}$ for the present study were 330, 240, and 210 ng/m³ for the close, middle, and far groups. Simcik et al. measured an average of 122 ng/m³ $\sum\text{PAH}_{20}$ in downtown Chicago, and an average of 21 ng/m³ in a rural location in Michigan.⁴⁴ Ravindra et al. measured average $\sum\text{PAH}_{14}$ levels of 90 ng/m³ near a petroleum refinery in an industrial Belgian location, and 9.4 ng/m³ in a rural Belgian location.⁴⁵ Khairy et al. used LDPE passive samplers to measure an average $\sum\text{PAH}_{14}$ of 110 ng/m³ in urban areas of Alexandria, Egypt during winter sampling campaigns.²⁹ Tidwell et al. used LDPE passive samplers to measure PAHs on the shore during the Deepwater Horizon Incident in the U.S. Gulf of Mexico. At the two shoreline sites closest to the incident (Louisiana and Mississippi), average $\sum\text{PAH}_{14}$ were 6.3 ng/m³ in observations immediately following the incident and 3.7 ng/m³ in all subsequent observations over the following year.⁴⁶ All of these studies measured PAHs in the vapor phase, making results comparable. Simcik and Ravindra et al. used active sampling to measure vapor phase PAHs, while Khairy and Tidwell et al. used LDPE passive sampling to measure PAHs in the vapor phase. Thus, results from these previous studies are directly comparable to the current work.

Thus, $\sum\text{PAH}$ in the present study are higher or comparable to most reported in published literature. Additionally, $\sum\text{PAH}$ in the close group are roughly an order of magnitude greater than levels previously measured in rural areas. The high density of NGE wells in the study area is important when interpreting these elevated PAH levels. Carroll County has more than 1 well per square mile. So, even samples in the far group have numerous active wells within 2 or 3 miles. This may partially explain why PAH levels at all sites are elevated.

PAH Sourcing Techniques. Sourcing ratios indicate that measured PAH mixtures have predominantly petrogenic signatures (Figure 3a-d). Petrogenic signatures suggest that PAHs were released directly from the earth, while pyrogenic signatures suggest that PAHs came from combustion. For both fluoranthene/pyrene and phenanthrene/anthracene, average ratios were petrogenic for all distance groups (Figure 3a, b). Fluoranthene/(fluoranthene+pyrene) ratios were petrogenic in the close group, and gained more pyrogenic influence as samples moved farther from NGE activity (Figure 3c). Anthracene/(anthracene+phenanthrene) ratios were all petrogenic (Figure 3d). Fluoranthene/pyrene and fluoranthene/(fluoranthene+pyrene) ratios both indicated that PAHs moved from strongly petrogenic toward more mixed or slightly

pyrogenic signatures as samplers moved farther from NGE activity (Figure 3a,c). Fluoranthene/(fluoranthene + pyrene) ratios between 0.4 and 0.5 are associated with liquid fossil fuel combustion.³⁵ This may suggest that PAH source becomes more affected by combustion as the sampler moves farther from active wells. Exploratory principle components analysis indicated that pyrene levels were negatively correlated with distance to the closest active well, reinforcing the sourcing ratio results (SI Figure S1). Additionally, average pyrene levels were significantly higher in the close group than the far group, reinforcing the association between NGE activity and pyrene (Welch's two sample *t* test, $p < 0.05$).

Average values for benzo[a]pyrene/benzo[g,h,i]perylene in the close, middle and far groups were 0.88, 1.1, and 1.2. Given that values >0.6 suggest traffic emissions, these data suggest that higher molecular weight PAHs (≥ 5 rings) measured in this study may be influenced by traffic emissions at all sites. However, these 5- and 6- ring PAHs only contribute 3.4% on average to $\sum\text{PAH}$ across all sites.

The predominant petrogenic signature suggests that PAH mixtures are heavily influenced by direct releases of hydrocarbons from NGE wells into the air, as opposed to other myriad anthropogenic processes which would produce pyrogenic signatures. It is reasonable to expect PAH emissions alongside natural gas extraction. This association was substantiated by a hydraulic fracturing simulation study, which demonstrated that nonmethane hydrocarbons, including aromatics, are emitted during natural gas extraction from shale.⁴⁷ Additionally, roughly half of the active wells were in the producing phase during the sampling period. This may further explain the predominant petrogenic signature, with PAHs mixtures being heavily influenced by direct release of hydrocarbons into the air, potentially as fugitive emissions during production. This may also partially explain the higher PAH load seen in the present study than in a previous study in which PAHs were only sampled during the drilling phase.¹⁵ The petrogenic signature of measured PAHs and the increased levels closer to NGE wells suggest that NGE activity may be impacting ambient PAH levels in this rural area.

Wood burning is another common source of PAHs in air. Retene is a PAH that is commonly used as an indicator of biomass combustion, especially wood.^{48,49} Interestingly, average retene levels did not show the same trend as other individual PAHs across distance groups. Rather, average retene levels were comparable across distance groups. This suggests that wood burning had a similar impact on PAH levels in all distance groups, and adds weight to the conclusion that elevated PAH levels may be related to NGE activity, not to wood burning.

Carcinogenic Potency. Carcinogenic potency of PAH mixtures decreases significantly in the far group, compared to the close group (Welch's two-sample *t* test, $p < 0.05$) (Figure 4). The average BaP_{eq} concentrations in the close, middle and far groups were 9.2, 8.0, and 6.3 ng/m³. Benzo[a]pyrene, fluoranthene, and benzo[b]fluoranthene were the main contributors to carcinogenic potency, collectively contributing over 80% to the total potency in all groups. Specific contributions to the average BaP_{eq} in the close, middle and far groups were as follows: benzo[b]fluoranthene contributed 2.2, 2.2, and 2.0 ng/m³, while fluoranthene contributed 2.4, 1.5, and 1.4 ng/m³. Benzo[a]pyrene's contributions were the same as are listed above in relation to Figure 1, because benzo[a]pyrene has a relative potency factor of 1.

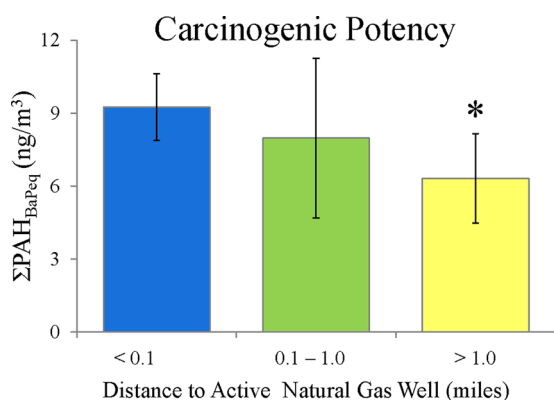


Figure 4. Average carcinogenic potency of measured PAHs, grouped by distance to the closest active natural gas well. The three distance groups are close ($n = 5$), middle ($n = 12$), and far ($n = 6$), defined in the text. Error bars represent one SD. The asterisk indicates a significant difference between the close and far groups, $p < 0.05$.

Average BaP_{eq} concentrations in all distance groups would potentially be concerning as chronic doses. While there are currently no regulatory levels for ambient PAH exposure in the U.S., the U.S. Clean Air Act specifies that a pollutant can be regulated when it is estimated to lead to more than 1 in a million excess cancers over the lifetimes of the most exposed individuals.⁵⁰ The World Health Organization suggested that 0.012 ng/m³ BaP in ambient air would produce 1 excess cancer in a million exposed individuals.⁵¹ Additionally, Caldwell et al. proposed 0.48 ng/m³ BaP as the benchmark concentration expected to cause excess cancer risk above 1 in a million.⁵⁰ Both WHO and the European Union have suggested 1.0 ng/m³ BaP as a guidance level for ambient air concentrations.^{24,52} If this guidance level were applied, ambient BaP_{eq} at all sites in this study would exceed this level.

Quantitative Risk Assessment. Quantitative risk assessment indicates that carcinogenic risk associated with inhalation decreases as samplers move farther from active wells. For the maximum residential exposure scenario of 24 h/day, estimated excess lifetime cancer risk (ELCR) decreases from 290 to 200 in a million when moving from the close to far group. For the minimum residential exposure scenario of 1 h/day, estimated ELCR decreases from 12 to 8.1 in a million when moving from the close to far group. The outdoor worker scenario was also calculated to approximate exposures working outside amidst NGE activity, such as farming or working on NGE wells. For this scenario, estimated ELCR decreases from 59 to 40 in a million when moving from the close to far group. These estimations depend heavily on exposure time, exposure frequency, and proximity to an active NGE well.

In all scenarios, the estimated ELCR decreases by about 30% when moving from the close group to far group, all other factors held constant. All of the estimated ELCRs were above 1 in a million, which is the conservative end of the range that the U.S. EPA considers acceptable. The estimated ELCRs for the maximum residential exposure convert to 2.9 in 10 000 and 2.0 in 10 000 for the close and far groups, respectively. These values exceed 1 in 10 000, which is the least conservative end of the U.S. EPA's acceptable range. This suggests that the maximum exposure scenario would produce risk levels above the U.S. EPA's acceptable range. Thus, PAH mixtures in areas heavily impacted by NGE may have higher than acceptable

cancer risk, and this risk increases as exposure moves closer to an active NGE well.

Quality Control Results. Carcinogenic PAHs were BLOD in all quality control (QC) samples. Of the noncarcinogenic PAHs, any instrument concentrations above the LODs in QC samples translated to <2.0 ng/m³ in air, on average. Any measurable levels in QC samples were averaged and subtracted from sample concentrations. Including field and laboratory blanks, >40% of analyzed samples were QC. PAH concentrations from the three codeployed samplers at the replicate site were averaged, with an average standard deviation of 0.77 ng/m³. Recoveries of laboratory surrogates ranged from 44 to 94%, averaging 76%. Instrument concentrations were surrogate-corrected. Instrument blanks were BLOD for all PAHs. Compounds were verified at $\pm 20\%$ of the true value for >80% of PAHs using verified standards before instrumental analyses of samples proceeded.

Additional Considerations. The LDPE passive samplers used in this study sample the vapor phase, but the particulate phase is typically enriched in carcinogenic PAHs. This is because the majority of carcinogenic PAHs are higher molecular weight, and the vapor phase typically contains a larger fraction of low molecular weight PAHs, while the particulate phase is typically enriched in high molecular weight PAHs.^{53,54} This may mean that the potency values and risk estimates presented here are under-representative of the actual carcinogenic risk associated with the air in the study area.

Sampling sites were on the private property of volunteer landowners. As a result, data do not represent a completely random sample of the population, and statistical inferences are only relevant to the portion of the population that was sampled.

As with any rapidly advancing technology, there are differences in the techniques used to perform NGE in different parts of the country and the world. It is possible that these differences could impact PAH emissions, and thus that these results may not be directly applicable to other regions. It has been observed, for instance, that NGE activities in different regions of the same state can have markedly different risks of leaks.⁵⁵ A recent commentary suggested that reasons for such differences may include differing geology, rates of development, techniques or implementation.⁵⁶ All of these areas would be worth exploring in efforts to minimize emissions from NGE in the future.

■ ASSOCIATED CONTENT

📄 Supporting Information

Additional details about sampling sites, sampling methods, analytical methods, and data analysis are included in the SI. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

PAH	polycyclic aromatic hydrocarbon
NGE	natural gas extraction
VOC	volatile organic compound
BTEX	benzene toluene ethylbenzene xylenes
NO _x	nitrogen oxides
LDPE	low-density polyethylene
OSU	Oregon State University
FSES	Food Safety and Environmental Stewardship
PRC	performance reference compound
LOD	limit of detection
LOQ	limit of quantitation
BLOD	below limit of detection
BaP _{eq}	benzo[a]pyrene equivalent
ELCR	excess lifetime cancer risk
QC	quality control

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