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Impact of natural gas extraction on PAH levels in ambient air

L. Blair Paulik[†], Carey E. Donald[†], Brian W. Smith[†], Lane G. Tidwell[†], Kevin A. Hobbie[†], Laurel Kincl[‡], Erin N. Haynes[§], Kim A. Anderson^{†}*

[†]Department of Environmental and Molecular Toxicology, Oregon State University, Corvallis, OR 97331

[‡]College of Public Health and Human Sciences, Oregon State University, Corvallis, OR 97331

[§]Department of Environmental Health, University of Cincinnati, Cincinnati, OH 45267

KEYWORDS: fracking, hydraulic fracturing, unconventional natural gas drilling, passive sampling, cancer risk assessment, air quality

1 **ABSTRACT**

2 Natural gas extraction, often referred to as “fracking,” has increased rapidly in the U.S. in
3 recent years. To address potential health impacts, passive air samplers were deployed in a rural
4 community heavily affected by the natural gas boom. Samplers were analyzed for 62 polycyclic
5 aromatic hydrocarbons (PAHs). Results were grouped based on distance from each sampler to
6 the nearest active well. PAH levels were highest when samplers were closest to active wells.
7 Additionally, PAH levels closest to natural gas activity were an order of magnitude higher than
8 levels previously reported in rural areas. Sourcing ratios indicate that PAHs were predominantly
9 petrogenic, suggesting that elevated PAH levels were influenced by direct releases from the
10 earth. Quantitative human health risk assessment estimated the excess lifetime cancer risks
11 associated with exposure to the measured PAHs. Closest to active wells, the risk estimated for
12 maximum residential exposure was 2.9 in 10,000, which is above the U.S. EPA’s acceptable risk
13 level. Overall, risk estimates decreased 30% when comparing results from samplers closest to
14 active wells to those farthest. This work suggests that natural gas extraction may be contributing
15 significantly to PAHs in air, at levels that are relevant to human health.

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22 INTRODUCTION

23 Natural gas extraction from shale, colloquially known as “fracking,” has increased
24 substantially in the United States in the past 15 years. U.S. shale gas production grew by 17%
25 annually from 2000-2006, and then grew by 48% from 2006-2010¹. This spike in activity has
26 been driven predominantly by improvements to the technologies of horizontal drilling and
27 hydraulic fracturing. Together, these processes enable companies to access gas reserves
28 previously out of reach. As of 2011, the U.S. Energy Information Administration estimated that
29 roughly 750 trillion cubic feet of natural gas were recoverable from shale reserves in the
30 contiguous United States using these approaches².

31 Despite this rapid expansion and implementation of technology, there has been relatively
32 little research into the environmental and health impacts these processes may have. There has
33 also been a lack of regulation, illustrated by the U.S. Energy Policy Act of 2005, which amended
34 portions of the U.S. Safe Drinking Water Act and Clean Water Act to give gas-drilling
35 companies more flexibility³. Concerns have arisen about the impacts that natural gas extraction
36 (hereafter NGE) may have on environmental and human health, due in part to this historic lack
37 of regulation⁴⁻⁷. In the past five years, studies have emerged assessing the impacts this activity
38 may have on water quality, air quality, and human health⁸⁻²⁰.

39 Many studies have acknowledged that impact to air quality may be the most significant
40 risk to communities living near NGE⁸⁻¹⁵. Shonkoff *et al* concluded that NGE has the potential to
41 pose health risks through both air and water emissions, and urged that many important data gaps
42 remain⁹.

43 Most of the air quality studies have focused on emissions of volatile organic compounds
44 (VOCs). McKenzie *et al* sampled air near NGE wells at different stages, measuring VOCs
45 including BTEX (benzene, toluene, ethylbenzene and xylenes) and aliphatic hydrocarbons¹⁰.
46 They performed a public health risk assessment and found an increased risk of cancer and non-
47 cancer endpoints for people living within 0.5 miles of NGE well pads¹⁰. In a subsequent study,
48 McKenzie *et al* assessed the correlation between decreased birth outcomes and NGE. They found
49 an increase in congenital heart defects and neural tube defects as mothers' residences got closer
50 to NGE wells¹¹. Roy *et al* estimated emissions from NGE in the Marcellus Shale, and predicted
51 that NGE contributes an average of 12% of all NO_x and VOC emissions to air in a given
52 location¹². Bunch *et al* studied regional VOC levels in a part of Texas with NGE¹⁴. Contrary to
53 the majority of the scientific literature, this study concluded that NGE is not polluting the air at
54 concerning levels. However, Bunch *et al* considered any risk estimates less than 1 in 10,000 not
55 to be concerning, which is the upper limit of risk that the EPA considers acceptable²¹.

56 Many studies have assessed the impacts of NGE on public health^{7, 9-11, 14, 16-20, 22}. Colborn
57 *et al* performed a hazard assessment of the chemicals that are used during NGE, and concluded
58 that over 70% of these chemicals are potentially risky to humans⁷. Other work has focused on the
59 impacts of NGE on communities^{18, 19, 22}. NGE often takes place in rural areas, where it may
60 present a larger change to ambient pollutant levels than it would in urban areas.

61 Other studies have reviewed the state of the science surrounding NGE, emphasizing the
62 need for more concerted field sampling and data generation. In one such review, Goldstein called
63 for toxicological studies to help characterize the potential risks of NGE activity¹⁷. Small *et al*
64 assessed the state of the science and regulation surrounding NGE in the U.S. They called for
65 improved characterization of air pollutants emitted from NGE and their potential health impacts,

66 and concluded that risks associated with NGE “remain under-analyzed”⁶. Despite the recent
67 surge of literature surrounding NGE, there are still many data gaps.

68 One data gap is the relationship between polycyclic aromatic hydrocarbons (PAHs) and
69 NGE. PAHs are pervasive environmental pollutants of concern, known to be associated with
70 both hydrocarbon extraction and negative health impacts^{23, 24}. The main categories of health
71 concerns associated with exposure to PAH mixtures are cancer risk and respiratory distress.
72 PAH-related cancer risk has received a great deal of attention in relation to oil spills, traffic
73 exhaust, wood smoke, and cooking. NGE involves extracting hydrocarbons from the earth, a
74 process that is often associated with PAH emissions. NGE also brings large volumes of truck
75 traffic into an area to move building materials, water, and product. Each of these stages could be
76 sources of PAHs. Goldstein and Adgate both specifically include PAHs as a potential health
77 concern at many or all stages of NGE^{8, 17}. Colborn *et al* sampled air near NGE well pads for 16
78 PAHs¹⁵. However, they ceased sampling PAHs after the drilling phase ended. They later
79 concluded that PAH levels during drilling were of concern to human health, citing that these
80 levels ($\Sigma\text{PAH}_{16} \sim 15 \text{ ng/m}^3$) were comparable to those associated with small but significant
81 decreases in IQ at 5 years of age in children exposed *in utero*²⁵. Colborn *et al* conclude that the
82 relationship between NGE and PAH emissions “deserves further investigation”¹⁵.

83 Passive sampling could fill this data gap. Low-density polyethylene (LDPE) passive
84 sampling devices sequester hydrophobic compounds through passive diffusion in a time-
85 integrated manner, and are well-suited to passively sample vapor phase PAHs from air. Since
86 this tool’s development in the 1990s, many studies have demonstrated its ability to measure
87 PAHs²⁶⁻²⁹. The objective of this study was to use passive sampling to assess the impact of NGE
88 on PAH levels in air a rural community.

89 MATERIALS AND METHODS

90 Site description and sampling design

91 This study took place predominantly in rural Carroll County, Ohio. As technology has
92 made gas in the Utica shale more accessible in the last five years, NGE in eastern Ohio has
93 increased. In 2011, Ohio had less than 50 horizontal natural gas drilling leases³⁰. As of June
94 2014, that number had jumped to 1,386, with 421 in Carroll County³¹.

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

111 **Passive sampler preparation, cleaning and extraction**

112 Details about chemicals and solvents are in the SI. Before deployment, LDPE was
113 cleaned using hexanes as described previously³². Each LDPE strip was infused with performance
114 reference compounds (PRCs) to enable calculation of *in situ* sampling rates and time-integrated
115 air concentrations³³. PRCs used in this study were fluorene-d10, pyrene-d10 and
116 benzo[b]fluoranthene-d12. PRCs were spiked into LDPE at 2-20 µg per strip. Samplers were
117 cleaned after deployment in two isopropanol baths, stored in amber jars at -20°C, and extracted
118 as described elsewhere³². Briefly, extractions were performed using two dialyses with n-hexane.
119 Prior to extraction, samples were spiked with deuterated PAHs to act as surrogate standards,
120 allowing for quantification of extraction efficiency. Surrogate standards are specified in SI Table
121 S1. Extracts were quantitatively concentrated to 1 mL using TurboVap® closed cell evaporators,
122 transferred to amber chromatography vials, and stored at -20°C.

123 **Chemical analysis**

124 LDPE extracts were quantitatively analyzed for 62 PAHs using an Agilent 7890A gas
125 chromatograph interfaced with an Agilent 7000 GC/MS-MS. An Agilent Select PAH column
126 was used. Each PAH was calibrated with a curve of at least five points, with correlations ≥ 0.99 .
127 Limits of detection (LODs) range from 0.33 to 1.67 ng/mL and limits of quantitation (LOQs)
128 range from 1.0 to 5.00 ng/mL. A list of PAHs, LODs and LOQs is included in SI Table S1.

129 **Air concentration calculation**

130 Air concentrations (ng/m³) of PAHs were calculated from instrument concentrations
131 (ng/mL) using PRCs. *In situ* sampling rates (R_S) were generated using calculations described by

132 Huckins *et al*³³. These calculations estimate the R_S of each PRC by incorporating deployment
133 time, average temperature, initial amount and K_{OA} . An R_S is then calculated for each PAH, using
134 the PAH's K_{OA} and the R_S of one of the PRCs. These calculations are included as SI equations
135 S1-S3.

136 **Data analysis**

137 Data was grouped by distance from each sampling site to the closest active well pad.
138 Three distance groups were created, with the “close” group <0.1 mile from an active well, the
139 “middle” group from 0.1 to 1.0 mile from an active well, and the “far” group >1.0 mile from an
140 active well. The close, middle and far groups had 5, 12 and 6 samples each. All results are
141 presented in these three distance groups. Distances were determined using Google Earth version
142 7.1.2.2041, and well status information was taken from the Ohio Department of Natural
143 Resource's website. A well was considered “active” if it was in the drilling, drilled, or producing
144 stages at the time of sampling.

145 Parent PAH isomer ratios were used to determine sources of PAHs. Two PAH isomer
146 pairs that are used to diagnose whether a PAH mixture is petrogenic or pyrogenic are
147 phenanthrene and anthracene, and fluoranthene and pyrene³⁴⁻⁴⁰. Phenanthrene/anthracene ratios
148 ≤ 10 indicate pyrogenic sources, while ratios ≥ 15 indicate petrogenic sources^{34, 36-38}.
149 Fluoranthene/pyrene ratios > 1 indicate pyrogenic sources, while ratios < 1 indicate petrogenic
150 sources^{34, 37, 38}. Ratios of one isomer to the sum of both isomers are also used in PAH sourcing.
151 Fluoranthene/(fluoranthene+pyrene) ratios ≥ 0.5 indicate pyrogenic sources, and ratios ≤ 0.4
152 indicate petrogenic sources^{36, 39}. Yunker suggests that ratios between 0.4 and 0.5 indicate liquid
153 fossil fuel combustion³⁵. Anthracene/(anthracene+phenanthrene) ratios < 0.1 indicate petrogenic

154 sources and ratios >0.1 indicate pyrogenic sources^{35, 39, 40}. A fifth ratio of two non-isomer parent
155 PAHs, benzo[a]pyrene/benzo[g,h,i]perylene, was used to obtain sourcing information for the 5-
156 and 6- ring PAHs measured in this study. For this ratio, values >0.6 are indicative of traffic
157 emissions while values <0.6 indicate non-traffic emission sources³⁹. There were samples in the
158 middle and far groups for which benzo[a]pyrene, benzo[g,h,i]perylene, or both were below limits
159 of detection (BLOD). So, the sample sizes for the close, middle, and far groups for this final ratio
160 are 5, 9, and 4, respectively.

161 **Risk assessment**

162 The carcinogenic potency of the PAH mixture at each site was calculated by multiplying
163 the concentration of each PAH by the relative potency factor (RPF) it was given by the U.S.
164 EPA²³. A list of the RPFs is in SI Table S2. This estimate of carcinogenic potency is referred to
165 as the benzo[a]pyrene equivalent concentration, or BaP_{eq}. These values were used in quantitative
166 risk assessments to estimate cancer risks of exposure to the measured PAHs through inhalation,
167 using the EPA's framework⁴¹. Exposure parameters were modeled after the "residential" and
168 "outdoor worker" examples presented to Superfund risk assessors by the EPA in 2014⁴².
169 Specifically, the average lifetime was set at 70 years for all exposure scenarios. For the
170 residential scenarios, exposure duration and exposure frequency were set at 26 years and 350
171 days/year, respectively. For the outdoor worker scenario, these parameters were set at 25 years
172 and 225 days/year. The residential assessment was performed for a worst-case and best-case
173 scenario, by adjusting the daily exposure time to 24 hours or 1 hour, while the outdoor worker
174 assessment was performed with daily exposure time set at 8 hours. Risk assessment equations are
175 included as SI equations S4-S5.

176 **Statistical analysis**

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

182 **Quality control**

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

193 **RESULTS AND DISCUSSION**

194 **PAH levels and trends**

195 The data show a common trend: PAH levels decrease as samplers get farther from active
196 NGE wells. Three distance groups were created, with the "close" group <0.1 mile from an active
197 well, the "middle" group between 0.1 and 1.0 mile from an active well, and the "far" group >1.0

198 mile from an active well. This trend is consistent when comparing averages in the three distance
199 groups for ΣPAH_{62} , benzo[a]pyrene, and phenanthrene (Figure 1a-c). Average ΣPAH_{62} were
200 390, 300, and 270 ng/m^3 for the close, middle, and far groups. Phenanthrene was the most
201 abundant PAH in all samples, contributing over 30% to average ΣPAH_{62} in all distance groups.
202 The next most abundant PAHs were fluorene, pyrene, and fluoranthene, collectively contributing
203 more than an additional 35% to average ΣPAH_{62} in all distance groups. The other 58 PAHs made
204 up the remaining ~30%.

205 The predominant health concerns associated with exposure to PAH mixtures are cancer
206 and respiratory distress, so benzo[a]pyrene and phenanthrene were chosen as representative
207 individual PAHs generally associated with each of these health endpoints. Benzo[a]pyrene has
208 been extensively studied in relation to its carcinogenicity and phenanthrene has been associated
209 with respiratory distress^{23, 43}. Average benzo[a]pyrene levels were 2.8, 2.7, and 1.9 ng/m^3 for the
210 close, middle, and far groups. Average phenanthrene levels were 130, 96, and 88 ng/m^3 for the
211 close, middle, and far groups. The close and far distance groups for benzo[a]pyrene were
212 significantly different (Welch's two sample t-test, $p < 0.05$). The close and far distance groups for
213 ΣPAH_{62} and phenanthrene were just above the $\alpha = 0.05$ significance level (Welch's two sample
214 t-tests, $p = 0.053$, and $p = 0.061$, respectively). Close and middle groups for phenanthrene were
215 also just above this significance level (Welch's two sample t-test, $p = 0.058$).

216 **Comparison to literature values**

217 Results from the present study were directly compared to the sum of 14 PAHs in the
218 reported in four previous studies (Figure 2). These 14 PAHs are listed in the SI. Average ΣPAH_{14}
219 for the present study were 330, 240, and 210 ng/m^3 for the close, middle, and far groups. Simcik
220 *et al* measured an average of 122 ng/m^3 ΣPAH_{20} in downtown Chicago, and an average of 21

221 ng/m³ in a rural location in Michigan⁴⁴. Ravindra *et al* measured average ΣPAH₁₄ levels of 90
222 ng/m³ near a petroleum refinery in an industrial Belgian location, and 9.4 ng/m³ in a rural
223 Belgian location⁴⁵. Khairy *et al* used LDPE passive samplers to measure an average ΣPAH₁₄ of
224 110 ng/m³ in urban areas of Alexandria, Egypt during winter sampling campaigns²⁹. Tidwell *et*
225 *al* used LDPE passive samplers to measure PAHs on the shore during the Deepwater Horizon
226 Incident in the U.S. Gulf of Mexico. At the two shoreline sites closest to the incident (Louisiana
227 and Mississippi), average ΣPAH₁₄ were 6.3 ng/m³ in observations immediately following the
228 incident and 3.7 ng/m³ in all subsequent observations over the following year⁴⁶. All of these
229 studies measured PAHs in the vapor phase, making results comparable. Simcik and Ravindra *et*
230 *al* used active sampling to measure vapor phase PAHs, while Khairy and Tidwell *et al* used
231 LDPE passive sampling to measure PAHs in the vapor phase. Thus, results from these previous
232 studies are directly comparable to the current work.

233 Thus ΣPAH in the present study are higher or comparable to most reported in published
234 literature. Additionally, ΣPAH in the close group are roughly an order of magnitude greater than
235 levels previously measured in rural areas. The high density of NGE wells in the study area is
236 important when interpreting these elevated PAH levels. Carroll County has more than 1 well per
237 square mile. So, even samples in the “far” distance group have numerous active wells within 2 or
238 3 miles. This may partially explain why PAH levels at all sites are elevated.

239 **PAH sourcing techniques**

240 Sourcing ratios indicate that measured PAH mixtures have predominantly petrogenic
241 signatures (Figure 3a-d). Petrogenic signatures suggest that PAHs were released directly from
242 the earth, while pyrogenic signatures suggest that PAHs came from combustion. For both
243 fluoranthene/pyrene and phenanthrene/anthracene, average ratios were petrogenic for all distance

244 groups (Figure 3a, b). Fluoranthene/(fluoranthene+pyrene) ratios were petrogenic in the close
245 group, and gained more pyrogenic influence as samples moved farther from NGE activity
246 (Figure 3c). Anthracene/(anthracene+phenanthrene) ratios were all petrogenic (Figure 3d).
247 Fluoranthene/pyrene and fluoranthene/(fluoranthene+pyrene) ratios both indicated that PAHs
248 moved from strongly petrogenic toward more mixed or slightly pyrogenic signatures as samplers
249 moved farther from NGE activity (Figure 3a,c). Fluoranthene/(fluoranthene+pyrene) ratios
250 between 0.4 and 0.5 are associated with liquid fossil fuel combustion³⁵. This may suggest that
251 PAH source becomes more affected by combustion as the sampler moves farther from active
252 wells. Exploratory principle components analysis indicated that pyrene levels were negatively
253 correlated with distance to the closest active well, reinforcing the sourcing ratio results (SI
254 Figure S1). Additionally, average pyrene levels were significantly higher in the close group than
255 the far group, reinforcing the association between NGE activity and pyrene (Welch's two sample
256 t-test, $p < 0.05$).

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

262 The predominant petrogenic signature suggests that PAH mixtures are heavily influenced
263 by direct releases of hydrocarbons from NGE wells into the air, as opposed to other myriad
264 anthropogenic processes which would produce pyrogenic signatures. It is reasonable to expect
265 PAH emissions alongside natural gas extraction. This association was substantiated by a
266 hydraulic fracturing simulation study, which demonstrated that non-methane hydrocarbons,

267 including aromatics, are emitted during natural gas extraction from shale⁴⁷. Additionally, roughly
268 half of the active wells were in the producing phase during the sampling period. This may further
269 explain the predominant petrogenic signature, with PAHs mixtures being heavily influenced by
270 direct release of hydrocarbons into the air, potentially as fugitive emissions during production.
271 This may also partially explain the higher PAH load seen in the present study than in a previous
272 study in which PAHs were only sampled during the drilling phase¹⁵. The petrogenic signature of
273 measured PAHs and the increased levels closer to NGE wells suggest that NGE activity may be
274 impacting ambient PAH levels in this rural area.

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

281 **Carcinogenic potency**

282 Carcinogenic potency of PAH mixtures decreases significantly in the far group,
283 compared to the close group (Welch's two-sample t-test, $p < 0.05$) (Figure 4). The average BaP_{eq}
284 concentrations in the close, middle and far groups were 9.2, 8.0, and 6.3 ng/m^3 . Benzo[a]pyrene,
285 fluoranthene, and benzo[b]fluoranthene were the main contributors to carcinogenic potency,
286 collectively contributing over 80% to the total potency in all groups. Specific contributions to the
287 average BaP_{eq} in the close, middle and far groups were as follows: benzo[b]fluoranthene
288 contributed 2.2, 2.2, and 2.0 ng/m^3 , while fluoranthene contributed 2.4, 1.5, and 1.4 ng/m^3 .

289 Benzo[a]pyrene's contributions were the same as are listed above in relation to Figure 1, because
290 benzo[a]pyrene has a relative potency factor of 1.

291 Average BaP_{eq} concentrations in all distance groups would potentially be concerning as
292 chronic doses. While there are currently no regulatory levels for ambient PAH exposure in the
293 U.S., the U.S. Clean Air Act specifies that a pollutant can be regulated when it is estimated to
294 lead to more than 1 in a million excess cancers over the lifetimes of the most exposed
295 individuals⁵⁰. The World Health Organization suggested that 0.012 ng/m³ BaP in ambient air
296 would produce 1 excess cancer in a million exposed individuals⁵¹. Additionally, Caldwell *et al*
297 proposed 0.48 ng/m³ BaP as the benchmark concentration expected to cause excess cancer risk
298 above 1 in a million⁵⁰. Both WHO and the European Union have suggested 1.0 ng/m³ BaP as a
299 guidance levels for ambient air concentrations^{24, 52}. If this guidance level were applied, ambient
300 BaP_{eq} at all sites in this study would exceed this level.

301 **Quantitative risk assessment**

302 Quantitative risk assessment indicates that carcinogenic risk associated with inhalation
303 decreases as samplers move farther from active wells. For the maximum residential exposure
304 scenario of 24 hours/day, estimated excess lifetime cancer risk (ELCR) decreases from 290 to
305 200 in a million when moving from the close to far group. For the minimum residential exposure
306 scenario of 1 hour/day, estimated ELCR decreases from 12 to 8.1 in a million when moving from
307 the close to far group. The outdoor worker scenario was also calculated to approximate
308 exposures working outside amidst NGE activity, such as farming or working on NGE wells. For
309 this scenario, estimated ELCRs decrease from 59 to 40 in a million when moving from the close
310 to far group. These estimations depend heavily on exposure time, exposure frequency, and
311 proximity to an active fracking well.

312 In all scenarios, the estimated ELCR decreases by about 30% when moving from the
313 close group to far group, all other factors held constant. All of the estimated ELCRs were above
314 1 in a million, which is the conservative end of the range that the U.S. EPA considers acceptable.
315 The estimated ELCRs for the maximum residential exposure convert to 2.9 in 10,000 and 2.0 in
316 10,000 for the close and far groups, respectively. These values exceed 1 in 10,000, which is the
317 least conservative end of the U.S. EPA's acceptable range. This suggests that the maximum
318 exposure scenario would produce risk levels above the U.S. EPA's acceptable range. Thus, PAH
319 mixtures in areas heavily impacted by NGE may have higher than acceptable cancer risk, and
320 this risk increases as exposure moves closer to an active NGE well.

321 **Quality control results**

322 Carcinogenic PAHs were BLOD in all quality control (QC) samples. Of the non-
323 carcinogenic PAHs, any instrument concentrations above the LODs in QC samples translated to
324 $<2.0 \text{ ng/m}^3$ in air, on average. Any measurable levels in QC samples were averaged and
325 subtracted from sample concentrations. Including field and laboratory blanks, $>40\%$ of analyzed
326 samples were QC. PAH concentrations from the three co-deployed samplers at the replicate site
327 were averaged, with an average standard deviation of 0.77 ng/m^3 . Recoveries of laboratory
328 surrogates ranged from 44 to 94%, averaging 76%. Instrument concentrations were surrogate-
329 corrected. Instrument blanks were BLOD for all PAHs. Compounds were verified at $\pm 20\%$ of the
330 true value for $>80\%$ of PAHs using verified standards before instrumental analyses of samples
331 proceeded.

332 **Additional considerations**

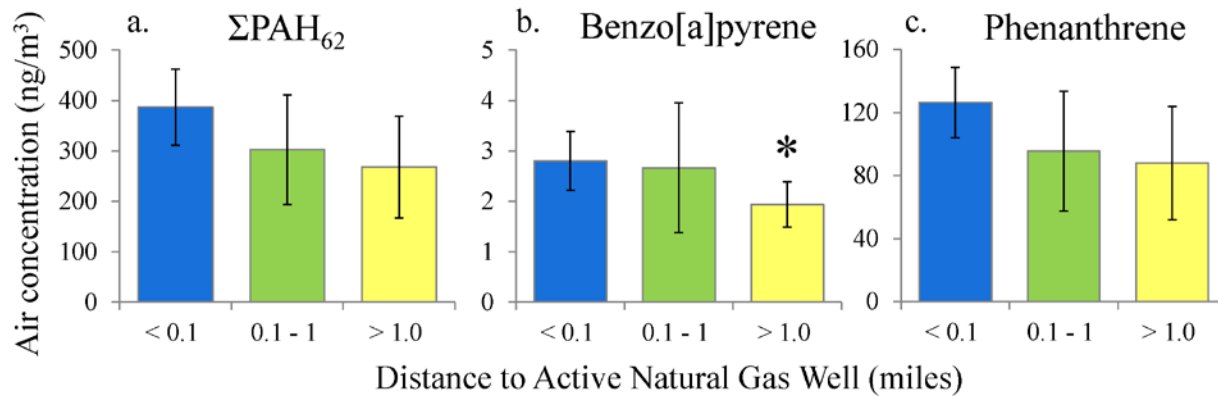
333 The LDPE passive samplers used in this study sample the vapor phase, but the particulate
334 phase is typically enriched in carcinogenic PAHs. This is because the majority of carcinogenic

335 PAHs are higher molecular weight, and the vapor phase typically contains a larger fraction of
336 low molecular weight PAHs, while the particulate phase is typically enriched in high molecular
337 weight PAHs^{53, 54}. This may mean that the potency values and risk estimates presented here are
338 under-representative of the actual carcinogenic risk associated with the air in the study area.

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

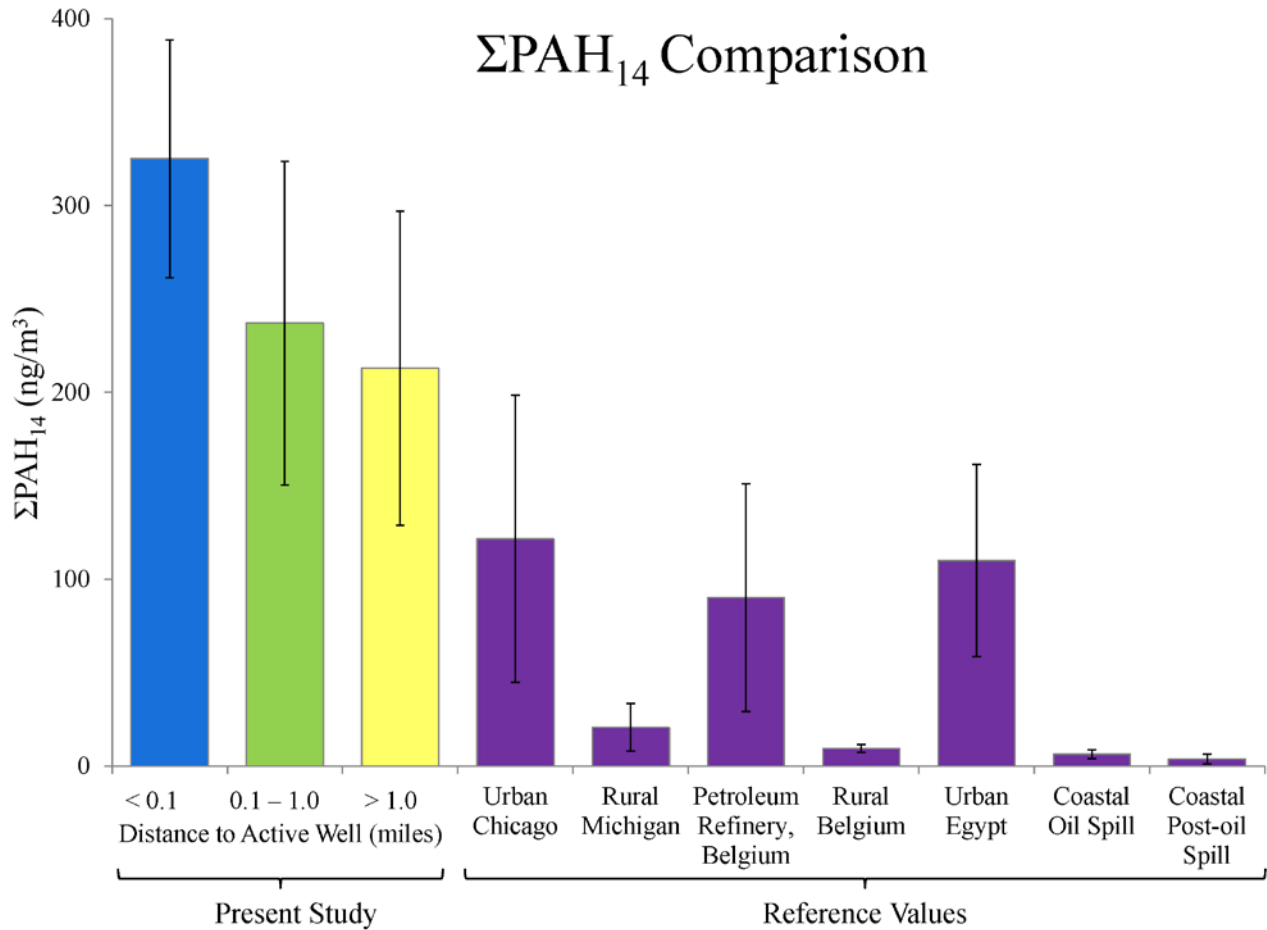
342 As with any rapidly advancing technology, there are differences in the techniques used to
343 perform NGE in different parts of the country and the world. It is possible that these differences
344 could impact PAH emissions, and thus that these results may not be directly applicable to other
345 regions. It has been observed, for instance, that NGE activities in different regions of the same
346 state can have markedly different risks of leaks⁵⁵. A recent commentary suggested that reasons
347 for such differences may include differing geology, rates of development, techniques or
348 implementation⁵⁶. All of these areas would be worth exploring in efforts to minimize emissions
349 from NGE in the future.

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

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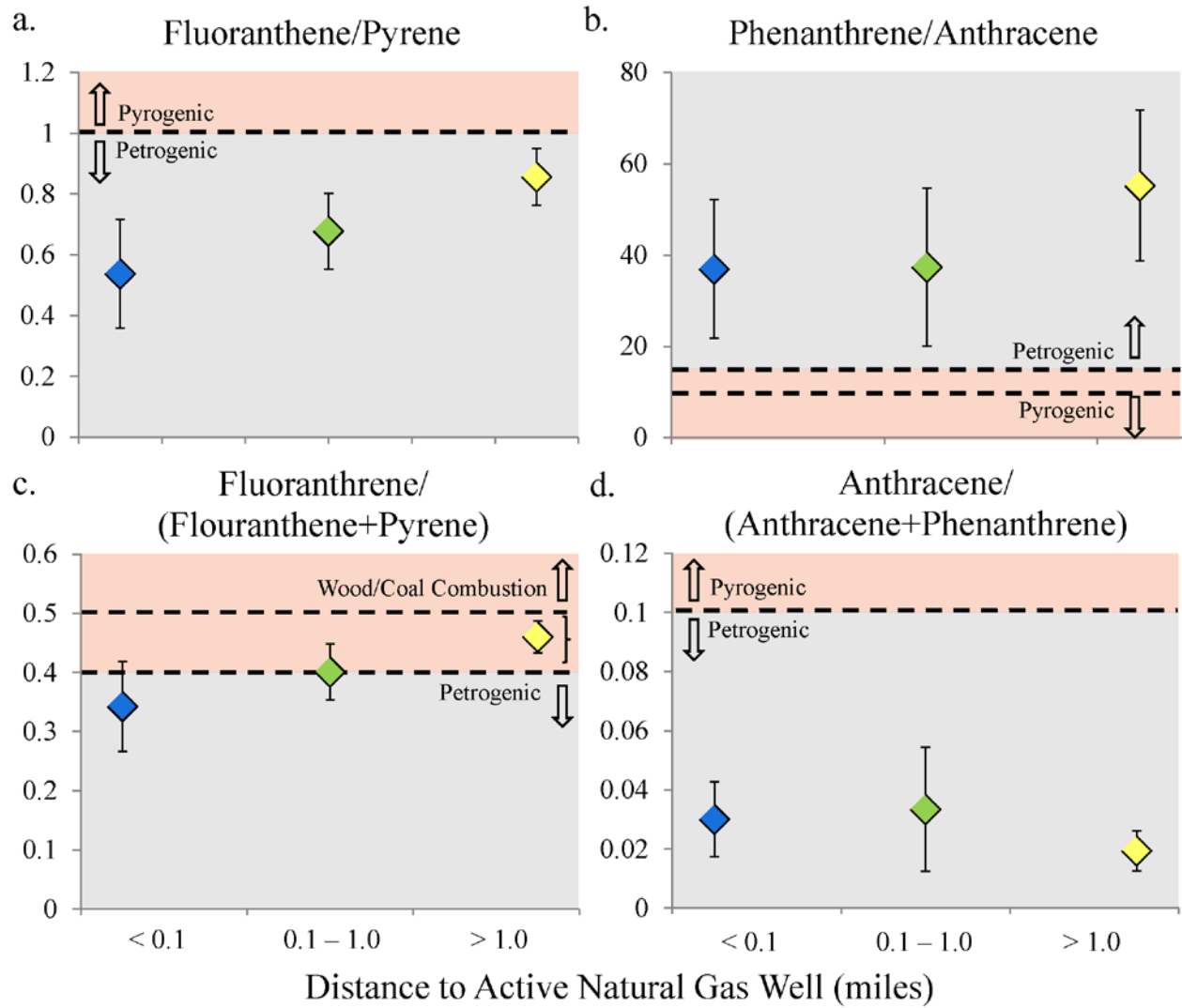
360 **Figure 2.** Average sum of 14 PAHs, grouped by distance to the closest active natural gas well,
 361 with comparisons to previous studies^{29, 44-46}. All data are vapor phase PAHs. The three distance
 362 groups in the present study are close (n=5), middle (n=12), and far (n=6), defined in the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

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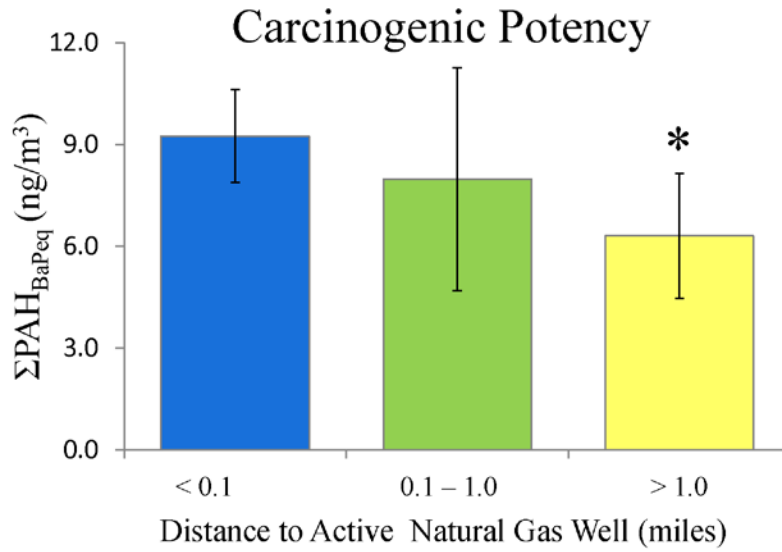
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369 **Figure 3.** Petrogenic vs. pyrogenic sourcing ratios, grouped by distance to the closest active
 370 natural gas well. a. Fluoranthene/pyrene, b. phenanthrene/anthracene, c.
 371 fluoranthene/(fluoranthene+pyrene) and d. anthracene/(anthracene+phenanthrene)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

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376 **Figure 4.** Average carcinogenic potency of measured PAHs, grouped by distance to the closest
 377 active natural gas well. The three distance groups are close (n=5), middle (n=12), and far (n=6).

378 Error bars represent one SD. Asterisks indicate significant differences, p < 0.05.

379 **ASSOCIATED CONTENT**

380 **Supporting Information**

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

384 **AUTHOR INFORMATION**

385 **Corresponding Author**

386 *E-mail: kim.anderson@oregonstate.edu, phone: 541-737-8501

387 **Notes**

388 The authors declare no competing financial interest.

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400 **ABBREVIATIONS**

401 PAH, polycyclic aromatic hydrocarbon; NGE, natural gas extraction; VOC, volatile organic
402 compound; BTEX, benzene toluene ethylbenzene xylenes; NO_x, nitrogen oxides; LDPE, low-
403 density polyethylene; OSU, Oregon State University; FSES, Food Safety and Environmental
404 Stewardship; PRC, performance reference compound; LOD, limit of detection; LOQ, limit of
405 quantification; BLOD, below limit of detection; BaP_{eq}, benzo[a]pyrene equivalent; ELCR,
406 excess lifetime cancer risk; QC, quality control.

407 **TOC Art**



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