Supplementary Information: Impact of natural gas extraction on PAH levels in ambient air

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Chemical information

Single PAH standards were purchased from Sigma Aldrich, in St. Louis, MO, Chiron, in Trondheim, Norway, or Fluka (part of Sigma-Aldrich). PAH mixes were purchased from Accustandard, in New Haven, CT. Labeled compounds used as performance reference compounds (PRCs), laboratory surrogates, or instrument internal standards were obtained from either CDN Isotopes, in Pointe-Claire, Quebec, Canada, Cambridge Isotope Laboratories, in Tewksbury, MA, or Fisher Scientific in Pittsburgh, PA. All solvents were Optima-grade (from Fisher Scientific, Pittsburgh, PA) or equivalent, and all laboratory glassware and other tools were baked at 450°C for 12 hours and/or solvent-rinsed before use. Water used to clean LDPE was filtered through a D7389 purifier purchased from Barnstead International, in Dubuque, IA.

Passive sampler handling

LDPE strips were cut from pre-sized polyethylene tubing that was approximately 2.7 cm wide. Each polyethylene strip was approximately 100 cm long and had a volume of 5.1 cm^3. LDPE was dried under filtered vacuum in stainless steel kegs, from AEB Kegs in Delebio, Italy. TurboVap® evaporators were from Biotage, in Charlotte, NC.

Site description and sampling design

A significant fraction of the Carroll County's residents earn their livings through farming. Carroll County also sits on both the Marcellus and Utica Shales. It has therefore been part of the natural gas boom occurring in the United States in recent years. The exact number of days that samplers were deployed ranged from 18 to 28. Welch Fluorocarbon, Inc. is in Dover, NH.

Volunteer training

Volunteer landowners were trained in passive sampler handling, retrieval, and documentation by Oregon State University and University of Cincinnati community outreach specialists. Training included demonstration of retrieving samplers, practicing the technique, and time for discussion of questions and concerns. Volunteers were given handouts with step-by-step instructions of the sampler retrieval process. Handouts included a website with access to training videos, as well as contact information for OSU and UC trainers who would be available to answer questions.

Chemical analysis

Agilent is located in Alpharetta, GA. The temperature profile in the GC/MS-MS analytical method was as follows: 60°C for 1 minute, increasing 40°C per minute to reach 180°C, then increasing 3°C per minute to reach 230°C, then increasing 1.5°C per minute to reach 235°C, then increasing 15°C per minute to reach 280°C, staying at 280°C for 10 minutes, then increasing 6°C per minute to reach 298°C, and finally ramping up 16°C per minute to reach 350°C and stay there for 4 minutes. The dimensions of the Agilent Select PAH column were: 30 m, 0.25 mm, 0.15 µm. Continuing calibration standards were run nominally every 10 samples, and/or at the end of the sample set. If a closing standard did not meet the criteria, samples were re-run after the standard was verified.

Air concentration calculations

Vapor phase air concentrations were determined using an empirical uptake model. Sampling rates were derived by measuring PRC loss, as described in Huckins *et al* 2006[1]. PRCs

allow for an accurate assessment of *in situ* uptake rates for a wide range of analytes in variable environmental conditions[2-4]. The uptake calculation does not make any assumptions about the analyte being at equilibrium, so this model was used for air concentration calculations for all PAHs. PRCs share similar physical and chemical properties with the target PAHs in this study and spanned a range of log K_{oa} values from 6.59 to 10.35[3]. Air concentrations (C_a) of PAHs were determined using equation S1:

$$\text{Eq. S1} \qquad C_a = \frac{N_{analyte}}{V_s K_{sa}\left(1-\exp\left(-\frac{R_s t}{V_s K_{sa}}\right)\right)}$$

In equation S1, C_a is the air concentration, $N_{analyte}$ is the mass of the compound of interest present in the sampler, V_s is the sampler volume, K_{sa} is the sampler-air partition coefficient, R_s is the compound specific sampling rate, and t is the duration of sampling. An analyte-specific K_{sa} was calculated for each target PAH and PRC using a regression based on individual octanol-air partition coefficients (K_{oa}). Sampling rates (R_s) of the PRCs were determined using equation S2:

$$\text{Eq. S2} \qquad R_s = -\frac{\ln\left(\frac{N}{N_0}\right)}{t} K_{sa} V_s$$

In equations S2 and S3, N_0 and N are the mass of PRC present at the beginning and ending of the sampling period, respectively. The sampling rate (R_s) for each analyte was calculated based on the R_s of the PRC with the most similar K_{oa}. Eq S3 uses compound class-specific modifiers (a) to compensate for compound-specific adjustments between the PRC and the target analyte.

$$\text{Eq. S3} \qquad R_{s,\text{target analyte}} = R_{s,PRC} * \frac{\alpha_{analyte}}{\alpha_{PRC}}$$

Sourcing ratios

Petrogenic PAH sources are typically enriched in the more thermodynamically stable isomer[5, 6]. In the two isomer pairs of PAHs used for PAH sourcing, phenanthrene and pyrene are the more thermodynamically stable isomers. Thus, a higher phenanthrene/anthracene, and a lower fluoranthene/pyrene ratio each indicate that the sample is predominantly petrogenic. A few samples had slightly pyrogenic signatures according to one ratio. However, more than one ratio should be used to confirm PAH source, as interpretation of values near the boundaries between sources can be less certain[5].

PAHs used in comparison

The 14 PAHs used in the comparison in Figure 2 were were Acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, benzo[g,h,i]perylene, and indeno[1,2,3-cd]pyrene. PAHs measured during the same season as the present study were used in this comparison where possible.

Quantitative risk assessment calculations

There were 10 PAHs that were above the detection limits and had nonzero RPFs (see Table S2). Thus, these were the 10 PAHs that were used in the carcinogenic risk assessment. These 10 PAHs were benzo[a]pyrene, benzo[b]fluoranthene, cyclopenta[c,d]pyrene, benzo[j]fluoranthene, benzo[a]anthracene, chrysene, fluoranthene, indeno[1,2,3-c,d]pyrene, benzo[k]fluoranthene, and benzo[g,h,i]perylene.

Risk assessment was performed using equations from the EPA's 2009 Risk Assessment Guidance for Superfund[7], using equations S4 and S5:

$$\text{Eq. S4} \qquad \mathrm{EC} = \frac{(\mathrm{CA\ x\ ET\ x\ EF\ x\ ED})}{\mathrm{AT}}$$

In equation S4, EC is the exposure concentration in ng/m^3, CA is the contaminant concentration in air in ng/m^3, ET is the exposure time in hours/day, EF is the exposure frequency in days/year, ED is the exposure duration in years, and AT is the averaging time. The AT includes the lifetime in years multiplied by 365 days/year and 24 hours/day.

$$\text{Eq. S5} \qquad \mathrm{ELCR} = \mathrm{IUR\ x\ EC}$$

In equation S5, ELCR is excess lifetime cancer risk, IUR is inhalation unit risk, and EC is the exposure concentration from Equation S4. In this study, an IUR of 8.7×10^{-5} ng/m3 was used. This is an IUR that was estimated for benzo[a]pyrene by the World Health Organization[8]. This was used because the U.S. EPA has no established an IUR for PAHs.

Overview and discussion of exploratory principle components analysis (PCA)

Exploratory data analysis was performed using a Principle Component Analysis (PCA) biplot showing scores and loadings plots together. All PAH variables that were above detection limits were used, in addition to the distance to closest well variable. Only sites previously classified as close or far were included. The data were first square root transformed and then mean centered and scaled. PC1 and PC3 were chosen as graph axes because the resulting PCA graph displayed good delineation between close and far sites and suggested which variables contributed most to this 'clumping'. PCA was performed using Primer-E version 6.1.13. A list of labels used in the PCA plot and the PAHs they correspond to can be found in Table S3.

Figure S1 shows that pyrene (p26) has the closest negative correlation with distance to the nearest active NGE well. This reinforces the results of the sourcing ratios in Figure 3. Given that pyrene is one of the PAHs used to indicate petrogenic signatures in the sourcing ratios, it is interesting that this is one of the main PAHs explaining the PAH data through PCA.

Figure S1 also shows samples in the close and far groups clumping separately. Looking closer at the clustering in the plot is also interesting. Samples in the far group are broken into two clusters of three samples. Far samples 1-3 cluster closer to the close samples, while far samples 4-6 cluster farther away from the rest of the samples. Interestingly, in the cluster that is closer to the close samples, two were located within 0.05 miles of heavily trafficked roads. This could potentially be a confounding factor.

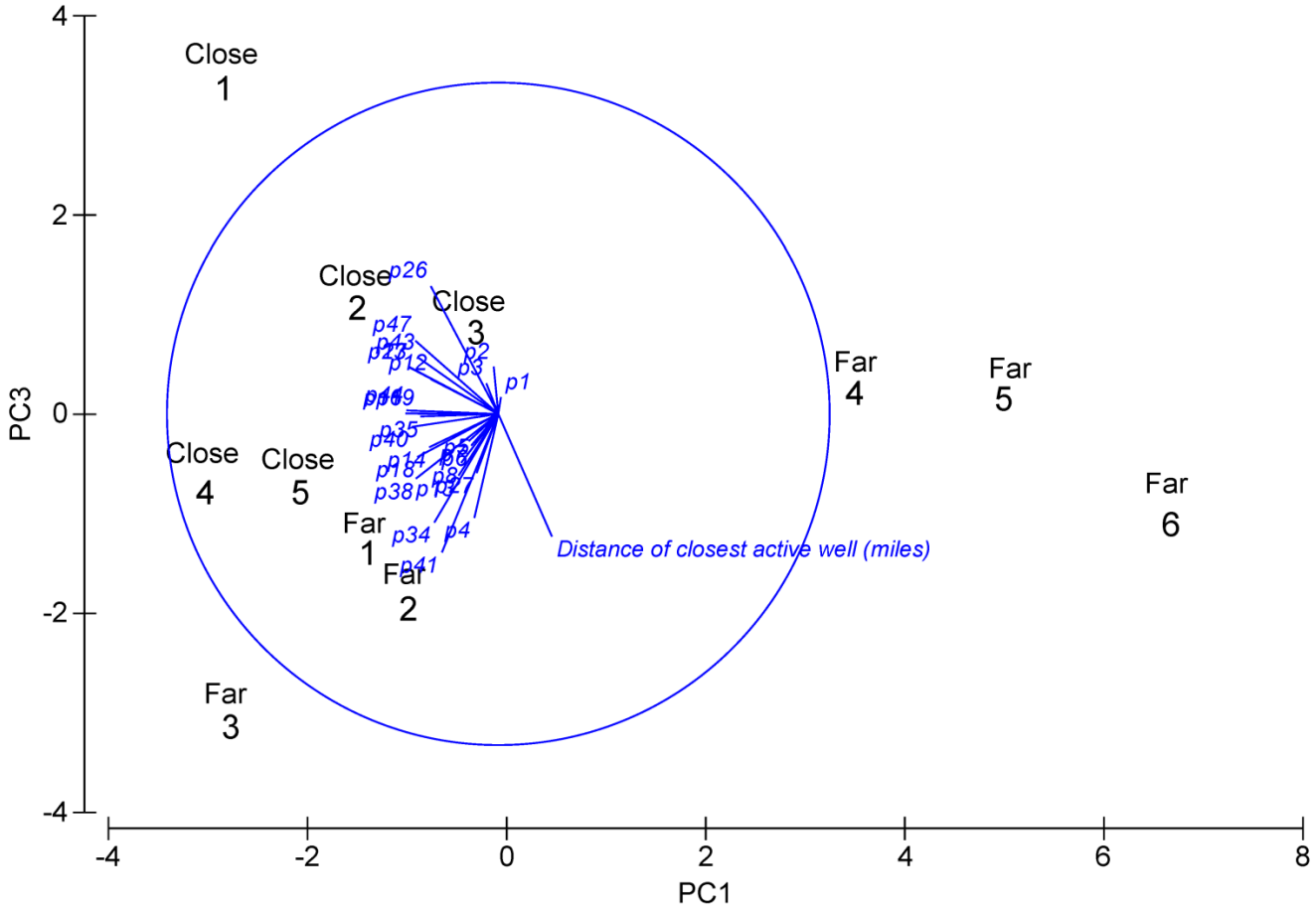

Figure S1. Exploratory principle components analysis (PCA) using PAHs and distance to closest active NGE well treated as covariates. The graph only includes data for samples in the close (n=5) and far (n=6) distance groups.

Table S1: List of performance reference compounds (PRCs), internal standard (IS), surrogates, and target polycyclic aromatic hydrocarbons (PAH) in the GC/MS Triple Quad method used for PAH analysis in this study, with limits of detection (LOD) and limits of quantification (LOQ).

PAH	Target, IS, PRC, or Surrogate?	CAS #	LOD (ng/mL)	LOQ (ng/mL)
Fluorene-d10	PRC	81103-79-9	.33	1
Pyrene-d10	PRC	1718-52-1	0.42	2.09
Benzo[b]fluoranthene-d12	PRC	205-99-2	1.67	5
Perylene-d12	IS	1520-96-3	1.67	
Naphthalene-d8	Surrogate	1146-65-2	.33	1
Acenaphthylene-d8	Surrogate	93951-97-4	.33	1
Phenanthrene-d10	Surrogate	1517-22-2	1.67	5
Fluoranthene-d10	Surrogate	93951-69-0	1.67	5
Chrysene-d12	Surrogate	1719-03-5	1.67	5
Benzo[a]pyrene-d12	Surrogate	63466-71-7	1.67	5
Benzo[ghi]perylene-d12	Surrogate	93951-66-7	1.67	5
Naphthalene	Target	91-20-3	1.04	5.20
2-Methylnaphthalene	Target	91-57-6	0.70	3.50
1-Methylnaphthalene	Target	90-12-0	0.28	1.39
2-Ethylnaphthalene	Target	939-27-5	0.97	4.84
2,6-Dimethylnaphthalene	Target	581-42-0	0.89	4.43
1,6-Dimethylnaphthalene	Target	575-43-9	0.81	4.05
1,4-Dimethylnaphthalene	Target	571-58-4	1.24	6.22
1,5-Dimethylnaphthalene	Target	571-61-9	1.19	5.93
1,2-Dimethylnaphthalene	Target	573-98-8	.94	4.70
1,8-Dimethylnaphthalene	Target	569-41-5	0.83	4.15
2,6-Diethylnaphthalene	Target	59919-41-4	0.81	4.06
Acenaphthylene	Target	208-96-8	2.33	11.65
Acenaphthene	Target	83-32-9	1.07	5.35
Fluorene	Target	86-73-7	0.79	3.97
Dibenzothiophene	Target	132-65-0	0.24	1.20
Phenanthrene	Target	85-01-8	0.46	2.31
Anthracene	Target	120-12-7	1.05	5.23
2-Methylphenanthrene	Target	2531-84-2	0.39	1.93
2-Methylanthracene	Target	613-12-7	0.47	2.36
1-Methylphenanthrene	Target	832-69-9	1.06	5.32

9-Methylanthracene	Target	779-02-2	0.87	4.37
3,6-Dimethylphenanthrene	Target	1576-67-6	0.42	2.08
2,3-Dimethylanthracene	Target	613-06-9	0.34	1.71
Fluoranthene	Target	206-44-0	0.54	2.72
9,10-Dimethylanthracene	Target	781-43-1	0.85	4.23
Pyrene	Target	129-00-0	0.42	2.09
Retene	Target	483-65-8	0.84	4.19
Benzo[a]fluorene	Target	238-84-6	1.67	5
Benzo[b]fluorene	Target	243-17-4	1.67	5
Benzo[c]fluorene	Target	205-12-9	0.30	1.50
1-Methylpyrene	Target	2381-21-7	0.38	1.90
Benz[a]anthracene	Target	56-55-3	0.75	3.77
Cyclopenta[c,d]pyrene	Target	27208-37-3	0.53	2.67
Triphenylene	Target	217-59-4	0.41	2.04
Chrysene	Target	218-01-9	0.50	2.49
6-Methylchrysene	Target	1705-85-7	0.89	4.44
5-Methylchrysene	Target	3697-24-3	1.67	5
Benzo[b]fluoranthene	Target	205-99-2	0.37	1.85
7,12-Dimethylbenz[a]anthracene	Target	57-97-6	0.94	4.71
Benzo[k]fluoranthene	Target	207-08-9	0.53	2.63
Benzo[j]fluoranthene	Target	205-82-3	0.56	2.79
Benz[j]&[e]aceanthrylene	Target	202-33-5 and 199-54-2	1.67	5
Benzo[e]pyrene	Target	192-97-2	0.71	3.53
Benzo[a]pyrene	Target	50-32-8	1.18	5.90
Indeno(1,2,3-c,d)pyrene	Target	193-39-5	0.26	1.32
Dibenzo[a,h]pyrene	Target	53-70-3	1.02	5.11
Picene	Target	213-46-7	0.74	3.72
Benzo[ghi]perylene	Target	191-24-2	0.34	1.71
Anthanthrene	Target	191-26-4	0.33	1.65
Naphtho[1,2-b]fluoranthene	Target	5385-22-8	1.67	5
Naphtho[2,3-j]fluoranthene	Target	205-83-4	1.67	5
Dibenzo[a,e]fluoranthene	Target	5385-75-1	0.47	2.36
Dibenzo[a,l]pyrene	Target	191-30-0	0.48	2.41
Naphtho[2,3-k]fluoranthene	Target	207-18-1	1.67	5
Naphtho[2,3-e]pyrene	Target	193-09-9	1.67	5

Dibenzo[a,e]pyrene	Target	192-65-4	6.44	32.22
Coronene	Target	191-07-1	0.70	3.49
Dibenzo[e,l]pyrene	Target	192-51-8	1.67	5
Naphtho[2,3-a]pyrene	Target	196-42-9	1.67	5
Benzo[b]perylene	Target	197-70-6	1.67	5
Dibenzo[a,i]pyrene	Target	189-55-9	1.42	7.10
Dibenz[a,h]anthracene	Target	189-64-0	0.52	2.60

Table S2: "PAHs with final RPFs based on tumor bioassay data," from the U.S. EPA's 2010 Development of a Relative Potency Factor (RPF) Approach for Polycyclic Aromatic Hydrocarbon (PAH) Mixtures[9].

PAH	Relative Potency Factor
Anthanthrene	0.4
Anthracene	0
Benz[a]anthracene	0.2
Benz[b,c]aceanthrylene	0.05
Benzo[b]fluoranthene	0.8
Benzo[c]fluorene	20
Benz[e]aceanthrylene	0.8
Benzo[g,h,i]perylene	0.009
Benz[j]aceanthrylene	60
Benzo[j]fluoranthene	0.3
Benzo[k]fluoranthene	0.03
Benz[l]aceanthrylene	5
Chrysene	0.1
Cyclopenta[c,d]pyrene	0.4
Cyclopenta[d,e,f]chrysene	0.3
Dibenzo[a,e]fluoranthene	0.9
Dibenzo[a,e]pyrene	0.4
Dibenz[a,h]anthracene	10
Dibenzo[a,h]pyrene	0.9
Dibenzo[a,i]pyrene	0.6
Dibenzo[a,l]pyrene	30
Fluoranthene	0.08
Indeno[1,2,3-c,d]pyrene	0.07
Naphtho[2,3-e]pyrene	0.3
Phenanthrene	0
Pyrene	0
Benzo(a)pyrene	1

Table S3: A list of labels used in the PCA plot in Figure S1, and the corresponding PAH names.

PCA Label	PAH
p1	Naphthalene
p2	2-Methylnaphthalene
p3	1-Methylnaphthalene
p4	2-Ethylnaphthalene
p5	2,6-Dimethylnaphthalene
p6	1,6-dimethylNaphthalene
p7	1,4-dimethylnaphthalene
p8	1,5-dimethylnaphthalene
p9	1,2-dimethylnaphthalene
p10	1,8-Dimethylnaphthalene
p11	2,6-Diethylnaphthalene
p12	Acenaphthylene
p13	Acenaphthene
p14	Fluorene
p15	Dibenzothiophene
p16	Phenanthrene
p17	Anthracene
p18	2-Methylphenanthrene
p19	2-Methylanthracene
p20	1-Methylphenanthrene
p21	9-Methylanthracene
p22	3,6-Dimethylphenanthrene
p23	Fluoranthene
p24	2,3-Dimethylanthracene
p25	9,10-Dimethylanthracene
p26	Pyrene
p27	Retene
p28	Benzo[a]fluorene
p29	Benzo[b]fluorene
p30	Benzo[c]fluorene
p31	1-Methylpyrene
p32	Benzo[a]anthracene
p33	Cyclopenta[cd]pyrene
p34	Triphenylene
p35	Chrysene
p36	6-Methyl chrysene
p37	5-Methylchrysene
p38	Benzo [b] fluoranthene
p39	7,12-Dimethylbenz[a]anthracene
p40	Benzo [k] fluoranthene
p41	Benzo [j] fluoranthene

p42	Benzo [e] pyrene
p43	Benzo [a] pyrene
p44	Indeno [1,2,3-c,d] pyrene
p45	Dibenzo [a,h] anthracene
p46	Benzo [a] chrysene
p47	Benzo [g,h,i] perylene
p48	Anthanthrene
p49	Naphtho[1,2-b]fluoranthene
p50	Naphtho[2,3-j]fluoranthene
p51	Dibenzo [a,e] flouranthene
p52	Dibenzo [a,l] pyrene
p53	Naphtho[2,3-k]fluoranthrene
p54	Naphtho[2,3-e]pyrene
p55	Dibenzo [a,e] pyrene
p56	Coronene
p57	Dibenzo[e,l]pyrene
p58	Naphtho[2,3-a]pyrene
p59	Benzo [b] perylene
p60	Dibenzo [a,i] pyrene
p61	Dibenzo [a,h] pyrene

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