

1 **Identifying and Quantifying Source Contributions of Air Quality Contaminants**  
2 **during Unconventional Shale Gas Extraction**

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43 **Abstract**

44 The United States experienced a sharp increase in unconventional natural gas (UNG)  
45 development due to the technological development of hydraulic fracturing. The  
46 objective of this study is to investigate the emissions at an active Marcellus Shale well  
47 pad at the Marcellus Shale Energy and Environment Laboratory (MSEEL) in  
48 Morgantown, Western Virginia, USA. Using an ambient air monitoring laboratory,  
49 continuous sampling started in September 2015 during horizontal drilling and ended in  
50 February 2016 when wells were in production. High resolution data were collected for  
51 the following air quality contaminants: volatile organic compounds (VOCs), ozone  
52 ( $O_3$ ), methane ( $CH_4$ ), nitrogen oxides (NO and  $NO_2$ ), carbon dioxide, ( $CO_2$ ), as well as  
53 typical meteorological parameters (wind speed/direction, temperature, relative  
54 humidity, and barometric pressure). Positive Matrix Factorization (PMF), a  
55 multivariate factor analysis tool, was used to identify possible sources of these  
56 pollutants (factor profiles) and determine the contribution of those sources to the air  
57 quality at the site. The results of the PMF analysis for well pad development phases  
58 indicate that there are three potential factor profiles impacting air quality at the site:  
59 *natural gas*, *regional transport/photochemistry*, and *engine emissions*. There is a  
60 significant contribution of pollutants during horizontal drilling stage to *natural gas*  
61 factor. The model outcomes show that there is an increasing contribution to *engine*  
62 *emission* factor over different well pad drilling through production phases. Moreover,  
63 model results suggest that the *regional transport/photochemistry* factor is more  
64 pronounced during horizontal drilling and drillout due to limited emissions at the site.

65 Keywords: ambient monitoring; natural gas; air pollution; source apportionment

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68 **Introduction**

69 There is a rapid increase in unconventional natural gas exploration by recent  
70 technological advances (USEIA 2020). The success of the US in exploiting  
71 unconventional natural gas has stimulated drilling activities in other countries. As a  
72 result, there is a growing attention by the public for the potential public health impacts  
73 of UNG extraction. In response to emerging public concern regarding the process of  
74 hydraulic fracturing for UNG extraction, several studies have investigated the potential  
75 public health risks of UNG development (Adgate et al. 2014; Hays et al. 2015; Hays et  
76 al. 2017; Werner et al. 2015). A part of adverse health effects are related to exposure of  
77 environmental pollution (Elliott et al. 2017; Elsner and Hoelzer 2016; Paulik et al.  
78 2016). The majority of environmental impact studies focus on water quality impacts of  
79 unconventional natural gas development (Annevelink et al. 2016; Butkovskyi et al.  
80 2017; Jackson et al. 2015; Torres et al. 2016). However, relatively fewer studies focus  
81 on air quality impacts (Hecobian et al. 2019; Islam et al. 2016; Ren et al. 2019;  
82 Swarthout et al. 2015; Williams et al. 2018). Some studies focus on collecting and  
83 analyzing data for pre-operational phase of fields to provide baseline dataset for future  
84 work that operational shale gas activities can be later evaluated (Purvis et al. 2019).  
85 Non-methane hydrocarbons (NMHC) and nitrogen oxides (NO<sub>x</sub>) are of most interest as  
86 some NMHC can be toxic (such as benzene) (Edwards et al. 2014), therefore, several  
87 studies focuses on increases in methane, NHMC, and ozone in oil and gas producing  
88 regions (Pacsi et al. 2015; Roest and Schade 2017). Another study explored the  
89 importance of the deployment autonomy of portable measurement systems by  
90 measuring exposure upwind, within and downwind of operation of hydraulic fracturing  
91 equipment to protect workers (Ezani et al. 2018). There are also more comprehensive  
92 studies for data collection. Swarthout et al. (2015) conducted a field campaign to  
93 investigate the impact of UNG production operations on regional air quality. Highest  
94 density of methane, carbon dioxide, and volatile organic carbons (VOCs) were

95 observed closer to UNG wells. A limited number of studies available on source  
96 apportionment for major air pollutants (Abeleira et al. 2017; Gilman et al. 2013; Majid  
97 et al. 2017; Prenni et al. 2016). These studies have lacked a comparison of the effects  
98 during distinct operational phases of natural gas extraction: well pad construction,  
99 drilling (vertical and horizontal), well stimulation (hydraulic fracturing followed by  
100 flowback), and production.

101 Several compounds are associated with emissions from each phase of well installation  
102 and development, depending on the activity and equipment in use for each phase.  
103 Activities that require the use of off-road diesel construction vehicles have emissions  
104 of coarse particulate matter ( $PM_{10}$  aerodynamic diameter  $\leq 10 \mu m$ ) from the suspension  
105 of dust from vehicle traffic on dirt and gravel roads, as well as volatile organic  
106 compounds (VOCs), nitrogen oxides ( $NO_x$ ) and fine particulate matter smaller than  $2.5$   
107  $\mu m$  in aerodynamic diameter ( $PM_{2.5}$ ) from the vehicle exhaust. During vertical and  
108 horizontal drilling, there are emissions of  $NO_x$ ,  $PM_{2.5}$ , and VOCs from diesel powered  
109 drilling rigs, and fugitive emissions of natural gas (methane ( $CH_4$ ) and other  
110 hydrocarbons). Hydraulic fracturing activities add emissions from truck traffic and  
111 diesel-powered compressors ( $NO_x$ ,  $PM_{10}$ ,  $PM_{2.5}$ , VOCs). Emissions of VOCs and  $CH_4$   
112 from water separation tanks, venting, and degassing of produced waters occur during  
113 flowback operations. In addition to these primary sources of emissions at the site,  
114 secondary production of ozone ( $O_3$ ) and  $PM_{2.5}$  from photochemistry can result from  
115 emissions during any of the operational phases.

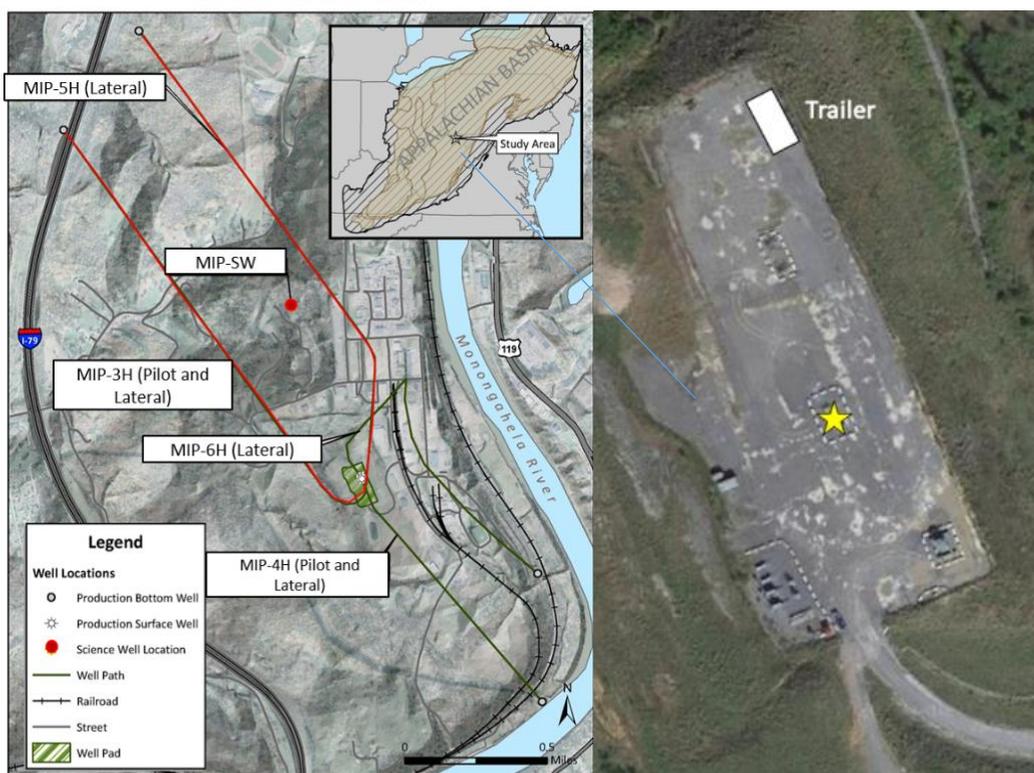
116 This is the first study, to our knowledge, to collect high time resolution ambient  
117 concentrations of compounds emitted from well pad activity on Marcellus Shale during  
118 various phases of operation such that the relative air quality effect of each phase of  
119 development can be investigated. This detailed information about the distribution of

120 emission sources' impact through a well pad's development phases is needed to manage  
121 the associated risks from emissions.

## 122 **Methods**

### 123 **Monitoring Location: Marcellus Shale Energy and Environment Laboratory**

124 The Marcellus Shale formation covers an area of approximately 240,000 km<sup>2</sup> across  
125 several states: New York, Pennsylvania, Ohio, West Virginia, Maryland, and Virginia  
126 (Kargbo et al. 2010) (Figure S1). The Marcellus Shale Energy and Environment  
127 Laboratory (MSEEL) is an approximately 14,000 m<sup>2</sup> study well pad in Morgantown,  
128 WV, USA (39.602° N, 79.976° W) (MSEEL 2019). The MSEEL is a multi-institutional,  
129 long-term collaborative field site where integrated geoscience, engineering, and  
130 environmental research have been conducted to assess environmental impacts and  
131 develop new technology to improve recovery efficiency as well as reduce  
132 environmental footprint of shale gas operations (MSEEL 2019). The MSEEL is the  
133 site of two horizontal production wells completed in 2011 (wells 4H and 6H, Figure 1)



134 and two horizontal production wells completed in 2015 (wells 3H and 5H, Figure 1).  
135 Production from the newer horizontal wells began in December 2015. Figure 1 shows  
136 the location of the trailer with respect to the location of the wells and the boundaries of  
137 the well pad. The distance between the wells and the trailer is 90 m. Dates and duration  
138 for phases of operation are shown in Figure S2, the total gas production for the four  
139 wells are shown in Figure S3. The vertical drilling was conducted using three diesel  
140 Caterpillar 3512 engines with 1365 kW generators. Horizontal drilling made use of two  
141 dual fuel (40% diesel and 60% natural gas) engines. All activities at the well pad  
142 followed industry's best management practices (MSEEL 2019).

### 143 **Air Quality and Meteorological Data Collection**

144 An ambient air monitoring laboratory (18' trailer with ambient air sampled from inlets  
145 on the trailer roof) was situated at the northeastern corner of the MSEEL well pad  
146 (Figure 1). With wind direction at this location most frequently from the southwest  
147 (Figure 2), this position optimized the occurrences of the laboratory being downwind  
148 of the well pad. Instrumentation in the laboratory and measured constituents are listed  
149 in Table 1. All instruments were maintained and calibrated according to manufacturer's  
150 recommended protocols. Details of the laboratory assembly and operation have been  
151 previously described (Pekney et al. 2014).

152 Data collected at the air monitoring site is classified by activity at the well pad.  
153 Horizontal drilling occurred September 8 – October 5, 2015, first at well 5H then at  
154 well 3H. Hydraulic fracturing occurred October 10 – November 16. Cleanout activities  
155 followed on November 20-26, which involved using a diesel-powered coil tubing rig to  
156 drill out plugs and flush out residue left in the wells.

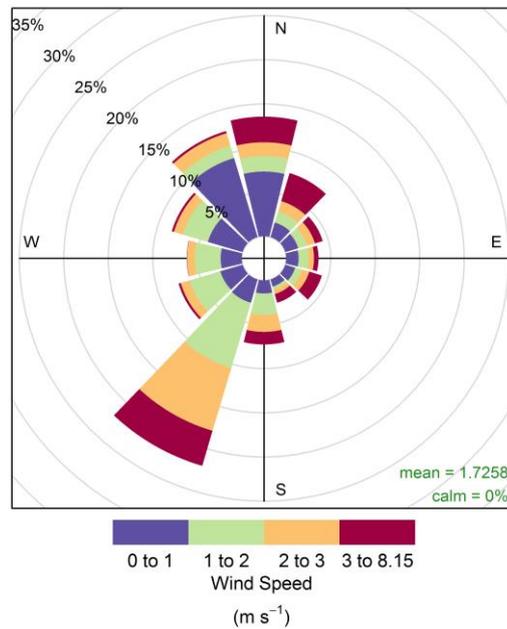


Figure 2. Wind speed and direction during ambient air monitoring campaign at MSEEL (September 2015-February 2016).

158 Flowback, the flowing of gas, formation fluid, and hydraulic fracturing fluid up the  
 159 wells to the surface, took place over December 10-14, after which both wells were in  
 160 production. A reduced emission completion (REC) was performed; gas produced  
 161 during this time was captured using portable equipment brought on site that separates  
 162 the gas from the liquids so that the gas can be retained as a product.

163 Air monitoring began September 18, 2015 and ended February 1, 2016. No data were  
 164 collected for the vertical drilling phase. Data collection was continuous except for  
 165 calibration and instrument downtime. The laboratory's meteorological station  
 166 measured relative humidity, temperature, rainfall, solar radiation, wind direction, wind  
 167 speed, and barometric pressure at an elevation of 10 m.

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172 Table 1. Constituents measured by the MSEEL mobile air monitoring laboratory  
 173 (Pekney et al. 2018).

Measurement	Unit	Resolution	Sampling Rate	Instrument	Measurement technique
VOCs (52 compounds, see Table S1 for full list)	ppb	0.4 ppb	1 hour	Perkin Elmer Ozone Precursor Analyzer (Waltham, Massachusetts)	Gas Chromatograph with Flame Ionization Detection (GC—FID) with thermal desorption
Ozone, NO <sub>x</sub>	ppb	0.4 ppb Ozone, 50 ppb NO <sub>x</sub>	1 minute	Teledyne-API Gas Analyzers T400 and T200U (San Diego, California)	UV absorption, Chemiluminescence
Methane, carbon dioxide	ppm	<5 ppb Methane, 1 ppm CO <sub>2</sub>	1 second	Picarro G2201-i (Santa Clara, California)	Cavity Ring-Down Spectrometry
Meteorological Parameters: wind speed and direction, temperature, relative humidity, barometric pressure, rainfall, and solar intensity	various	Various; 1 degree for wind direction/ 0.45 m/s for wind speed for Vantage Pro2 Plus; 0.1 degree for wind direction/ 0.01 m/s wind speed for R.M. Young 81000	1 minute	Davis Instruments Vantage Pro2 Plus (Oakland, California) and R.M. Young 81000 ultrasonic anemometer (Traverse City, Michigan)	Various

174 **Source-Receptor Modeling**

175 Positive Matrix Factorization (PMF), a factor analysis method (Figure S7), was applied  
 176 to hourly averaged ambient concentrations of measured species to identify possible  
 177 sources and patterns for the stages of development. PMF decomposes the sample data  
 178 into two matrices: factor profiles (representative of *sources*) and factor contributions  
 179 (Brown et al. 2015; Norris et al. 2014). The fundamental objective of PMF is to solve  
 180 the chemical mass balance (Equation 1) between measured species concentrations and  
 181 source profiles while optimizing goodness of fit (Equation 2):

182 Mass balance (Evans and Jeong 2007):

$$183 \quad x_{i,j} = \sum_{k=1}^p g_{ik} f_{kj} + e_{ij}$$

184 [1]

185 where  $x_{i,j}$  is the data matrix with dimensions of  $i$  (observations) by  $j$  (chemical species),  
186  $p$  is the optimum number of factors,  $g_{ik}$  is the factor contribution to the observation,  $f_{kj}$   
187 is the species profile of the factor,  $k$  is the factor, and  $e_{i,j}$  is the residual concentration  
188 for each observation.

189 Goodness of fit:

$$190 \quad Q = \sum_{i=1}^n \sum_{j=1}^m \left( \frac{x_{ij} - \sum_{k=1}^p g_{ik} f_{kj}}{s_{ij}} \right)^2$$

191 [2]

192 where  $Q$  is the goodness of fit,  $n$  is the total number of observations,  $m$  is the total  
193 number of chemical species, and  $s_{ij}$  is the uncertainty for each observation. Summary  
194 of methods for uncertainty calculations are provided in Supplemental Information.  
195 Missing values within the data set are replaced with the median value of that species;  
196 also, uncertainty for missing values is set at four times the species-specific median by  
197 the program. Multiple runs with different numbers of factors are executed for each data  
198 set. The output of the PMF analysis needs to be interpreted by the user to identify the  
199 number of factors that may be contributing to the samples and the possible sources they  
200 represent. One of the main strengths of PMF analysis is that each sample is weighted  
201 individually, which allows the user to adjust the influence of each sample based on the  
202 measurement confidence.

203 Signal-to-noise ratio (S/N), an indicator of the accuracy of the variability in the  
204 measurements, can be used to identify a species as “Strong”, “Weak”, or “Bad”.

205 Generally, if this ratio is greater than 0.5 but less than 1 that species has a “Weak”  
206 signal. “Strong” is the default value for all species with an assumption of S/N greater  
207 than 1. “Bad” category excludes the species from the rest of the analysis. We considered  
208 the number of samples that are missing or below the detection limit when choosing the  
209 category for each species. (Norris et al. 2014). The expected goodness of fit ( $Q_{expected}$ )  
210 is calculated for each scenario (Norris et al. 2014):

211 Expected goodness of fit:

$$212 \quad Q_{expected} = (i \times j) - \{(p \times i) + (p \times j)\} \quad [3]$$

213

214 where  $(i \times j)$  is the number of non-weak data values in  $X_{ij}$  and  $(p \times i)$  and  $(p \times j)$  are the  
215 number of elements in G and F, respectively.  $Q_{robust}$  is the calculated goodness-of-fit  
216 parameter that excludes points that are not fit by the model. The lowest  $Q_{robust}/Q_{expected}$   
217 is calculated to compare different factor scenarios; when changes in Q become small  
218 with increasing factors, it can indicate that there may be too many factors in the solution  
219 (Brown et al. 2015).

220 In addition to these calculated parameters, factor profiles and error estimation  
221 diagnostics are used to compare the output of different simulations. Marker species  
222 (chemical species that are unique to a particular source) and temporal or seasonal  
223 variations can be used to aid in identifying the possible emission sources (Figure 3).  
224 Associations between factors can also provide useful information for profile  
225 characterization. Moreover, meteorological data can provide useful information about  
226 the geographic location of the sources.

227 In order to perform the PMF analysis, we utilized a user-friendly graphical user  
228 interface (GUI) developed by the U.S. Environmental Protection Agency (EPA), EPA  
229 PMF 5.0 (Norris et al. 2014). Hourly average data was used for each pollutant to unify

230 the measurement intervals. All pollutants included in the matrix were identified as  
231 “strong” (signal to noise:  $S/N > 2$ ). Fifty base runs were performed, and the run with  
232 the minimum Q value was selected as the base run solution. In each case, the model  
233 was run in the robust mode with a number of repeat runs to ensure the model least-  
234 squares solution represents a global rather than a local minimum. First, the rotational  
235 (linear transformation) Fpeak variable was held at the default value of 0.0. However,  
236 there can be almost infinite possibilities of F and G matrices that produces the same  
237 minimum Q value, but the goal is producing a unique solution. As a result, rotational  
238 freedom is one of the main sources of uncertainty in PMF solutions (Paatero et al.  
239 2014). Therefore, Fpeak values were adjusted (-1.0, -0.5, 0.5, and 1.0) to explore how  
240 much rotational ambiguity exists in PMF solutions. In other words, the model adds  
241 and/or subtracts rows and columns of F and G matrices based on the Fpeak value, which  
242 is typically between -5 and +5 (Norris et al. 2014). Positive Fpeak values cause a  
243 sharpened F-matrix and smeared G-matrix; negative Fpeak values result in subtractions  
244 in the G-matrix. The factor contributions were analyzed to find the optimum Fpeak  
245 value.

246 The PMF analysis was completed with error estimation. We used three methods of  
247 error estimation: Bootstrap (BS), Displacement (DISP), and BS-DISP, which guide  
248 understanding the stability of the PMF solution (Norris et al. 2014). BS analysis is  
249 used to determine whether a set of observations affect the solution disproportionately.  
250 The main idea of BS analysis is resampling different versions of the original data set  
251 and perform PMF analysis. Random errors and rotational ambiguity affect BS error  
252 intervals. The main reason of rotational ambiguity is the existence of infinite solutions  
253 similar to the solution generated by PMF solution. DISP analysis helps to analyze the  
254 PMF solution in detail. Only rotational ambiguity affects DISP error intervals.  
255 BS-DISP is a hybrid method that gives more robust results than DISP results.

## 256 **Results and Discussion**

### 257 **Overview of Results for Measured Compounds**

258 Figure 3 shows a box-and-whisker graph of the measured NO<sub>x</sub>, NO, NO<sub>2</sub>, Ozone, and  
259 ethane during the whole monitoring campaign at the study site. Similarly, Figure 5  
260 shows a statistical summary of methane and carbon dioxide. The y-axis represents  
261 concentrations and the x-axis represents the phases of the well development. The black  
262 line on each of the boxes represents the median for that particular data set. The small  
263 circles represent outliers. The blue circles represent the mean. Since most of the VOCs  
264 concentrations measured were consistently below 10 ppb, only ethane is included.  
265 There was an increase for NO<sub>x</sub> (25<sup>th</sup> percentile (q1)=12.5 ppb) and NO (q1= 2.7 ppb)  
266 during the *fracturing* phase compared to other phases. The whiskers show the high  
267 variability for this phase, which can be a result of small sample size for the *fracturing*  
268 phase. NO/NO<sub>2</sub> ratio for 25<sup>th</sup> and 75<sup>th</sup> percentiles was 1.2, indicating fresher, less  
269 oxidized emissions. The skewness of the data for this phase indicates that the data may  
270 not be normally distributed. NO<sub>2</sub> graph shows a similar trend for the *fracturing* phase.  
271 We did not observe significant differences for different development phases for ozone,  
272 which is not surprising as it is a secondary pollutant and it can be related to winter  
273 season of the data collection period (Edwards et al. 2014). There was a dramatic  
274 increase for the *flowback* phase for ethane concentration. This 25<sup>th</sup> percentile was 24  
275 ppb, while this concentration ranged between 0 and 11 ppb for other phases. The 75<sup>th</sup>  
276 percentile was 89 ppb, which is a significantly higher value compared to other phases.  
277 We observed a similar trend for methane concentration. The 25<sup>th</sup> percentile (2.5 ppm)  
278 and the 75<sup>th</sup> percentile (4.3 ppm) were significantly higher than other phases.  
279 Differences for development phases for CO<sub>2</sub> were not statistically significantly

280 different. CO<sub>2</sub> has many emissions sources and variable background concentrations so  
 281 distinguishing emissions from the well pad activities is difficult.

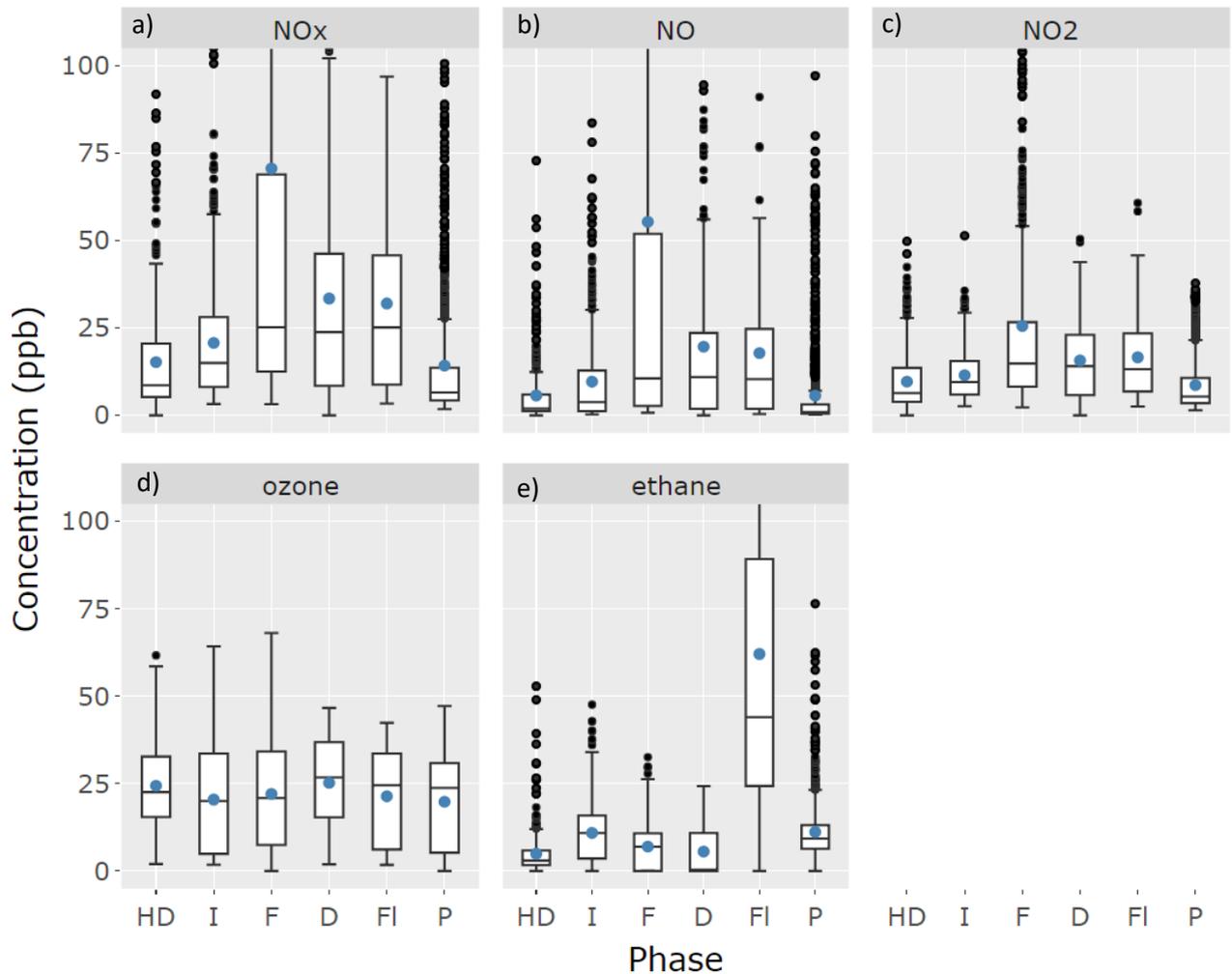
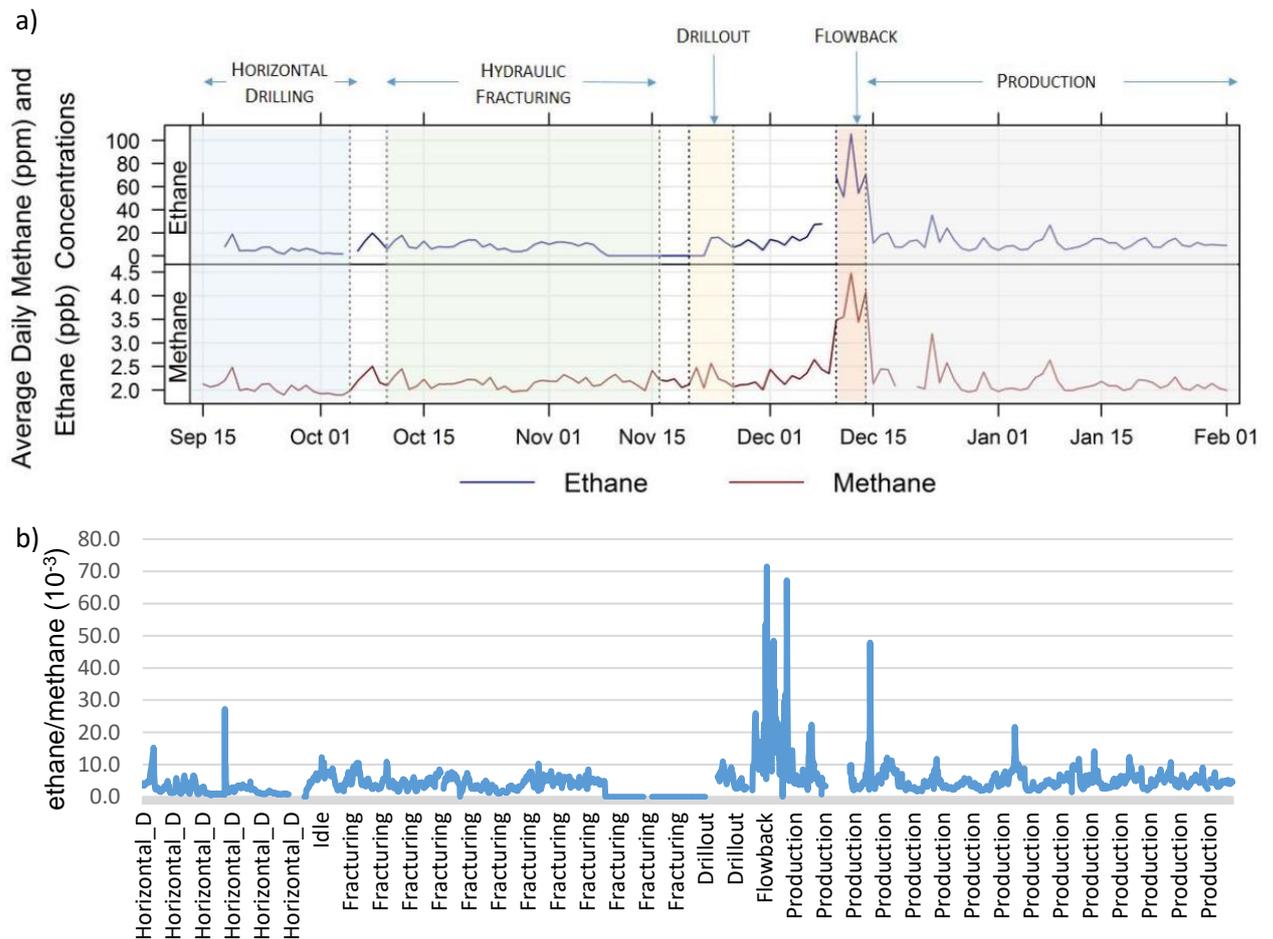


Figure 3. Summary statistics of input parameters for (a) NO<sub>x</sub>, (b) NO, (c) NO<sub>2</sub>, (d) Ozone, (e) ethane (HD: Horizontal Drilling, I: Idle, F: Fracturing, D: Drillout, FI: Flowback, P: Production). The idle phase consists of gaps of time between other operational phases, when there was little to no emissions-generating activity on the well pad.

282 The average concentrations of methane and ethane for the entire monitoring campaign  
 283 are shown in Figure 4a. The highest ethane concentrations occurred during the  
 284 *flowback* stage (565.7 ppb). A mean that is significantly higher than the median comes  
 285 from a distribution that is skewed due to peak events (mean<sub>ethane</sub>= 11.4 ppb,  
 286 median<sub>ethane</sub>= 8.5 ppb). Figure 4b shows the time series of ethane to methane ratios  
 287 throughout the operational phases. The lowest average ratio occurred at *horizontal*  
 288 *drilling* with 2.5, while the highest ratio occurred at *flowback* phase with 17.4 average

289 ratio. The average ethane/methane ratio for *fracturing*, *drillout*, and *production* phases  
290 are 3.4, 3.2, and 5.1 respectively.



291

292

293 Figure 4. (a) Ethane and methane 24-hour average concentrations (b) the ratio of ethane  
294 to methane from Drilling through Production Monitoring Period of well pad activity.

295 The hourly concentration graphs of NO<sub>x</sub>, O<sub>3</sub>, and CH<sub>4</sub>, and CO<sub>2</sub> were used to analyze  
296 the factor solutions (Figure S8). Hecobian et al. (2019) investigated the emissions  
297 during different well pad development phases to analyze emission rates in the Denver-  
298 Julesburg and Piceance basins in Colorado, US. They observed that emission rates of  
299 benzene and most VOCs were highest during flowback for both basins, on the other  
300 hand, they had much lower emission rates from the production phase, which can be  
301 related to the differences in duration of each phase (days to weeks). Light alkanes and  
302 benzene concentrations were higher during hydraulic fracturing. It is difficult to directly  
303 compare the results of the two studies, because the proposed study is based on

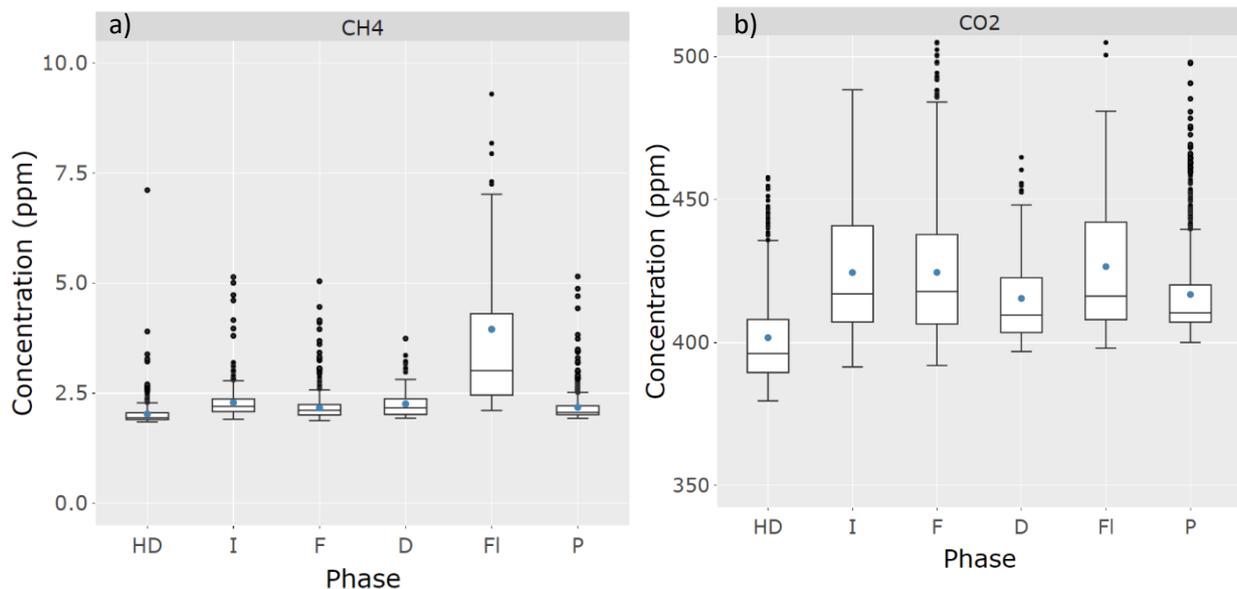
304 continuous data during each phase while Hecobian et al. (2019) collected 374  
305 measurements from five drilling, eight fracking, nine flowback, one liquids load out,  
306 and 11 production sites to analyze emission rate.

307 Figure S4 shows the dominant wind directions on overall concentrations, as well as  
308 giving information on the different concentration levels. Pollution roses show which  
309 wind directions contribute most to overall mean concentrations. For all air quality  
310 species, southwestern winds controlling the overall mean concentrations at the well pad.  
311 To explore the relationship between methane and ethane, we conditioned ethane by  
312 methane. Figure S5 indicates that higher ethane concentrations are associated with the  
313 SW and higher methane concentrations. The results also show that lower ethane and  
314 methane concentrations contributed from the east; the highest methane concentrations  
315 were obscured by a relatively high ethane background. The highest contribution to the  
316 factors were provided from the SW data (Figure S6).

### 317 **Factor Profiles**

318 The three-factor model was chosen for the PMF analysis based on the interpretation of  
319 the factor profiles,  $Q_{\text{robust}}/Q_{\text{expected}}$  ratios (Table S3), factor contributions, error  
320 estimation results (Table S4, Figure S9), and hourly peak concentrations of pollutants.  
321 The three-factor solution was resolved to the following factors: *natural gas* for the  
322 natural gas-related emissions sources; *regional transport/photochemistry* for the  
323 atmospheric regional molecular transport and oxidized background air; and *engine*  
324 *emissions* for emissions from vehicles, drill rigs, generators, and pumps used at the site  
325 (Figure 5). The summary of PMF models with various  $F_{\text{peak}}$  values for well  
326 development activities are shown in Table S4. The DISP, BS, and BS-DISP results for  
327 2, 3, and 4 factor PMF solutions are summarized in Table S2. For the 3-factor analysis,

328 the DISP results indicate that there are no swaps and the PMF solution is stable, which  
 329 means there are no exchange factor identities and it is a well-defined solution for the  
 330 case. According to BS results, there is a small uncertainty; this can be an impact of high  
 331 variability in concentration. BS-DISP captures both random errors and rotational  
 332 ambiguity; these results also indicate that the solution is reliable because there are no  
 333 swaps between factors for the PMF model. Error estimation summary plots (Figure S9)  
 334 show range of concentration by species in each factor: Base Value, BS 5th, BS Median,  
 335 BS 95th, BS-DISP 5th, BS-DISP Average, BS-DISP 95th, DISP Min, DISP Average,  
 336 and DISP Max.



337 Figure 5. Summary statistics of input parameters for methane (a) and carbon dioxide  
 338 for (b) (HD: Horizontal Drilling, I: Idle, F: Fracturing, D: Drillout, FI: Flowback, P:  
 339 Production).

### 340 Source Profiles

341 **The natural gas factor** was named as such due to its composition of species that are  
 342 present in natural gas: 89% CO<sub>2</sub>, 1% methane, 3% ethane, 1.5% propane, 0.5%  
 343 isobutane, 1% n-butane, 0.1% pentane, and 0.2% isopentane (Figure S10). Ethane is a  
 344 particularly good marker for natural gas emissions sources due because its atmospheric  
 345 sources are almost exclusively from natural gas extraction, production, processing and

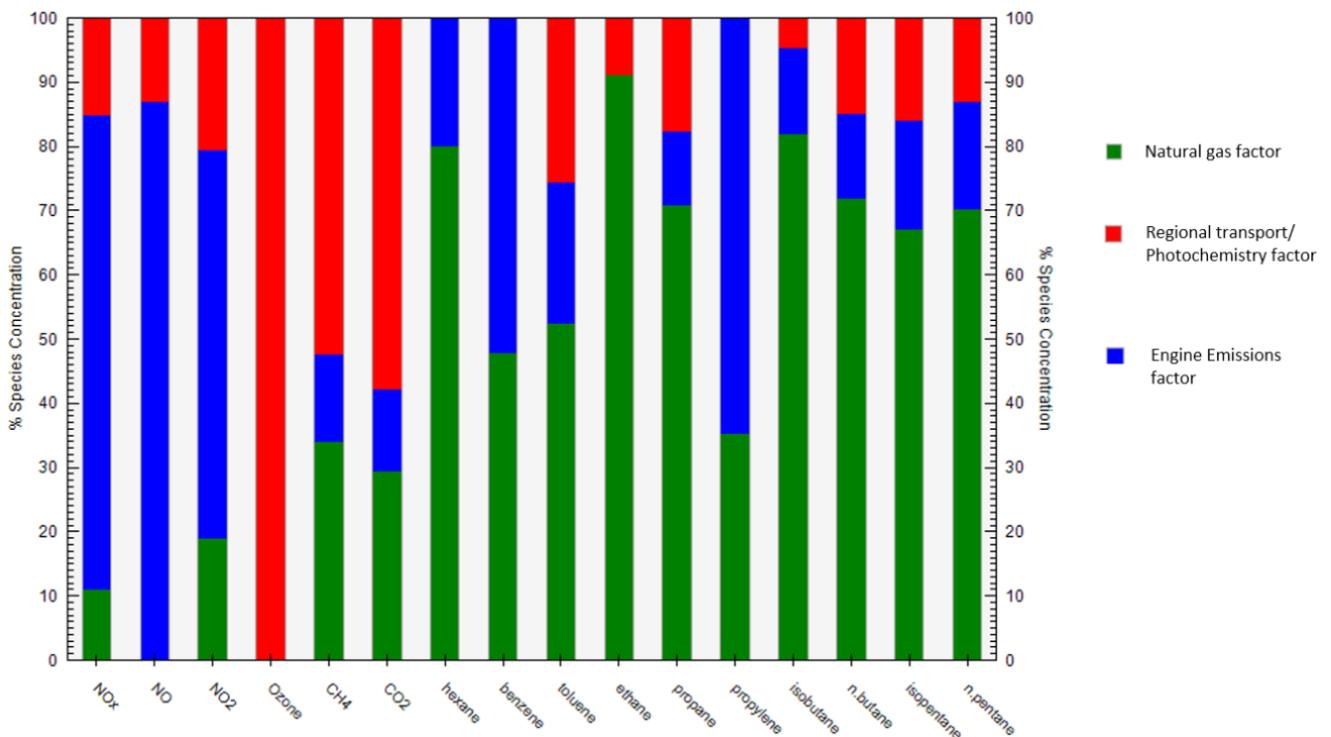
346 use (Liao et al. 2017). Ninety-two percent of ethane mass is explained by the natural  
347 gas factor (Figure 6). The highest contribution for this factor occurred during the  
348 *flowback* phase.

349 **The regional transport/photochemistry factor** was characterized by high  
350 contributions from ozone (12%), methane (1%), and CO<sub>2</sub> (86%) (Figure S10). Ninety-  
351 nine percent of the ozone mass was explained by this factor (Figure 6). Ozone is a  
352 product of photochemistry and not directly emitted by any of the sources on the well  
353 pad. Although CH<sub>4</sub> and CO<sub>2</sub> would be emitted by well pad sources, they are also present  
354 in background ambient air and could be transported to the monitoring location from  
355 other sources in the region. Contributions of this factor were relatively steady for all  
356 phases of operation during the entire monitoring campaign.

357 **The engine emissions factor** was composed of 39% NO<sub>x</sub>, 33% NO, and 11% NO<sub>2</sub> as  
358 well as 0.02% toluene and 0.04% benzene (Figure S10). The portions of the mass of  
359 these species explained by this factor are 74%, 87%, 60%, 20%, and 54%,  
360 respectively (Figure 6). Toluene is released mainly from motor vehicle emissions and  
361 chemical spills (Gierczak et al. 2017). Another important emission source is oil and  
362 gas extraction (EPA, 1993). Contribution of this factor was significantly highest  
363 during hydraulic fracturing, when there were emissions from many diesel engines  
364 operating continuously on the well pad. Contribution during *flowback* was also  
365 elevated. Several peaks of contribution were observed during production, which could  
366 be due to maintenance vehicles and other short-lived vehicle-based activities on the  
367 well pad.

368 The main limitation of the study is having uneven number of data points for each  
369 operational phase. This limitation affects the analyses; however, we do not have control  
370 of the durations of the operational phases. PMF models have several limitations. First,  
371 it needs large datasets. In this study, the number of data varies based on the duration of

372 the activity (Figure S2). Therefore, the contribution to the factors is not same for each  
 373 phase. This is the main reason behind the uncertainty of defined factors. Second, the  
 374 accuracy and precision of measured species limit the analysis. The determination of the  
 375 number and character of factors is based on an expert’s interpretation. Comprehensive  
 376 information is needed on source profiles to verify the defined source profiles. Finally,  
 377 the pre-set parameters are playing an important role on the model results. As a future  
 378 work, integrating more data from different fields can decrease the inherent uncertainty.



379 Figure 6. The three-factor solution fingerprints for Drilling through Production  
 380 Monitoring Period,  $F_{peak}=1$ .

### 381 Conclusion

382 We investigated the effect of unconventional natural gas development activities on local  
 383 air quality by using ambient air monitoring laboratory near Marcellus Shale well pad in  
 384 Morgantown, Western Virginia. The results of PMF solutions for well pad development  
 385 phases show that there were three potential factor profiles as outlined in Figure 5:  
 386 *natural gas*, *regional transport/photochemistry*, and *engine emissions*. Horizontal  
 387 drilling stage had an important contribution to the *natural gas* factor. In addition, there  
 388 was a significant concentration contribution at the end of the horizontal drilling phase.

389 An increasing contribution to *engine emission* factor was observed over different well  
390 pad drilling through production phases. The peak concentration was observed during  
391 the drillout stage. Even though it is difficult to compare the *regional*  
392 *transport/photochemistry* contributions due to high variability, highest contributions  
393 occurred during horizontal drilling and drillout.

394 As determined by the PMF analysis, a measurable increase in natural gas-related  
395 pollutant concentrations and the associated natural gas factor contribution from  
396 different stages of active phase was not observed. At the downwind distance of 600m  
397 from the well pad center to the air monitoring laboratory, the emissions from the well  
398 pad were not easily distinguishable from typical variations in ambient background  
399 concentrations. West Virginia has many natural gas wells that contribute to the ambient  
400 background, as evidenced by ethane concentrations that are higher than typical global  
401 background (Rinsland et al. 1987; Rudolph et al. 1996). Short-lived peak events that  
402 were observed when the wind direction was coming from the well pad show that  
403 emissions can be dispersed downwind and detected at this distance, but when  
404 concentrations are averaged and analyzed with a PMF analysis the peak events were  
405 not significant enough to result in a measurable impact of the well pad emissions at the  
406 receptor location. Understanding the air quality impacts of operational phases is  
407 important since it has potential to help inform future decision-making and constrain  
408 cumulative impact assessments.

#### 409 **Conflicts of interest**

410 There are no conflicts to declare.

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#### 430 **Author Contribution**

431 **Nur H Orak:** Conceptualization, Methodology, Software. Visualization, Writing  
432 **Natalie J. Pekney:** Supervision, Methodology, Writing. **Matthew Reeder:**  
433 Methodology, Validation.

#### 434 **Code/Data availability**

435 Model simulations presented in this paper are available upon request.

436

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