Supplement of Atmos. Chem. Phys., 21, 4729–4739, 2021
https://doi.org/10.5194/acp-21-4729-2021-supplement

Atmospheric Chemistry and Physics
Open Access

Supplement of

Identifying and quantifying source contributions of air quality contaminants during unconventional shale gas extraction

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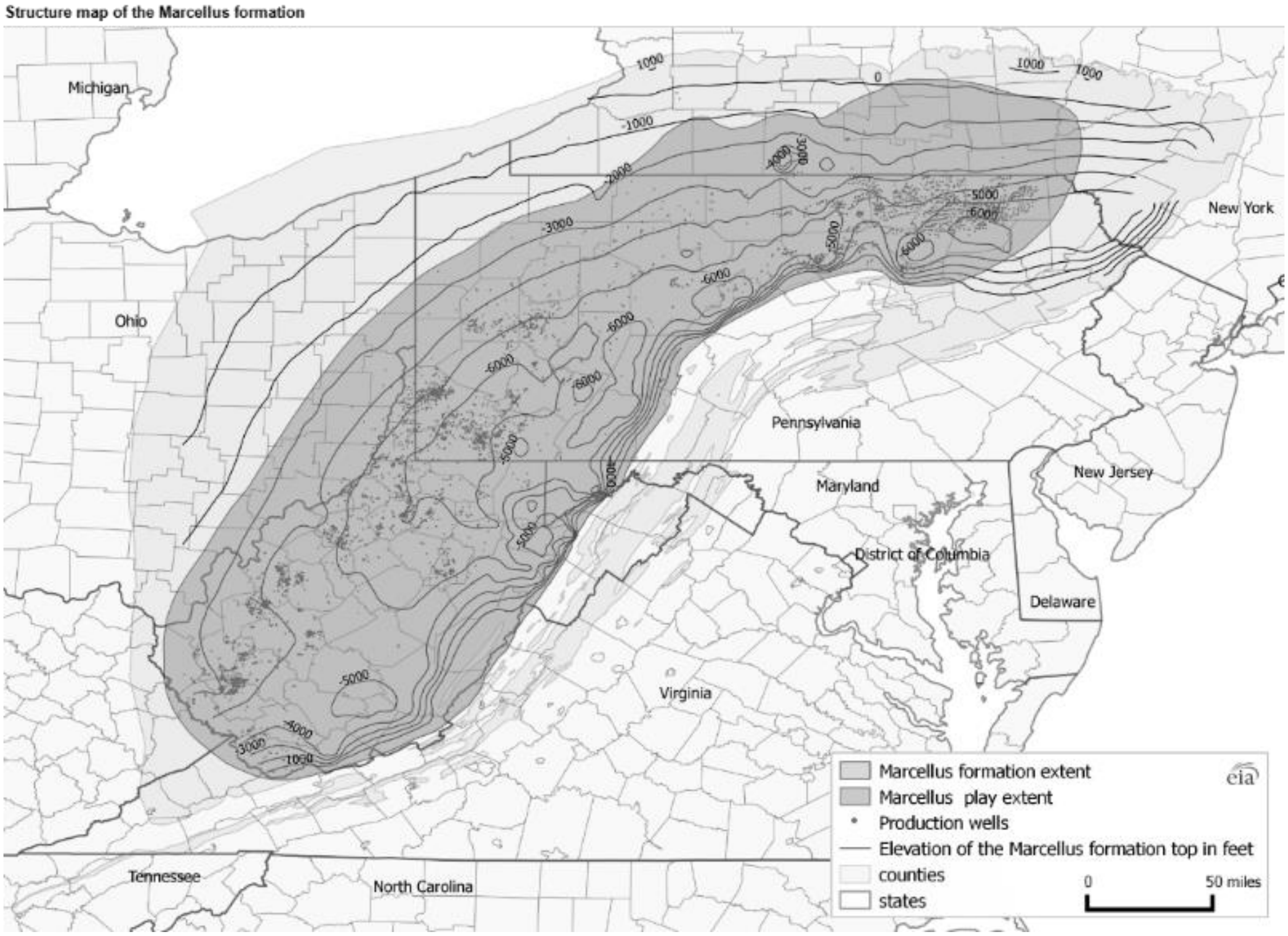


Figure S1. Structure map of the Marcellus formation (EIA 2015a).

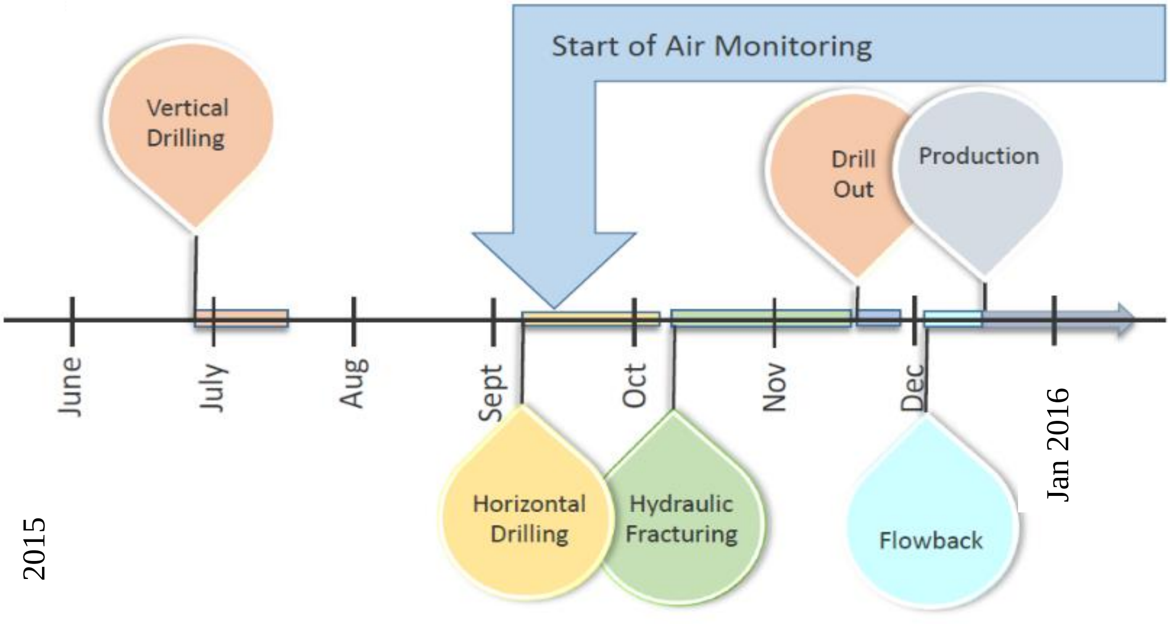


Figure S2. Unconventional natural gas production process activity diagram.

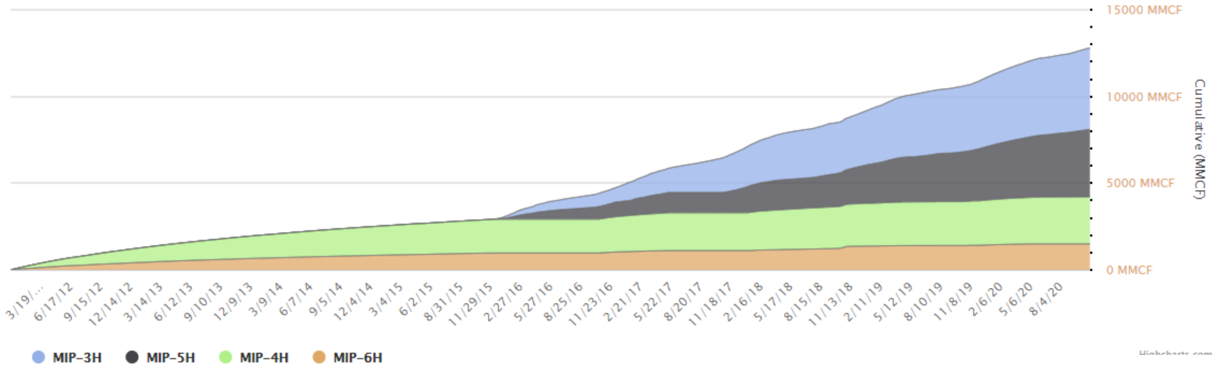


Figure S3. The time series of the total gas production for the four wells (mseel.org).

Table S1. List of Measured volatile organic compounds.

Compound	Compound	Compound
Acetylene	Trans-2-pentene	Methylcyclohexane
n-Butane	Propane	Methylcyclopentane
1-Butene	Propylene	2-Methylheptane
Cis-2-butene	Benzene	3-Methylheptane
Trans-2-butene	Cyclohexane	2-Methylhexane
Cyclopentane	n-Decane	3-Methylhexane
2,2-Dimethylbutane	m-Diethylbenzene	n-Nonane
2,3-Dimethylbutane	p-Diethylbenzene	n-Propylbenzene
Ethane	2,3-Dimethylpentane	Styrene
Ethylene	2,4-Dimethylpentane	Toluene
1-Hexene	n-Dodecane	1,2,3-Trimethylbenzene
Isobutane	Ethyl Benzene	1,2,4-Trimethylbenzene
Isopentane	o-Ethyltoluene	1,3,5-Trimethylbenzene
Isoprene	m-Ethyltoluene	2,2,4-Trimethylpentane
n-Pentane	p-Ethyltoluene	2,3,4-Trimethylpentane
1-Pentene	n-Heptane	n-Undecane
2-Methylpentane	n-Hexane	o-Xylene
3-Methylpentane	Isopropylbenzene	m-Xylene
Cis-2-pentene	n-Octane	p-Xylene

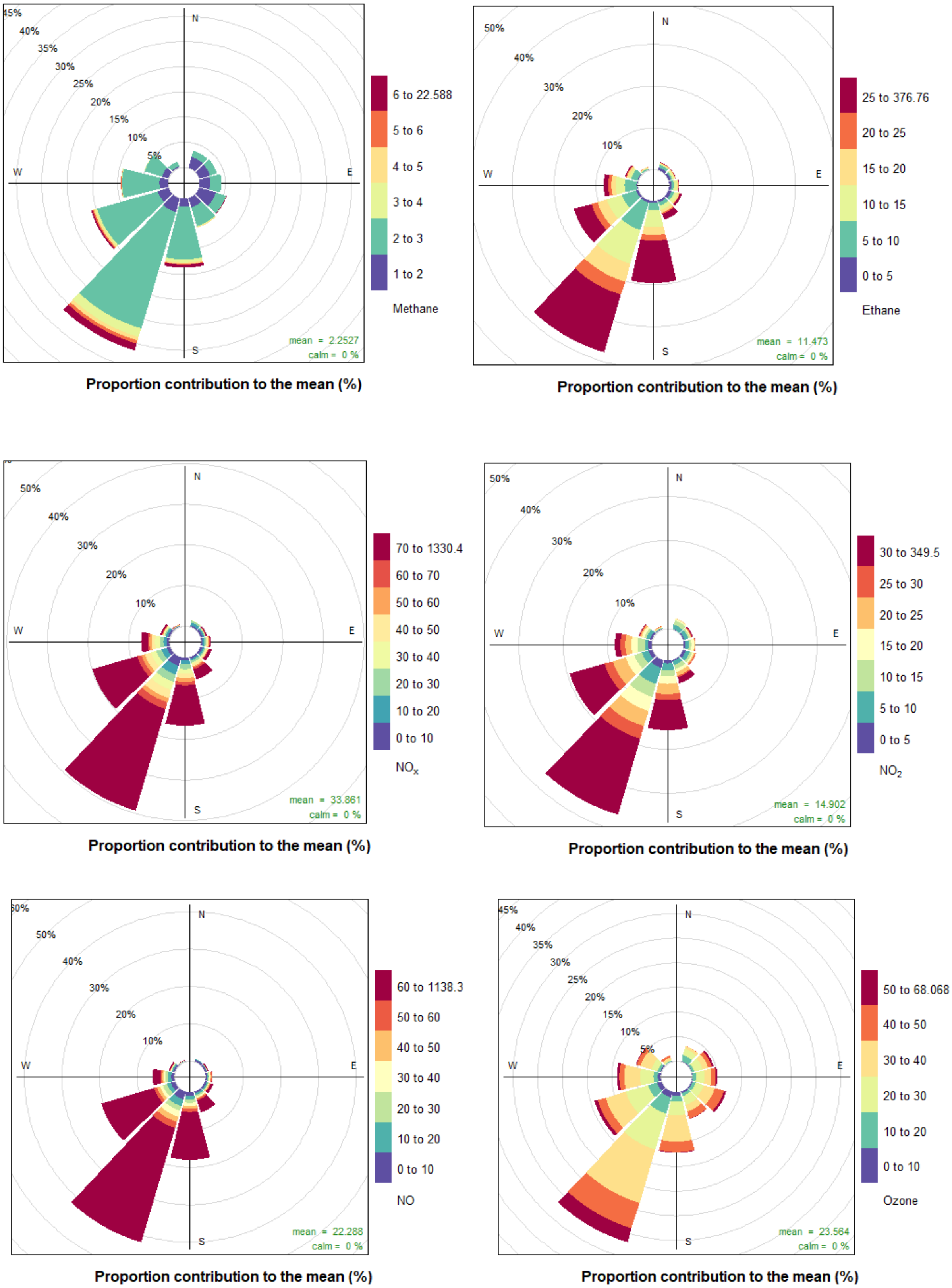


Figure S4. Methane, Ethane, NOx, NO2, NO, and Ozone pollution roses

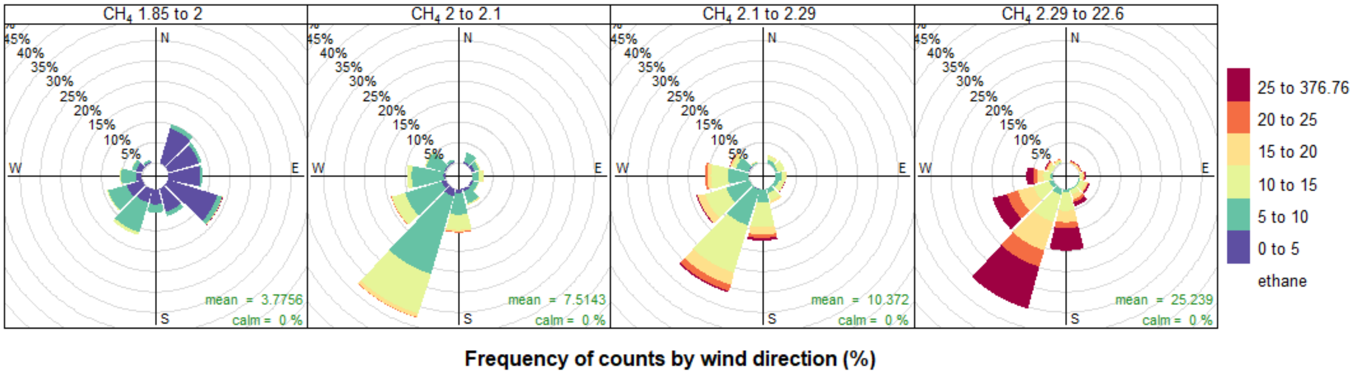


Figure S5. Ethane pollution rose conditioned by Methane concentration.

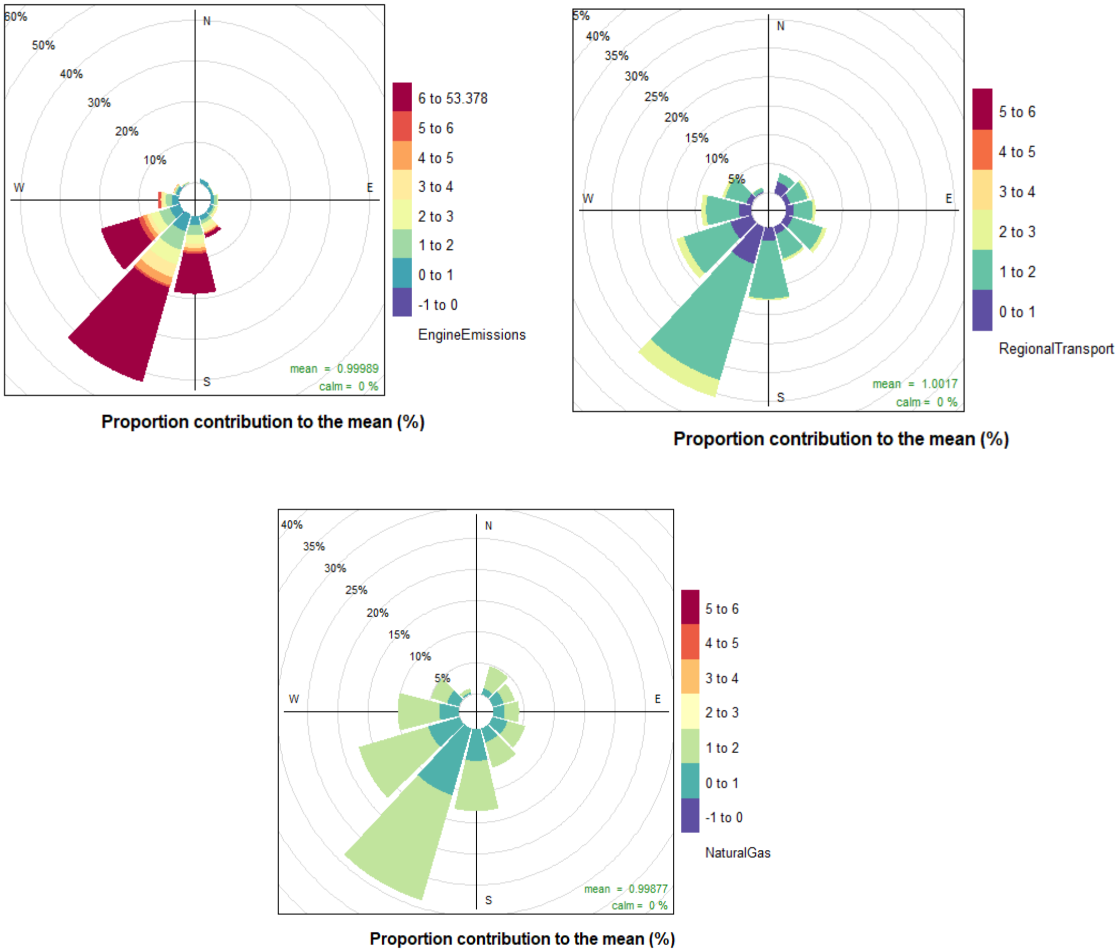


Figure S6. The PMF factor contribution roses for Engine Emissions factor, Regional Transport/ Photochemistry factor, and Natural Gas factor.

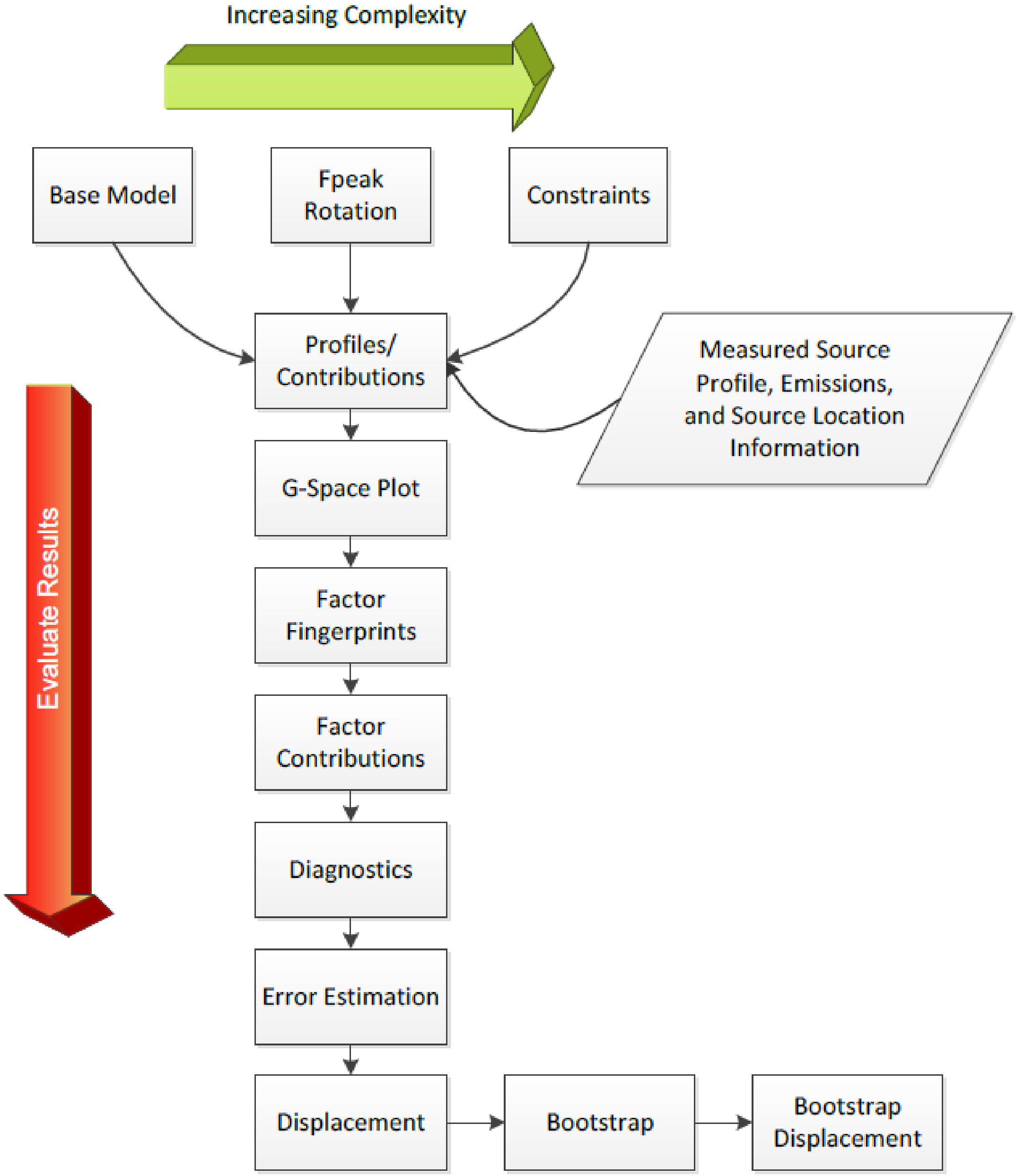


Figure S7. PMF Evaluation Process, adapted from Norris and Duvall 2014.

Table S2. Average concentrations (ppb) of the most significant volatile organic compounds in different operational phases

Pollutants	**Horizontal_D**	**Idle**	**Fracturing**	**Drillout**	**Flowback**	**Production**
hexane	0.0	0.4	0.1	0.1	0.2	0.1
benzene	0.0	0.0	0.0	0.0	0.0	0.0
toluene	0.6	0.7	0.6	0.4	0.7	0.3
ethane	5.4	13.5	7.3	7.1	70.3	11.4
propane	4.9	24.4	13.2	5.9	18.7	8.6
propylene	0.1	0.3	0.3	0.4	0.1	0.1
isobutane	2.6	63.3	3.8	1.5	4.1	3.3
n.butane	3.4	5.8	6.5	2.7	8.2	5.0
isopentane	0.5	0.8	0.6	0.5	0.9	0.5
n.pentane	0.2	0.5	0.4	0.3	0.6	0.4

Table S3. Evaluation of PMF solutions for drilling through production phases.

Diagnostic	**2 factors**	**3 factors**	**4 factors**
$Q_{expected}$	45,594	42,319	39,044
Q	561,925	354,642	213,876
Q_{robust}	353,713	248,477	161,946
$Q_{robust}/Q_{expected}$	12.3	5.9	5.5
DISP %dQ	-0.001	0	-0.015
DISP swaps	0	0	0
Factors with BS mapping	99%	95%	74%
BS-DISP % cases with swaps	0	0	3

The base run was automatically selected by the program based on the lowest Q_{robust}. Since finding a rotationally unique solution is rare, it is acceptable to observe an increasing Q_{value} due to the F_{peak} rotation with a less than 5% change in Q (dQ).

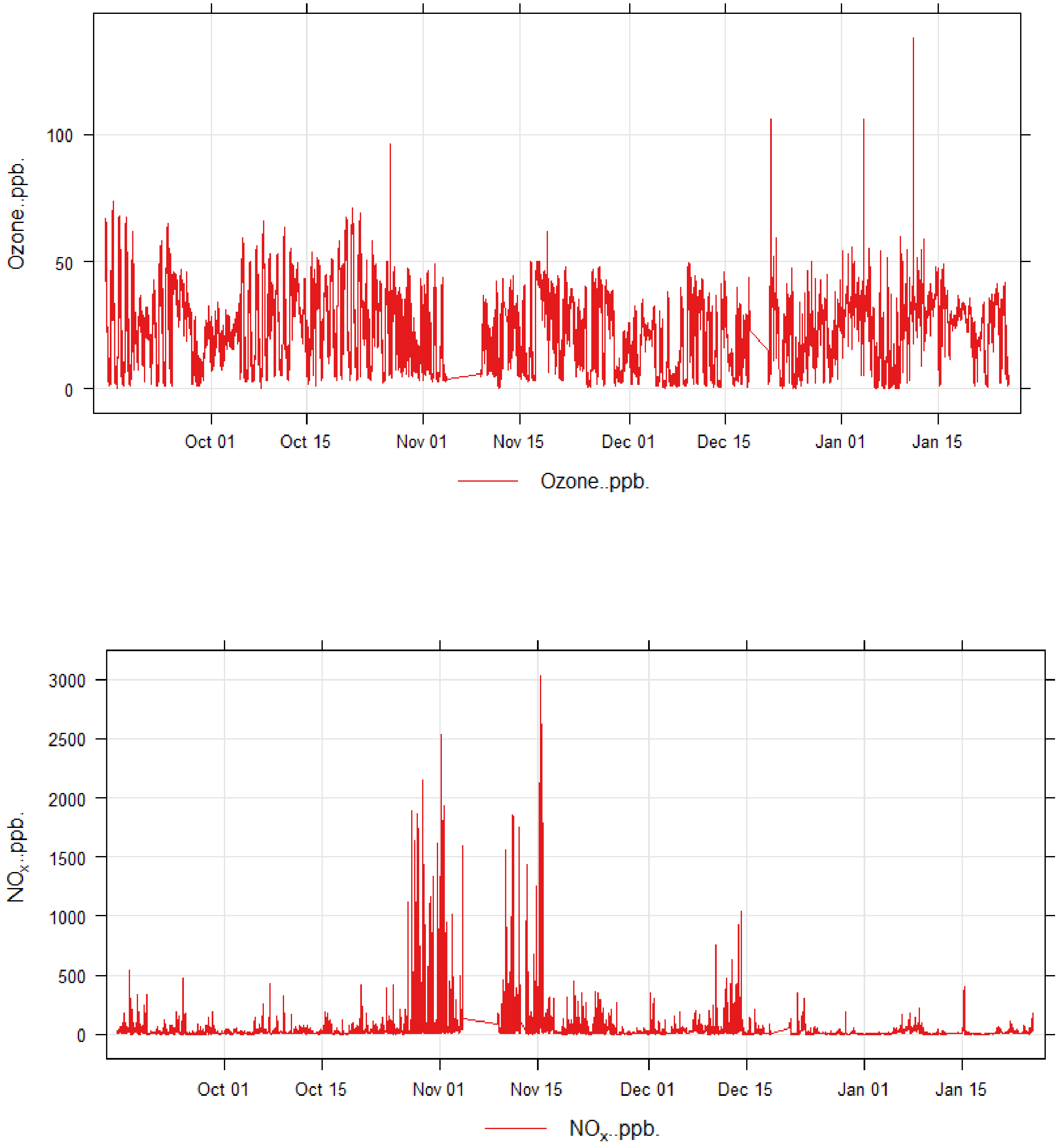
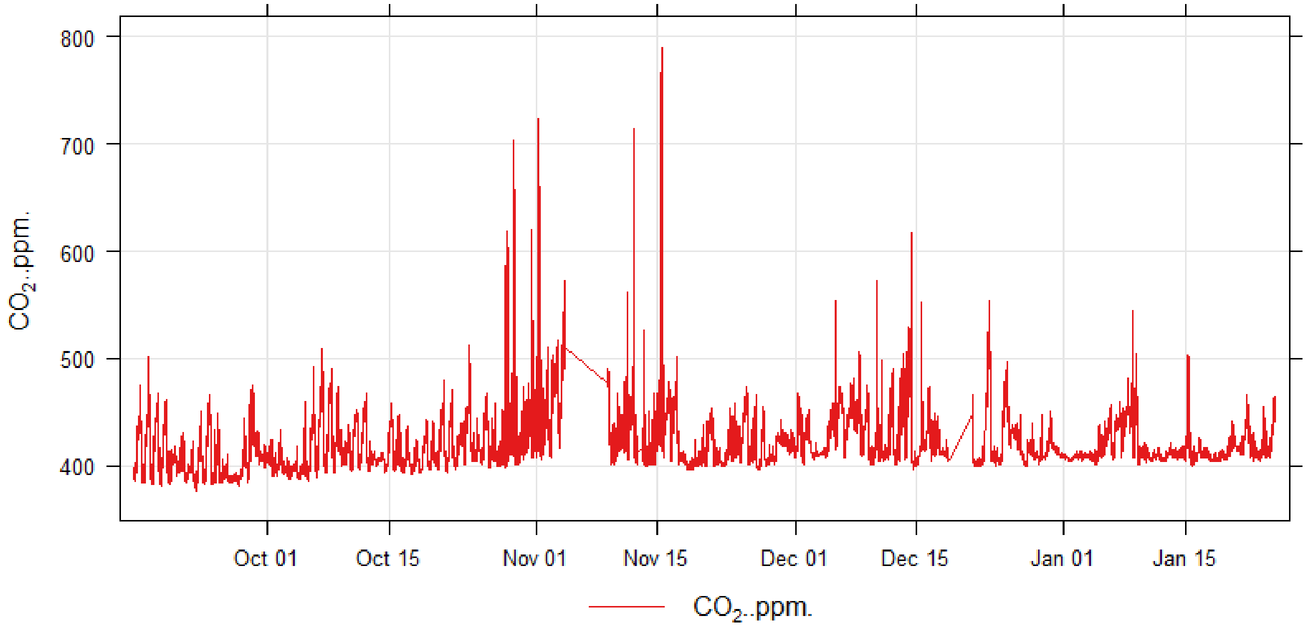


Figure S8. O_3, NOx, CO_2, and CH_4 concentration time series at well pad development site.



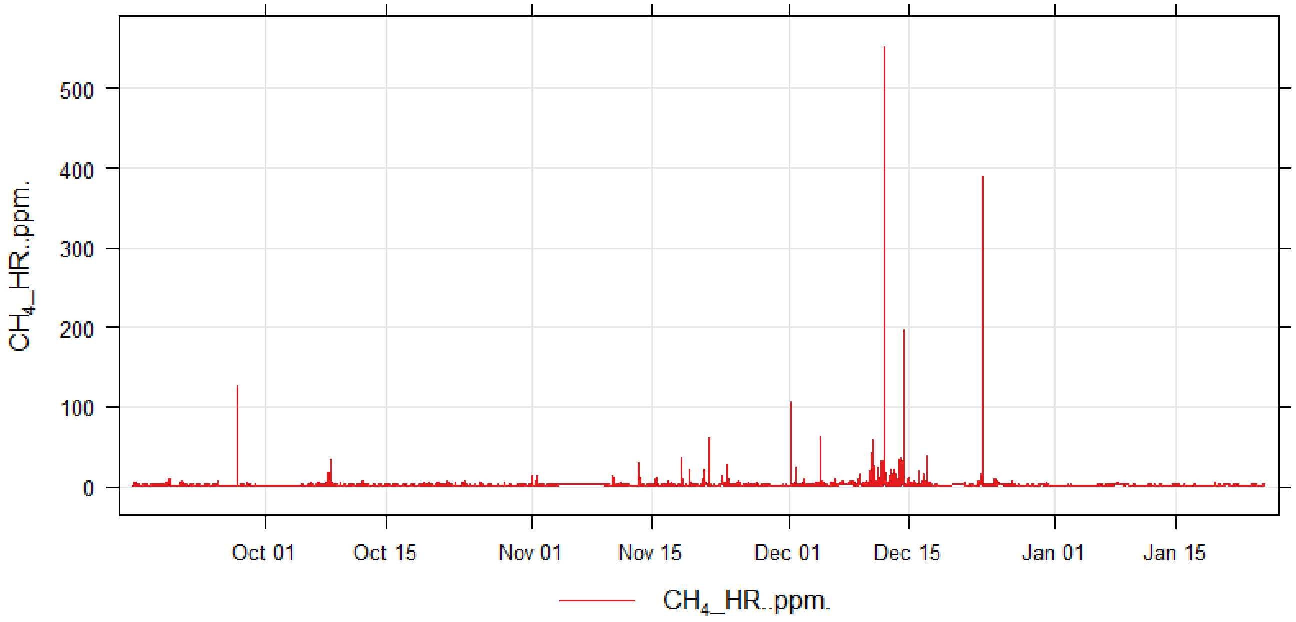


Figure S8 (continue). O_3, NOx, CO_2, and CH_4 concentration time series at well pad development site.

Table S4. F_{peak} Summary.

Drilling through Production Phases					
Strength	**dQ (Robust)**	**Q (Robust)**	**% dQ (Robust)**	**Q (Aux)**	**Q**
-1.0	10.0	23047	0	7.7	329063
-0.5	5.0	230042	0	3.7	329064
0.5	4.0	230041	0	4.5	329066
1.0	6.0	230043	0	7.4	329068

For both time period results, Q values did not vary significantly with F_{peak} values of -1.0, -0.5, 0.5, and 1.0); therefore, we can consider all four model results for evaluation. Factor profiles and contributions were examined to determine the impact of the rotation by comparing to the base run results. As a result, for baseline conditions some optimization is gained using an F_{peak} of 1.0. There is a small deviation in species for the three factors. Furthermore, F_{peak}-rotated factor fingerprints were compared with the base model outputs. The optimized distribution of pollutants in the three factors provides more interpretable source profiles with respect to marker species. Also, there is small improvement with the source profiles for the well pad drilling through production phases.

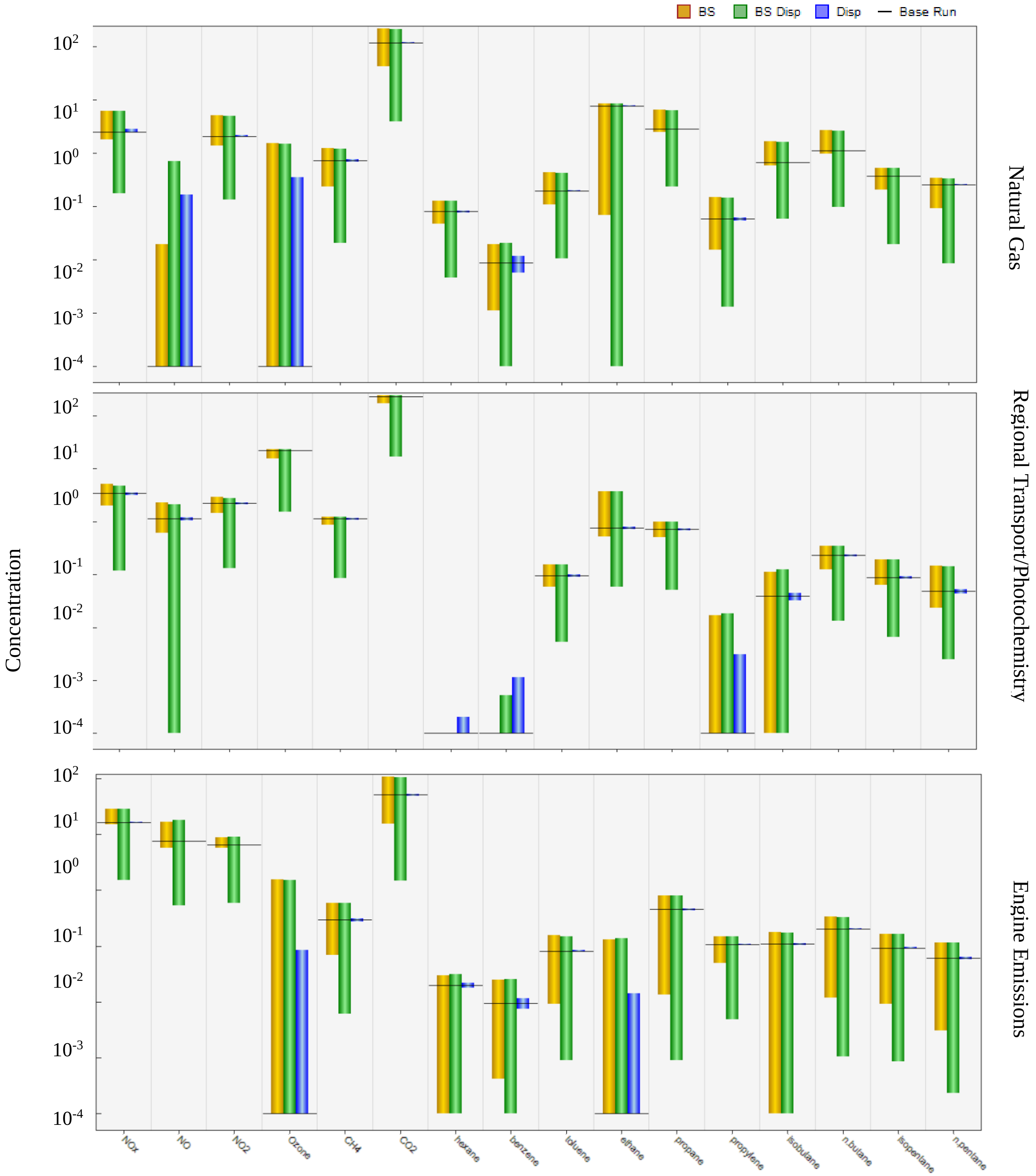


Figure S9. Error estimation summary plot of range of concentration by pollutants in each factor, active phase.

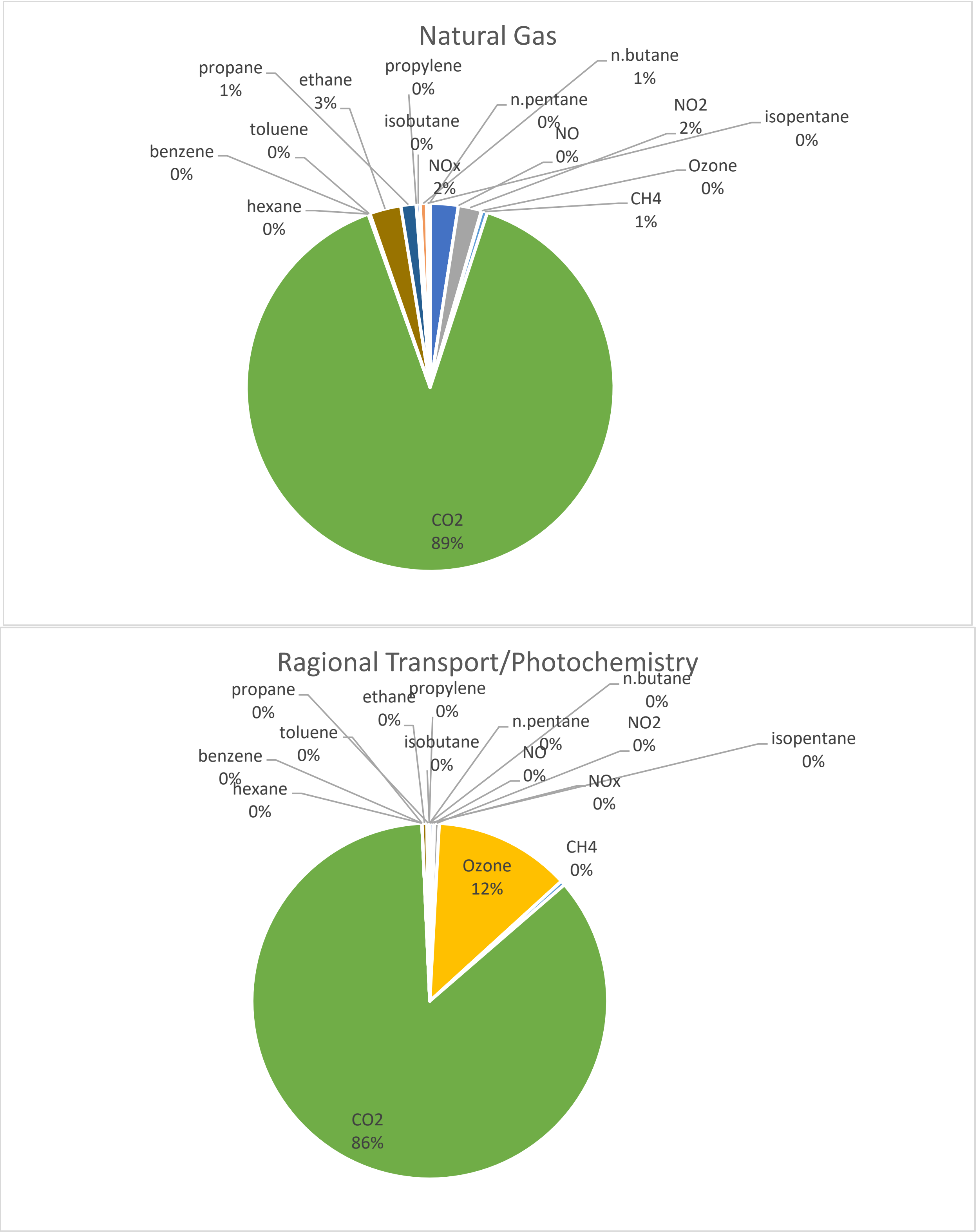


Figure S10. Factor profiles for natural gas, regional transport/photochemistry, and engine emissions factors.

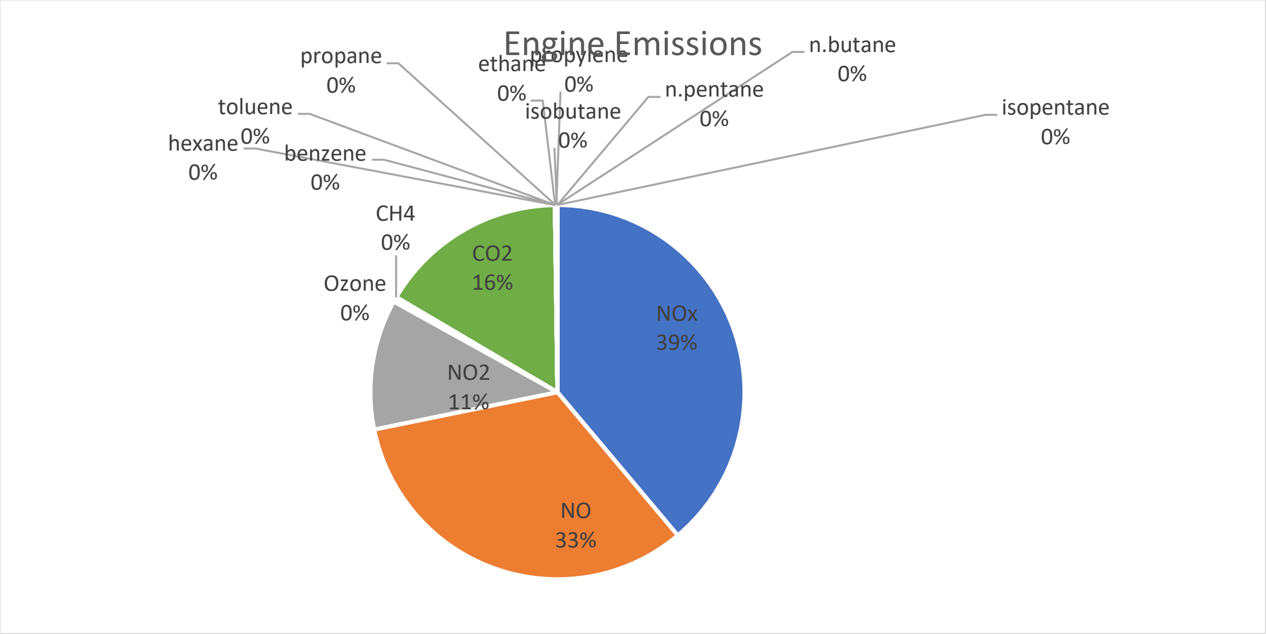


Figure S10 (continue). Factor profiles for natural gas, regional transport/photochemistry, and engine emissions factors.

Methods/rationale for uncertainty calculations

All parameters have instrument error (2 x detection limit) as the base uncertainty.

Uncertainty is added based on the number of measurements included in the average (as standard error). For the TEOM and VOCs data, where only two measurements are used and the standard error becomes “range/2”, an additional factor is calculated to account for the time-weighted averages.

In special cases, where there is missing data before or after a given measurement (as a result of instrument malfunction, power failure, etc), an additional uncertainty is added based on the number of minutes of available data relative to the total number of minutes possible.

TEOM

IE: Instrument error (2*detection limit) = 0.2

SE: Standard error (for n=2)

IE+SE =range/2

multiplied by a factor to account for the averages being weighted based on the number of minutes at each concentration (quadratic equation): (range/2)*(ax^2+bx+c)

where x is the number of minutes for the measurement within the target hour (for example: for an original data point at “02:41”, x = 41) and a, b, c are constants that were calculated based on the following criteria:

-Maximum added uncertainty for measurements at x=30 (“02:30” “03:30” etc.)

-No added uncertainty for measurements at x=0/60 (“02:00” “03:00” etc.)

Factor related to the number of minutes used in the average:

60 minute sample = no added uncertainty

Largest increase in uncertainty for samples where the adjacent sample is missing (before or after)=((60/minutes used)-1)*(hourly averaged concentration$^{0.5}$)

VOCs

IE: Instrument error (2*detection limit) = 0.2
SE: Standard error (for n=2)
IE+SE = range/2

multiplied by a factor to account for the averages being weighted based on the number of minutes at each concentration (quadratic equation)=(range/2)*(ax^2+bx+c)

where x is the number of minutes for the measurement within the target hour (for example: for an original data point at “02:41”, x = 41) and a,b,c are constants that were calculated based on the following criteria:

-Maximum added uncertainty for measurements at x=30 (“02:30” “03:30” etc)

-No added uncertainty for measurements at x=0/60 (“02:00” “03:00” etc)

Factor related to the number of minutes used in the average:

40-minute sample (sample collection starts and is injected within the same hour) = no added uncertainty

35-minute sample (start and injection in consecutive hours) – slight increase in uncertainty

Largest increase in uncertainty for samples where the adjacent sample is missing (before or after): ((40/minutes used)-1)*(hourly averaged concentration$^{0.5}$)

NO/NO2/Ozone/SO2

IE: Instrument error (2*detection limit): NO/NO2=0.1 Ozone= 0.8

IE+SE=standard deviation/(number of measurements$^{0.5}$)

Number of measurements in average, relative to the maximum available (42)=((42/number of measurements)-1)*(hour averaged concentration$^{0.5}$)