CSU studies of air quality impacts of oil and gas development from local to regional scales

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Natural gas offers a cleaner burning alternative to coal, with lower emissions of:
- SO$_2$
- NO$_x$
- Particulate Matter (PM)

The higher energy intensity of natural gas also reduces CO$_2$ emissions.

CO$_2$ emissions by fuel:
- Coal
- Diesel/fuel oil
- Gasoline
- Propane
- Natural gas

Source: U.S. Energy Information Administration (EIA)
Potential air quality impacts

- **Climate**
  - Methane (CH$_4$)
  - Black carbon

- **Criteria Pollutants**
  - O$_3$ (VOC + NO$_x$ + sunlight)
  - PM$_{2.5}$ (particles < 2.5 microns)

- **Air toxics**
  - VOCs such as BTEX (benzene, toluene, ethylbenzene, xylenes)

VOCs (volatile organic compounds) and NO$_x$ (nitrogen oxides) are both emitted by O&G operations.
Fine particle formation and haze

- Nitric acid production
  - $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$
  - $\text{NO}_2 + \text{OH} \rightarrow \text{HNO}_3$

- Ammonium nitrate production
  - $\text{NH}_3(g) + \text{HNO}_3(g) \rightleftharpoons \text{NH}_4\text{NO}_3(p)$
  - Particles favored at low $T$, high RH

- Ammonium nitrate particles
  - Submicron
  - Remain several days in the atmosphere
  - Important cause of haze
PM$_{2.5}$ nitrate concentration trends

- NO$_x$ emissions reductions greatly reduced PM$_{2.5}$ nitrate in much of U.S.
- Increasing winter nitrate in some regions

- Increases in U.S. oil and gas production may be relevant
Spatial patterns of methane and ethane

Methane elevated in oil and gas production and some other regions; ethane tied more directly to oil and gas
VOC signatures of oil and gas

- Ratio of i-pentane to n-pentane is unique for each oil and gas or urban region
- Measurements at all Bakken sites indicate regional influence from oil and gas activity
Bakken haze episodes

- Ammonium nitrate particles dominate winter haze
- Form over several hours during stagnation periods
- Key ingredients are NO$_x$ and ammonia

Evanoski-Cole et al., *Atmos Env.* 2017
Colorado development has occurred mainly in Weld (Denver-Julesburg Basin) and Garfield (Piceance Basin) counties.
Garfield County Well Drilling

Hydraulic Fracturing

Flowback

Production

Objectives

• Quantify emissions of chemical compounds (air toxics, ozone precursors, and methane) from oil and gas operations

• Characterize how these compounds are dispersed in the atmosphere downwind of the site

• Produce a public, high quality emissions dataset

Front Range

Well Drilling

Hydraulic Fracturing

Flowback

Production
Several monitoring platforms to locate and sample emissions plume

Tracer ratio method used to characterize methane and VOC emissions
Why measure emissions?

- Emissions are the amount of material emitted by an activity per unit time (e.g., grams per second)

- Air pollutant concentrations depend on
  - Emissions
  - Location
  - Weather conditions

- While concentrations are easier to measure, they provide information only for a single place and time
  - A meteorological model can be used to predict concentrations from known emissions for any place and time
Methane emissions in Front Range study

Methane emissions: flowback & liquids load out > production > fracking

![Graph showing methane emission rates and normalized frequencies for different operations.]

<table>
<thead>
<tr>
<th>Operation Type</th>
<th>Mean (g s(^{-1}))</th>
<th>Median (g s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fracking</td>
<td>0.29</td>
<td>0.051</td>
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<tr>
<td>Flowback</td>
<td>7.6</td>
<td>2.8</td>
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<tr>
<td>Production</td>
<td>5.7</td>
<td>0.60</td>
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<tr>
<td>Liquids load out</td>
<td>13.0</td>
<td>4.8</td>
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</table>
Methane emissions comparison

- Flowback and liquids load out >> drilling, fracking, and production
- During well completion: Front Range < Garfield County

<table>
<thead>
<tr>
<th>Activity</th>
<th>Median emission rate (g/s)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Garfield County</td>
</tr>
<tr>
<td>Drilling</td>
<td>2.0</td>
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<tr>
<td>Fracking</td>
<td>2.8</td>
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<tr>
<td>Flowback</td>
<td>40</td>
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<tr>
<td>Liquids Load Out</td>
<td>NA</td>
</tr>
<tr>
<td>Production</td>
<td>NA</td>
</tr>
</tbody>
</table>

Garfield County wells are gas producers
Front Range wells produce oil and gas
Nearly all methane emission rates observed from production sites were below 1% of methane produced, with a mean < 0.4%
VOC emissions – Front Range study (all operations)

- VOC emissions vary widely by compound and for a given compound.

Emission Rates (g s⁻¹)

ethane, propane, i-butane, n-butane, i-pentane, n-pentane, 2,3-dimethylpentane, 2,4-dimethylpentane, 2,2,4-trimethylpentane, 2,3,4-trimethylpentane, n-hexane, 2-methylhexane, 3-methylhexane, n-heptane, 2-methylheptane, 3-methylheptane, n-octane, n-nonane, n-decane, ethene, propene, t-2-butene, 1-butene, c-2-butene, t-2-pentene, 1-pentene, c-2-pentene, cyclopentane, cyclohexane, methylcyclohexane, isoprene, benzene, toluene, ethylbenzene, m+p-xylene, o-xylene, styrene, i-propylbenzene, n-propylbenzene, 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, 1,3-diethylbenzene, 1,4-diethylbenzene, 2-ethyltoluene, 3-ethyltoluene, 4-ethyltoluene

All sampling locations n = 231
Some VOCs of interest

- **Alkanes** – ethane, propane, butane, pentane, ...
  - Important constituents of natural gas
  - Small alkanes not a major direct health concern
  - React slowly, but can be important contributors to ozone production when abundant

- **BTEX** – benzene, toluene, ethylbenzene, xylenes
  - Air toxics → possible health concern
  - Can be emitted from oil and gas deposits and from combustion processes
 Liquids load out and flowback have highest BTEX emissions

 Production has lowest BTEX emissions
BTEX emissions comparison

- **Flowback**
  - Front Range and Garfield County BTEX emissions similar

- **Fracking**
  - Front Range BTEX emissions < Garfield County
Translating emissions to concentrations

- Modeled benzene concentration maps for a Front Range site
  - constant 0.001 g/s benzene emissions

- CDPHE-sponsored study now completing a more sophisticated health risk assessment using CSU Garfield and Front Range emissions

Comparison: current Fort Collins benzene concentrations ~ 0.1–0.4 ppbv
Variable meteorology produces wide range of concentrations at a given point
- 1 yr simulation, Front Range location 2000’ from hypothetical pad, emissions typical of Front Range production site

Average concentration increase is small
- Individual hours occasionally significantly elevated at night

Median Measured Conc. = 0.18 ppbv
Avg increase = 0.33 ppbv
0.02 ppbv
Source contributions to ambient air pollution

- 2018/19 CSU project with Garfield County
- Determine source contributions to ambient VOCs
  - Analyze variability in ambient VOC data to identify source profiles
  - Measure source profiles and fit them to ambient VOC data

Liu et al. (2016) Env. Poll.
Concluding thoughts

- CSU has examined O&G impacts on air quality at local to regional scales
  - PM$_{2.5}$ and haze
  - Methane
  - Ozone
  - Air toxics
- At neighborhood scales, hourly air toxics exposure evaluation highest priority
  - Average conc. increase often modest compared to risk thresholds
  - Highest emissions come from limited-duration activities
  - Watch for forthcoming CDPHE O&G health risk assessment
- Ozone & PM$_{2.5}$ increases potential concern on a regional scale
  - A few hours required to form these pollutants from direct emissions
- Climate forcing (methane) is a global-scale issue