Source Influences on Ambient Ozone Precursor Concentrations in the Colorado Front Range

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Colorado Front Range

Denver-Julesburg Basin

Cities & Counties

Area of Interest

from Colorado Oil & Gas Conservation Commission (COGCC) Interactive Map
Measurement Campaign

- Conducted by Colorado Department of Public Health & Environment (CDPHE) Air Pollution Control Division Ozone Precursor Study

- Flasks analyzed for 79 non-methane organic compounds
  - co-elution of 1-butene and isopentane in sampling led to their exclusion

- 3-hr samples acquired from 6 a.m. to 9 a.m. M.S.T.
  - methane and carbonyls separately measured and analyzed

<table>
<thead>
<tr>
<th>Samples</th>
<th>2013</th>
<th>2014</th>
</tr>
</thead>
<tbody>
<tr>
<td>Denver</td>
<td>57</td>
<td>58</td>
</tr>
<tr>
<td>Platteville</td>
<td>51</td>
<td>56</td>
</tr>
</tbody>
</table>

Data courtesy of Gordon Pierce (CDPHE)
Wells*
Cities
Platteville measurement site
Denver measurement site

from COGCC Interactive Map (Oct 2016)
*actual directional/horizontal well bottomhole
Platteville Measurement Site
Denver Measurement Site
Evaluating Source Influences

\[ E_{ik} = \sum_{j=1}^{p} A_{ij} B_{jk} + \epsilon_{ik} \quad i = 1, 2, \ldots, m; k = 1, 2, \ldots, n \]

- Positive Matrix Factorization (PMF)
- \( A_{ij} \), source profile: loading of compound \( i \) on factor \( j \)
- \( B_{jk} \), normalized source contribution: \( j^{th} \) factor’s contribution for the total \( k^{th} \) observation
- \( p \), total factors
  - [4-6 evaluated]
- \( i \), compound observed and attributed
  - [79 NMVOCs]
- \( k \), observation
  - [~55 per site per year]
Five Physically-meaningful Factors

Percent of Species Sum in Factor

- Factor 1
- Factor 2
- Factor 3
- Factor 4
- Factor 5

Species included:
- 1-Nonene
- 1-Octene
- 1-Pentene
- 1,2,3-Trimethylbenzene
- 1,2,4-Trimethylbenzene
- 1-3-Butadiene
- 2-Octane
- 2-Methyl-1-butene
- 2-Methyl-2-butene
- 2-Methylheptane
- 2-Methylhexane
- 2-Methylpentane
- 2,2-Dimethylbutane
- 2,2,3-Trimethylpentane
- 2,2,4-Trimethylpentane
- 2,3-Dimethylbutane
- 2,3-Dimethylpentane
- 2,3,4-Trimethylpentane
- 2,4-Dimethylpentane
- 3-Methylheptane
- 3-Methylhexane
- 3-Methylpentane
- a_Pinene
- Acetylene
- Benzene
- cis_2-Butene
- cis_2-Pentene
- Cyclohexane
- Cyclopentane
- Ethane
- Ethylbenzene
- Ethylene
- Isobutane
- Isoprene
- m_Ethyltoluene
- m_Xylene/p_Xylene
- Methylcyclohexane
- Methylcyclopentane
- n_Butane
- n_Decane
- n_Heptane
- n_Hexane
- n_Nonane
- n_Octane
- n_Pentane
- n_Propylbenzene
- n_Undecane
- o_Ethyltoluene
- o_Xylene
- p_Ethyltoluene
- Propylene
- Toluene
- trans_2-Butene
- trans_2-Hexene
- trans_2-Pentene
- sumNMVOC
acetylene and ethylene

Percent of Species Sum in Factor

Factor 1  Factor 2  Factor 3  Factor 4  Factor 5
lighter, branched, and cyclic alkanes
branched and straight heavier alkanes
Key Species Robust to Error Testing

- **alkenes, alpha-pinene, & branched BTEX**
- **alkenes, particularly acetylene & ethylene**
- **isoprene**
- **lighter, branched, & cyclic alkanes**
- **branched & straight heavier alkanes; BTEX**

Bootstrap: + 5th / 95th percentile □ 25th / 75th percentile ★ 50th percentile
Displacement: ◀ Minimum ◀ Average ▶ Maximum

Percent of Species Sum in Factor

- **Factor 1**
- **Factor 2**
- **Factor 3**
- **Factor 4**
- **Factor 5**
Contributions from Each Factor & Site to Sum of the NMVOCs

- Denver
- Platteville

Factors:
- Factor 1
- Factor 2
- Factor 3
- Factor 4
- Factor 5

Concentration-based Contribution (ppbC)
Contributions from Each Factor & Site to BTEX Compounds

Concentration-based Contribution (ppbC)

- benzene
- xylene
- toluene

Factors:
- Factor 1
- Factor 2
- Factor 3
- Factor 4
- Factor 5

Sites:
- Denver
- Platteville
Time Series of Contributions: Benzene and Toluene

![Graph showing contributions of benzene and toluene over time](image)

- Contribution of Species per Factor (ppbC)
- Factors: Factor 1, Factor 2, Factor 3, Factor 4, Factor 5
- Denver benzene, Platteville benzene, Denver toluene, Platteville toluene

**Legend:**
- Green: Factor 1
- Orange: Factor 2
- Blue: Factor 3
- Brown: Factor 4
- Gray: Factor 5
- Green: Denver benzene
- Orange: Platteville benzene
- Green: Denver toluene
- Orange: Platteville toluene

**Notes:**
- Contribution values range from 0 to 25 (ppbC).
- Values for benzene and toluene are compared to their respective factors.
- Levels are indicated by 10 times greater and 10 times smaller markers.
Time Series of Contributions: Benzene and Toluene

Denver benzene
Platteville benzene
Denver toluene
Platteville toluene
Time Series of Contributions: Benzene and Toluene
Time Series of Contributions: Acetylene and Isoprene

2 times greater

10 times smaller
Time Series of Contributions: Acetylene and Isoprene
Time Series of Contributions: Acetylene and Isoprene

Contribution of Species per Factor (ppbC)
Time Series of Contributions: Acetylene and Isoprene

Contributions of Species per Factor (ppbC)

- Denver acetylene
- Platteville acetylene
- Denver isoprene
- Platteville isoprene

Factors 1 to 5 are represented on the graph.
Western Regional Air Partnership
Phase III O+G Speciation Profiles

- Surveyed O+G producers in intermountain west basins for gas chromatography / mass spectrometry-based speciation

- Provided SPECIATE profiles with molar VOC content standard deviation to U.S. EPA (Shah et al., memo, 2015)
Evaluation of VOC Profile for DJ Flashed and Produced Gas Emissions

DJ Flash and Produced gas VOC profiles from the Western Regional Air Partnership

Error bars: 1.45% standard deviation for DJ profiles | bootstrap 5th / 95th percentile

Shah et al., memo (2015)
Conclusions & Next Steps

- 2013-2014 observations of factors composed of VOCs characteristic of oil and gas development were much higher in Platteville than in Denver.

- PMF suggests that BTEX compounds arise from other sources in addition to the oil and gas activity.

- The WRAP Phase III VOC emissions profiles for the Denver-Julesburg flashed and produced gas align well with the oil and gas factor from PMF.

- Consider 2015 observations and implications for ozone based on VOC reactivity.
Acknowledgements

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