Speciated VOC Sampling to Understand VOCs and Sources Contributing to Ozone Formation in Maricopa County

Joshua Uebelherr, Senior Air Quality Planner
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Overview

- Background
- Purpose
- Methods
- Summary sampling results
- Receptor modeling
  - Purpose
  - EPA Chemical Mass Balance (CMB) model
  - Results
Large areas of Maricopa County are classified as moderate ozone nonattainment areas:

- 2008 National Ambient Air Quality Standards (NAAQS)
- 2015 NAAQS (pending)
Speciated volatile organic compounds (VOC) sampling was conducted in order to gain a better understanding of how VOC sources contribute to ozone formation in Maricopa County.
Methods

• Collected 24-hour air samples
  o SUMMA canisters
  o 2,4 dinitrophenylhydrazine (DNPH) cartridges

• May 4 to September 25, 2021
  o Sampling every 6 days at each site

• Samples were analyzed by Eastern Research Group
  o 88 VOC species
  o Total non-methane hydrocarbons
Sampling Locations
Study Limitation

- Nearly 5,300 square mile nonattainment area
  - Four sample locations
  - Samples more heavily influenced by nearby sources
- Sampling dates may not be representative
- Analytical method identifies 88 out of thousands of VOC species in the atmosphere
- Not all species are equally reactive for ozone formation
- Limited availability of current source profiles for receptor modeling
Sample Completeness

- Sampling scheduled using 1-in-6 days schedule for Photochemical Assessment Monitoring Stations (PAMS)
- 25 sample days from May 4 through September 25, 2021

<table>
<thead>
<tr>
<th>Site</th>
<th>Number of Valid Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Buckeye</td>
<td>22</td>
</tr>
<tr>
<td>Mesa</td>
<td>25</td>
</tr>
<tr>
<td>North Phoenix</td>
<td>24</td>
</tr>
<tr>
<td>Pinnacle Peak</td>
<td>24</td>
</tr>
</tbody>
</table>
Sampling Results Summary

<table>
<thead>
<tr>
<th>Location</th>
<th>Total NMOC</th>
<th>Unknown VOCs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mesa North</td>
<td>648</td>
<td>557</td>
</tr>
<tr>
<td>Phoenix</td>
<td>455</td>
<td>366</td>
</tr>
<tr>
<td>Buckeye Pinnacle</td>
<td>422</td>
<td>236</td>
</tr>
<tr>
<td>Peak</td>
<td>570</td>
<td>397</td>
</tr>
</tbody>
</table>
## Sampling Results Summary

<table>
<thead>
<tr>
<th>Location</th>
<th>Aromatics</th>
<th>Carbylons</th>
<th>Olefins</th>
<th>Paraffins</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mesa</td>
<td>0</td>
<td>179</td>
<td>84</td>
<td>113</td>
</tr>
<tr>
<td>North Phoenix</td>
<td>0</td>
<td>10</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Buckeye</td>
<td>0</td>
<td>20</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Pinnacle Peak</td>
<td>0</td>
<td>15</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

**Concentration (ppbC)**
Relative Ozone Impact

- Aromatics
- Carbonyls
- Olefins
- Paraffins

MIR Weighted Concentration (µg/m³)

Locations:
- Mesa
- North Phoenix
- Buckeye
- Pinnacle Peak

Graph showing data points and error bars for each location across different categories.
Receptor Modeling

• Receptor modeling uses multivariate statistical techniques with speciated monitoring data to identify sources of pollution

• EPA Chemical Mass Balance (CMB) model, version 8.2 compares monitoring data to emission source profiles
  o Takes unknown VOC into account

• Source profiles extracted from the EPA SPECIATE database, version 5.1
Preparation of Data for CMB

- Screening of ambient data to determine reliable measurements for VOC species
  - Exclude species with all non-detects and high percentage measured below detection limits
- Extract multiple source profiles from SPECIATE database for source categories likely to affect ambient VOC concentrations
- Reformat ambient and source profile data to CMB requirements
Modeling Approach

• CMB models each sample separately to compare concentrations against source profiles
• Days were classified and data averaged based on ozone concentrations and exceptional event status
  o Moderate days (17 days)
  o Exceedance days not flagged for wildfire smoke influence (2 days)
  o Wildfire smoke exceptional events (6 days)
• Outlier days excluded from some averages
  o Spikes in specific VOCs
  o Unknown VOC over 70% of TNMOC
North Phoenix

Modeled Source Contribution (ppbC)

- Wildfire Smoke
- Biogenic VOC
- Secondary VOC
- Consumer Products
- Other Solvent Use
- Architectural Coatings
- Natural Gas Combustion
- Gasoline Vapor
- Diesel Truck Exhaust
- Gasoline Vehicle Exhaust

* Excluding June 3 and August 8, 2021
North Phoenix

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- Diesel Truck Exhaust
- Gasoline Vehicle Exhaust

* Excluding May 4, June 3, and August 8, 2021
** Excluding June 9, 2021
Buckeye

Modeled Source Contribution

<table>
<thead>
<tr>
<th>Source Category</th>
<th>Moderate Days*</th>
<th>Exceedance Days**</th>
<th>Smoke Affected Exceedance Days</th>
<th>All Days</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wildfire Smoke</td>
<td>9.8%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Animal Waste Decomposition</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Biogenic VOC</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Consumer Products</td>
<td></td>
<td></td>
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<tr>
<td>Diesel Truck Exhaust</td>
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<tr>
<td>Gasoline Vehicle Exhaust</td>
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<tr>
<td>Total</td>
<td>100%</td>
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* Excluding May 4 and August 8, 2021
** Excluding June 9, 2021
Pinnacle Peak

![Bar chart showing modeled source contribution (ppbC) for different days and exceedance days. The categories include:
- Wildfire Smoke
- Animal Waste Decomposition
- Biogenic VOC
- Secondary VOC
- Consumer Products
- Other Solvent Use
- Architectural Coatings
- Natural Gas Combustion
- Gasoline Vapor
- Diesel Truck Exhaust
- Gasoline Vehicle Exhaust

The chart compares contributions on moderate days, exceedance days, smoke affected exceedance days, and all days.}
Pinnacle Peak

Modeled Source Contribution

- Wildfire Smoke
- Animal Waste Decomposition
- Biogenic VOC
- Secondary VOC
- Consumer Products
- Other Solvent Use
- Architectural Coatings
- Natural Gas Combustion
- Gasoline Vapor
- Diesel Truck Exhaust
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<th>Moderate Days</th>
<th>Exceedance Days</th>
<th>Smoke Affected Exceedance Days</th>
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<tbody>
<tr>
<td>Wildfire Smoke</td>
<td>10.9%</td>
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Summary

Patterns that stand out include:

- Dominance of solvent related source categories on moderate days
- Mobile sources more dominant on exceedance days at the urban sites
- Wildfire smoke is significant for days after June 15, 2021
Average All Samples

- Wildfire Smoke: 13.9%
- Animal Waste Decomposition: 8.3%
- Biogenic VOC: 7.2%
- Secondary VOC: 11.1%

Mesa:
- Modeled Source Contribution:
  - Wildfire Smoke: 13.9%
  - Animal Waste Decomposition: 8.3%
  - Biogenic VOC: 7.2%
  - Secondary VOC: 11.1%

Phoenix:
- Modeled Source Contribution:
  - Wildfire Smoke: 13.9%
  - Animal Waste Decomposition: 8.3%
  - Biogenic VOC: 7.2%
  - Secondary VOC: 11.1%

Buckeye:
- Modeled Source Contribution:
  - Wildfire Smoke: 13.9%
  - Animal Waste Decomposition: 8.3%
  - Biogenic VOC: 7.2%
  - Secondary VOC: 11.1%

Pinnacle Peak:
- Modeled Source Contribution:
  - Wildfire Smoke: 13.9%
  - Animal Waste Decomposition: 8.3%
  - Biogenic VOC: 7.2%
  - Secondary VOC: 11.1%

- Other Solvent Use: 13.9%
- Architectural Coatings: 8.3%
- Natural Gas Combustion: 7.2%
- Gasoline Vapor: 11.1%
- Gasoline Vehicle Exhaust: 13.9%
- Diesel Truck Exhaust: 8.3%
Questions
Thank you.

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