What drives high wintertime ozone in the oil and natural gas fields of the western U.S.?

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During some winters over rural areas with high oil and natural gas production in Wyoming and Utah high O$_3$ episodes were observed (Schnell et al., 2009; Oltmans et al., 2014).

Carter and Seinfeld (2012) and Edwards et al. (2014) used detailed chemical mechanisms in box models to study high wintertime O$_3$ production observed in Wyoming and Utah, respectively. The authors stressed the need for full 3D air quality models to address the high wintertime O$_3$ episodes.

NOAA/ESRL and other groups conducted two intensive field campaigns - Uinta Basin Winter Ozone Study (UBWOS) in January-February, 2012 (warmer, little or no snow conditions) and 2013 (colder and snowy) to study meteorology, oil/gas emissions and atmospheric chemistry in the Uinta Basin. In 2013 the highest O$_3$ concentration in the U.S. was observed in the Uinta Basin during winter!
The region is sparsely populated (~50,000 people). The urban VOC and NO\textsubscript{x} emissions are not high.
Objectives of our modeling study

- Model the wintertime meteorological conditions in 2012 and 2013 over the Uinta Basin (UB), Utah; Focus on cold pool type stagnations during 2013;
- Estimate emissions of NO\textsubscript{x} and VOCs for the oil/gas sector in the UB using the atmospheric measurements from the UBWOS field campaigns;
- Conduct air quality simulations using both bottom-up (EPA NEI-2011) and top-down emission scenarios;
- Investigate the major driving factors of high the wintertime ozone in the UB;

A high resolution meteorology-chemistry modeling using WRF-Chem (with RACM gas chemistry) was conducted for January – February, 2012 and 2013. The dry deposition and photolysis schemes in WRF-Chem were modified to take into account effect of snow cover.
Examples of CH$_4$ regressions, VOC/NO$_y$ measurements at the Horse Pool site – The basis of the Top-Down inventory

Daytime CH$_4$ regressions for:
- **49** Primary VOCs (GC and PTRMS)
- **10** Oxygenated VOCs
- NO$_y$

Primary VOC regressions are:
- Very robust ($0.85 < r^2 < 0.98$)
- The same for 2012 and 2013

NO$_y$ – CH$_4$ regression:
- Combine 2012/2013 data
- $r^2 = 0.66$
- Slope used as “Best Guess” in the top-down inventory
Anthropogenic emission scenarios used in the WRF-Chem model: Emission totals for the oil and gas sector in the Uinta Basin

<table>
<thead>
<tr>
<th>Emission inventories</th>
<th>Inventory source</th>
<th>$\text{CH}_4$ (tons/year)</th>
<th>VOC (tons/year)</th>
<th>$\text{NO}_x$ (tons/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bottom-up</td>
<td>EPA NEI-2011</td>
<td>110,539</td>
<td>111,536</td>
<td>18,131</td>
</tr>
<tr>
<td>Top-down</td>
<td>Regression analysis</td>
<td>531,457</td>
<td>203,389</td>
<td>4,583</td>
</tr>
</tbody>
</table>

Total $\text{CH}_4$ flux estimate is from Karion et al., 2013

Top-down: Using $\text{NO}_y/\text{CH}_4$ and VOC/CH$_4$ ratios from surface observations during winters of 2012 and 2013

Total $\text{CH}_4$ and VOC emissions in NEI-2011 are lower by a factor of 4.8 and 1.8 than in the top-down estimates respectively!

Conversely, $\text{NO}_x$ emissions are 4.0 times higher in the NEI-2011 inventory!

Ahmadov et al. (2014), ACPD
Anthropogenic **methane** emissions in the 4km resolution grid over the Uinta Basin (two inventories)

Bottom-up (NEI-2011)

Top-down

Oil and gas well locations are from Utah Department of Environmental Quality
Observed and modeled methane time series at the Horse Pool site in 2013

Daytime (9-17MST) statistics:
Bottom-up case: $r = 0.29$, med. bias = -5.1 ppm, med. (mod./obs.) = 0.31
Top-down case: $r = 0.37$, med. bias = -2.9 ppm, med. (mod./obs.) = 0.61
Observed and modeled ozone time series at the Horsepool site
observed and modeled ozone time series at the Horsepool site, 2013

Daytime (9-17MST) statistics:
Bottom-up case: $r = 0.33$, med. bias = -39.8 ppb, med. (mod./obs.) = 0.51
Top-down case: $r = 0.85$, med. bias = -5.3 ppb, med. (mod./obs.) = 0.93

Ahmadov et al. (2014), ACPD
Nighttime and Early Morning
- Strong drainage flow
- Complicated circulation within Basin
- $O_3$ from previous day trapped

Daytime
- Light winds within Basin
- Low Mixing Heights
- Significant $O_3$ buildup in shallow layers

Ahmadov et al., ACPD, 2014
O$_3$ distribution over Horse Pool on February 5th, 2013

Tethersonde observations

Model

O$_3$, ppb

hour, MST

hour, MST
Model $O_3$ comparisons against the aircraft measurements (Feb. 5, 2013)

**Bottom-up (NEI2011)**

$20130205$, 9-17LT, 25-500m AGL

**Top-down**

$20130205$, 9-17LT, 25-500m AGL

$\alpha = 0.814 \pm 0.023$
Horse Pool measurements used for model/inventory verification

$O_x$ versus PAN at the Horsepool site, 2013

$O_x$ – PAN relationship
Depends on:
VOC/$O_x$ ratios
Photochemical mechanism

NO$_x$ emission inventory assessment

<table>
<thead>
<tr>
<th>Year</th>
<th>NO$_x$ (ppbv)</th>
<th>Top-Down</th>
<th>Bottom-up (NEI-2011)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Observed Median</td>
<td>Median Mod/Obs Ratio</td>
<td>$r$ coefficient</td>
</tr>
<tr>
<td>2012</td>
<td>4.81</td>
<td>0.70</td>
<td>0.64</td>
</tr>
<tr>
<td>2013</td>
<td>17.16</td>
<td>0.75</td>
<td>0.46</td>
</tr>
</tbody>
</table>

Ahmadov et al., ACPD, 2014
Is $O_3$ photochemistry sensitive to Bonanza power plant emissions and snow albedo?

Bonanza power plant: No
Snow albedo: Yes
### Highlights of perturbation/sensitivity analysis

#### Physical Processes - Perturbation Case

<table>
<thead>
<tr>
<th>Impact on model O$_3$ from oil/gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare ground surface albedo (no snow) 104%</td>
</tr>
<tr>
<td>Bare ground O$_3$ surface deposition 48%</td>
</tr>
</tbody>
</table>

**Snow is essential for high O$_3$**

#### NO$_x$ Emission Perturbation Case

<table>
<thead>
<tr>
<th>Impact</th>
</tr>
</thead>
<tbody>
<tr>
<td>Top-Down Oil&amp;Gas NOx Emission Reduced 30% 1%</td>
</tr>
<tr>
<td>Top-Down Oil&amp;Gas NOx Emission Reduced 67% 14%</td>
</tr>
<tr>
<td>Top-Down Oil&amp;Gas NOx Emission Reduced 100% 45%</td>
</tr>
</tbody>
</table>

**High O$_3$ events are insensitive to NO$_x$ reductions**

#### VOC Emission Perturbation Case

<table>
<thead>
<tr>
<th>Impact</th>
</tr>
</thead>
<tbody>
<tr>
<td>Top-Down Oil&amp;Gas VOC emis. Reduced 30% 33%</td>
</tr>
<tr>
<td>&gt;C-2 Alkane VOC emis. set to zero 44%</td>
</tr>
<tr>
<td>Aromatic VOC emis. set to zero 37%</td>
</tr>
</tbody>
</table>

**O$_3$ is VOC limited**

Aromatics have a disproportionate influence

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*Ahmadov et al., ACPD, 2014*
Model $O_3$ sensitivity to emissions of radical precursors
(Horse Pool site, Jan 29 to Feb 9, 2013, daytime)

<table>
<thead>
<tr>
<th>Base Case $NO_x$ emissions:</th>
<th>Impact Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO: 90%</td>
<td></td>
</tr>
<tr>
<td>NO$_2$: 8%</td>
<td></td>
</tr>
<tr>
<td>HONO: 2%</td>
<td></td>
</tr>
<tr>
<td>All $NO_x$ emissions were included as NO</td>
<td>5%</td>
</tr>
</tbody>
</table>

The model can predict high O3 concentrations without primary HONO emissions!

CH$_2$O Statistics: Median Model/Observed Ratio = 0.53

<table>
<thead>
<tr>
<th>CH$_2$O primary emissions set to zero</th>
<th>Impact Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_2$O primary emissions set to zero</td>
<td>18%</td>
</tr>
</tbody>
</table>

CH$_2$O Median Model/Observed Ratio = 0.36 after emissions removal

The primary formaldehyde emissions need to be considered!
Observed and modeled **ozone** time series at the Horsepool site, 2012

The same model settings and emissions for the 2012 and 2013 cases were used!

Ahmadov et al. (2014), ACPD
The emission inventories (CH$_4$, VOCs, NO$_x$) for the oil/gas sector can be significantly improved by using the top-down emission estimates.

The model is able to simulate high O$_3$ episodes in winter of 2013 using the top-down inventory, but not the bottom-up (NEI-2011) inventory.

The sensitivity simulations show reducing the VOC emissions would be an efficient way to mitigate wintertime O$_3$ problem in the Uinta Basin.

High ozone in the Uinta Basin are primarily caused by the very high VOC versus NO$_x$ emissions from the oil/gas sector, persistent stagnation episodes and high surface albedo and reduced deposition effect due to snow cover.
Thank you for your attention!

Uintah Basin, 2013

Photo by S. Sandberg