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Recent Work

**Title**
Ozone Sensitivity to Emissions and Changes of Limiting Reagents

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Regional control strategy options for reducing ozone change temporally and spatially in Central California where air pollution is particularly serious. The rate of ozone production is a complex function of the concentrations of volatile organic compounds (VOCs) and nitrogen oxides (NOx) as well as meteorological conditions. As a result, ozone formation exhibits a very non-linear dependence on its precursors. Determining the relative benefits of controlling NOx emissions or VOC emissions remains a challenging problem. Current practice of modeling 3 to 5 day episodes does not capture the changes in limiting reagents since they represent a limited sample of the diverse meteorology and human behavior that affect air pollution.

We are using CMAQ, the EPA’s Community Multiscale Air Quality Model, to model a season of air quality in Central California for the summer of 2000 to illustrate some limitations of current practice. We have modeled a 15-day period and, in concert with the modeling, we have also used the Decoupled Direct Method to compute ozone sensitivities to NOx and VOC emissions. Emissions have been disaggregated differently to extract mechanistic information regarding limiting reagents, and to explore issues of long range transport. We have computed ozone sensitivities to total NOx emissions and VOC emissions for the entire modeling domain, NOx emissions, and NOX emissions from specific air basins, as well as emissions from specific air basins for specific time intervals. We demonstrate how the computed sensitivity coefficients of ozone to the various emission types may be used to demonstrate and understand limiting reagent changes throughout the modeling domain.

Ozone Sensitivity to Domain-wide Emissions

- More site-hours exceed 8 hour average standard (84 ppb) than 1 hour standard (120 ppb). In general, sites that violate 1-hour standard also violate 8-hour standard.
- Reduced emissions (mostly NOx) on weekend can cause increased ozone levels at VOC controlled sites (weekend effect). We see that weekend effect contributes more to the 1-hour violations than to the 8-hour averages in both episode and non-episode (Fig. 4).
- There is a greater fraction (Fig. 4) of non-episode hour-sites in exceedance of the 8-hour standard than the 1-hour standard.
- Control strategies would not be significantly different for episodes and non-episodes for this 15-day period.

San Francisco Bay Area (SFB) is about 100% VOC controlled for both 1-hour and 8-hour average exceedances. Picture in the valley (SJV) is quite different. VOC control dominates 1-hour exceedances.

Summary of 1-hr and 8-hr exceedances in SJV

Episode: Jul 29 ~ Aug 2, 2000

<table>
<thead>
<tr>
<th>Weekday</th>
<th>Non-episode</th>
<th>Weekday</th>
<th>Non-episode</th>
<th>Weekend</th>
<th>Non-episode</th>
</tr>
</thead>
<tbody>
<tr>
<td>NOx</td>
<td>8%</td>
<td>NOx</td>
<td>50%</td>
<td>NOx</td>
<td>21%</td>
</tr>
<tr>
<td>VOC</td>
<td>4%</td>
<td>VOC</td>
<td>18%</td>
<td>VOC</td>
<td>8%</td>
</tr>
</tbody>
</table>

Limiting reagents for cases (a), (b), and (c) defined in Figure 5: weekend indicated by dotted pattern.
- VOC control is more effective, and part of the time, NOx control is more effective, e.g., PLR. The southern part is far downwind and is in a NOx limited regime, e.g., BAC.
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Definition of Limiting Reagent and Ozone Control Strategy

- Semi-normalized ozone sensitivity coefficients (1) and (2)
- Sensitivity of hourly ozone is calculated by Decoupled Direct Method (DDM 4.5).
- VOC control dominates for both 1-hour and 8-hour average exceedances. Picture in the valley (SJV) is quite different. VOC control dominates 1-hour exceedances, while for 8-hour exceedances, the strategy shifts toward controlling NOx.
- Palomar Mountain (PCP), Bakersfield (BAC), Arvin (ARV), Arom (ARV), KRV.

Table 1: Limiting regime and control strategy

<table>
<thead>
<tr>
<th>Case</th>
<th>Limiting Regime</th>
<th>Control Strategy</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>&lt;0</td>
<td>VOC sensitive</td>
</tr>
<tr>
<td>(2)</td>
<td>&gt;0</td>
<td>VOC dominant</td>
</tr>
<tr>
<td>(3)</td>
<td>NOx sensitive</td>
<td>NOx dominant</td>
</tr>
</tbody>
</table>

Conclusions

- Emissions from the SFB area affect domain wide NOX budgets more than NOX budgets.
- The influence of afternoon emissions from the SFB area persists for longer time periods (>20hr) than morning emissions (~10hr).
- VOC sensitivity is reduced to nearly zero before ozone peaks (~1-3pm), while NOx remain sensitive to the afternoon emissions from the SFB of the previous day.
- NOx sensitivity is reduced to nearly zero before ozone peaks (~1-3pm), while VOCs remain sensitive to the afternoon emissions from the SFB of the previous day.

Acknowledgement

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