#MO09 Evaluation of explicit NO<sub>x</sub> chemistry methods in AERMOD using a new compressor station dataset

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Guideline on Air Quality Models: Planning Ahead

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Background

• For some industrial installations, demonstrating compliance with the 1-hour NO$_2$ National Ambient Air Quality Standard (NAAQS) using AERMOD can be difficult.

• AERMOD Tier 3 chemistry methods, OLM (Ozone Limiting Method) and PVMRM (Plume Volume Molar Ratio Method), can predict overly conservative concentration values for some model configurations.

• A new explicit NO$_x$ chemistry method for AERMOD ‘Atmospheric Dispersion Modelling System Method’ (ADMSM) has been implemented in a previous version of AERMOD. ADMSM was evaluated using available NO$_2$ databases (Empire Abo, Palaau, Wainwright and Prudhoe Bay)*.

• This presentation provides results of additional ADMSM assessment using a new compressor station evaluation dataset.

### Chemistry schemes

#### NO\textsubscript{x} chemistry

- **‘Ozone titration’**
  \[
  \text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2
  \]

- **‘Photolysis’**
  \[
  \text{NO}_2 + \text{sunlight} \rightarrow \text{NO} + \text{O}_3
  \]

#### Main sources of inaccuracy of predicted NO\textsubscript{2}

<table>
<thead>
<tr>
<th>Item</th>
<th>OLM (Ozone-Limiting Method)</th>
<th>PVMRM (Plume Volume Molar Ratio Method)</th>
<th>ADMSM (ADMS Method)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hourly background</td>
<td>O\textsubscript{3}</td>
<td>O\textsubscript{3}</td>
<td>O\textsubscript{3}, NO\textsubscript{x}, NO\textsubscript{2}</td>
</tr>
<tr>
<td>Method for ‘O\textsubscript{3} titration’</td>
<td>100% conversion</td>
<td>100% conversion</td>
<td>Explicit calculation</td>
</tr>
<tr>
<td>Method for ‘photolysis’</td>
<td>Neglects</td>
<td>Neglects</td>
<td>Explicit calculation</td>
</tr>
<tr>
<td>Method for entrainment of O\textsubscript{3} into the plume</td>
<td>Fully entrained into <em>ensemble</em> plume</td>
<td>Limited entrainment (volume-based approach) into <em>instantaneous</em> plume</td>
<td>Limited entrainment (cross-sectional area-based approach) into <em>instantaneous</em> plume</td>
</tr>
<tr>
<td>Main sources of inaccuracy of predicted NO\textsubscript{2}</td>
<td>Full entrainment into <em>ensemble</em> plume so upper bound for NO\textsubscript{2}</td>
<td>Neglects reaction rates; assumptions relating to entrainment method</td>
<td>Reaction rates; assumptions relating to entrainment method</td>
</tr>
</tbody>
</table>
Campaign set up


Flat, scrubby grassland

- 4 main NO₂ sources:
  - 2 compressor engine stacks
  - 1 boiler
  - 1 emergency generator

Meteorological instruments on 30 m tower

- 4 monitors:
  - ‘North Fence’ and ‘Field’ in alignment with the stacks and the prevailing wind
  - ‘East Fence’
  - ‘Tower’

Buildings adjacent to compressor engine stacks of similar height to one of the stacks

Parametric Emissions Monitoring Systems (PEMS) recorded hourly engine parameters (compressor engines only)
Meteorological data

- Recorded wind speed, wind direction, temperature, solar radiation, pressure, precipitation and humidity
- Standard deviation of the horizontal wind direction (sigma theta) derived from 1-minute wind direction data
- 2 m, 10 m and 30 m measurements
- Good quality data:
  - On-site
  - Away from significant buildings
  - Located to record prevailing conditions

13 month wind rose
## Source and emissions data

<table>
<thead>
<tr>
<th>Source</th>
<th>No. operational hours (out of 9528)</th>
<th>Av. NO\textsubscript{x} emission rate when operational (g/s)</th>
<th>Exit Temp. (°C)</th>
<th>Exit vel. (m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clark TCV-12 comp. engine</td>
<td>1862</td>
<td>12.8</td>
<td>316</td>
<td>17.4 (average)</td>
</tr>
<tr>
<td>Cooper-Bessemer comp. engine</td>
<td>1833</td>
<td>1.75</td>
<td>277</td>
<td>19.8</td>
</tr>
<tr>
<td>Boiler (with rain cap)</td>
<td>5134</td>
<td>0.062</td>
<td>427</td>
<td>10.9</td>
</tr>
<tr>
<td>Emergency generator (EG)</td>
<td>86</td>
<td>0.29</td>
<td>538</td>
<td>13.1</td>
</tr>
</tbody>
</table>

**Emergency Generator (8 m)**

**Boiler (7 m)**

**Cooper-Bessemer (21 m)**

**Clark TCV-12 (10 m)**

**13 m building**

**11 m building**

Clark TCV-12 compressor engine emissions dominate
In-stack ratios

<table>
<thead>
<tr>
<th>Source</th>
<th>Supplied in-stack ratio</th>
<th>Modelled in-stack ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clark TCV-12 comp. engine</td>
<td>0.16 (PEMS)</td>
<td>0.08 (ambient monitoring data)</td>
</tr>
<tr>
<td>Cooper-Bessemer comp. engine</td>
<td>0.3 (PEMS)</td>
<td>0.3 (PEMS)</td>
</tr>
<tr>
<td>Boiler</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Emergency generator (EG)</td>
<td>0.1</td>
<td>0.1</td>
</tr>
</tbody>
</table>

- This is a scientific evaluation study - not a regulatory assessment
- Consider ambient monitoring data from the closest monitor with the highest frequency and magnitude of concentrations (North Fence)
- Filter data for when the Cooper-Bessemer is not operational
- Minimum $\text{NO}_2/\text{NO}_x$ asymptotes to 0.08
Analysis methodology

• Analyse NO\textsubscript{x} performance then analyse NO\textsubscript{2} performance:
  – Are the predictions of NO\textsubscript{2} consistent with NO\textsubscript{x}? (e.g., if NO\textsubscript{x} is overpredicted then NO\textsubscript{2} should also be overpredicted, and vice versa.)
  – Are the NO\textsubscript{2} predictions consistent with the chemistry scheme formulation?

• Consider:
  – Statistics
  – Quantile-quantile (Q-Q) plots
  – Variation of the ratio of modelled to observed NO\textsubscript{2} against ratio of modelled to observed NO\textsubscript{x}*

• Analyse data where emissions are high and the wind advects from the source(s) to the monitor(s); i.e., filter by wind direction

Statistical results: average concentrations

Tables: data paired in space and time

• **NO\textsubscript{x}** performance

<table>
<thead>
<tr>
<th>Monitor</th>
<th>N</th>
<th>R</th>
<th>Fac 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>East Fence</td>
<td>238</td>
<td>0.67</td>
<td>0.54</td>
</tr>
<tr>
<td>North Fence</td>
<td>803</td>
<td>0.57</td>
<td>0.45</td>
</tr>
<tr>
<td>Field</td>
<td>576</td>
<td>0.59</td>
<td>0.51</td>
</tr>
<tr>
<td>Tower</td>
<td>149</td>
<td>0.47</td>
<td>0.45</td>
</tr>
</tbody>
</table>

• **NO\textsubscript{2}** performance

Underline performance better than NO\textsubscript{x}

<table>
<thead>
<tr>
<th>Monitor</th>
<th>R</th>
<th>Fac 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>ADMSM</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVMRM</td>
<td></td>
<td></td>
</tr>
<tr>
<td>OLM</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ADMSM</td>
<td>ADMSM</td>
<td></td>
</tr>
<tr>
<td>PVMRM</td>
<td>PVMRM</td>
<td></td>
</tr>
<tr>
<td>OLM</td>
<td>OLM</td>
<td></td>
</tr>
<tr>
<td>East Fence</td>
<td>0.71</td>
<td>0.61</td>
</tr>
<tr>
<td>North Fence</td>
<td>0.57</td>
<td>0.50</td>
</tr>
<tr>
<td>Field</td>
<td>0.61</td>
<td>0.62</td>
</tr>
<tr>
<td>Tower</td>
<td>0.56</td>
<td>0.59</td>
</tr>
</tbody>
</table>
Consider:
- the ratio of modelled to observed mean: highest 10 values

ADMSM shows more consistency between NO\textsubscript{x} and NO\textsubscript{2} concentrations than other schemes e.g. modelled NO\textsubscript{x} at North Fence less than half observed value, so modelled NO\textsubscript{2} should be significantly under-predicted.
Quantile-quantile plots

Field

- Clark TCV-12 distance to monitor: 425 m
- PVMRM and ADMSM NO$_2$ broadly consistent with NO$_x$
- High NO$_2$ PVMRM values higher than corresponding ADMSM values
**Quantile-quantile plots**

**North Fence**

- Clark TCV-12 distance to monitor: 140 m
- ADMSM NO₂ broadly consistent with NOₓ
- PVMRM NO₂ higher than corresponding NOₓ and exceed OLM concentrations for some values

![Quantile-quantile plots](image.png)
Ratio plots

- If NO\textsubscript{x} is overpredicted then NO\textsubscript{2} should also be overpredicted, but not by quite so much due to the non-linearity in the chemical equations, and vice versa.
- Consider Modelled NO\textsubscript{2} / Observed NO\textsubscript{2} against Modelled NO\textsubscript{x} / Observed NO\textsubscript{x}

### Diagram

- **Modelled NO\textsubscript{2} / Observed NO\textsubscript{2}**
- **Modelled NO\textsubscript{x} / Observed NO\textsubscript{x}**

- **NO\textsubscript{2} accuracy the same as NO\textsubscript{x} accuracy**
- **Categorised by observed NO\textsubscript{x} concentration (µg/m\textsuperscript{3})**
Field

- Clark TCV-12 distance to monitor: 425 m
- ADMSM values better aligned with blue triangles than PVMRM
- Some under-prediction of PVMRM for high NO₂ concentrations (red points)
- Clear over-prediction of NO₂ relative to NOₓ for OLM

Points coloured by NOₓ concentration (µg/m³)

+ <20
+ 20-50
+ >50
Ratio plots

North Fence

- Clark TCV-12 distance to monitor: 140 m
- ADMSM and PVMRM much better aligned in the blue triangles than OLM
**North Fence**

- Clark TCV-12 distance to monitor: 140 m

*Zooming in to NO\textsubscript{x} values within a factor of 10*

- ADMSM has a tighter grouping of high concentration values (representing better R)
- PVMRM has some high NO\textsubscript{2} predictions that correspond to low-moderate NO\textsubscript{x} concentrations (seen on Q-Q plot)

Points coloured by NO\textsubscript{x} concentration (µg/m\textsuperscript{3})

- + <20
- + 20-100
- + 100-500
- + >500
Conclusions (1 of 2)

- Superior dataset for evaluation of NO\textsubscript{x} chemistry schemes, with short source to monitor distances, and two monitors aligned with the prevailing wind.
- NO\textsubscript{x} evaluation: AERMOD performs well at some monitors
- NO\textsubscript{2} evaluation:
  - PVMRM and ADMSM perform better than OLM; OLM overpredicts
  - PVMRM and ADMSM broadly replicate near-field NO\textsubscript{2}/NO\textsubscript{x} ratios
  - PVMRM predicts some high NO\textsubscript{2} concentrations exceeding the ‘upper bound’ OLM values – likely related to entrainment method rather than lack of explicit chemistry
  - ADMSM NO\textsubscript{2} statistics more consistent with NOx than PVMRM; ADMSM shows better performance in ratio plots
Next steps
• Further chemistry scheme evaluation is planned using other new datasets
• ADMSM to be incorporated within the latest version of AERMOD

Other uses for this dataset
• Building downwash evaluation
• Sensitivity of model results to sigma-theta

Suggestion for future measurement campaigns
• More downwind monitors in the range 0.5 – 1 km and further, to evaluate performance in terms of the variation of NO$_2$/NO$_x$ with distance
## Co-authors

<table>
<thead>
<tr>
<th>Cambridge Environmental Research Consultants</th>
<th>AECOM</th>
<th>American Petroleum Institute</th>
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<tbody>
<tr>
<td>• David Carruthers</td>
<td>• Robert Paine</td>
<td>• Cathe Kalisz</td>
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<tr>
<td>• Steve Smith</td>
<td>• Christopher Warren</td>
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<td>• Martin Seaton</td>
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## Acknowledgements

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<tbody>
<tr>
<td>• Funded study</td>
<td>• Provided compressor station dataset</td>
<td>• Chris Owen</td>
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<td>• Chris Rabideau (Chair of API Modeling Group)</td>
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Questions?

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