APPLICATION OF A MASTER CHEMICAL MECHANISM (MCM) TO OZONE POLICY ASSESSMENTS IN EUROPE

Dick Derwent
rdscientific

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AIM OF THE STUDY

Emission inventories
UK & Europe

UK Photochemical Trajectory Model

Science focus
Why is the chemical mechanism important?

Policymakers focus

Ozone and PM Health impacts
UK PHOTOCHEMICAL TRAJECTORY MODEL

• moving box model

• box height changes with time of day

• emissions of $\text{SO}_2$, $\text{NO}_x$, CO, CH$_4$, organic compounds

• spatial resolution is 10 km x 10 km, 50 km x 50 km and 150 km x 150 km depending on distance from arrival point

• single standard 5 – day trajectory case from Austria to the UK
GRIDDED EMISSION INVENTORIES
SPECIATION OF THE EMISSIONS OF ORGANIC COMPOUNDS

• UK National Atmospheric Emissions Inventory NAEI

• 248 separate emission source categories

• each emission source has a separate species profile

• species profiles contain 663 individual VOC species

• UK PTM utilises the 248 x 663 speciation matrix

• http://www.naei.org.uk
SPECIATION MATRIX

Emission source categories

Policy makers

Organic species

Science community

[1,1]

[248,663]
UK PTM uses MCMv3.1

- 176 emitted organic compounds
- 4,414 reaction products
- 12,871 chemical reactions

Detailed near-explicit chemical mechanism MCM v3.1 to represent the contribution made by methane and 136 individual organic species to ozone formation.

MCM-CRI common reactive intermediates mechanism (Jenkin et al.) used for addition 40 organic species

- 248 x 176 matrix of category x species
- 90% coverage of total VOC mass emissions
- fractional speciation held constant across Europe
MASTER CHEMICAL MECHANISM

Generates the same picture of regional ozone formation across Europe as other mechanisms such as CBM-4

Used here because it is the only mechanism that treats enough emitted organic species in explicit detail

VOC emission source categories can only be treated explicitly with a chemical mechanism that treats each species in detail
UK PHOTOCHEMICAL TRAJECTORY MODEL
REACTIVITY SCALES

Incremental reactivity

• this is the increase in ozone $\Delta O_3$ in ppb divided by the fractional increase in the emissions from that source category:

$$IR_i = \frac{\Delta O_3}{\Delta VOC_i}$$

Incremental reactivities depend on the environmental conditions and are not geophysical quantities
An additional emission was added in turn for each of the 176 VOC emission source categories across Europe and the model was rerun. The extra emission amounted to a 2.9% increase in the emissions for that VOC species.

The increase in emission was applied everywhere across Europe.

The increase in ozone above the base case $\Delta O_3$ was different for every VOC species.
PHOTOCHEMICAL OZONE CREATION POTENTIAL
POCP

Incremental reactivity for $VOC_i$ expressed relative to ethylene = 100

They depend on environmental conditions such as $NO_x$ and VOC emissions and some policy assumptions.

Determined for:

• single-day Los Angeles situation

• multi-day European situation
COMPARISON OF MIR REACTIVITIES FOR THE ALKANES
WITH POCP INDICES
FOR LOS ANGELES SINGLE-DAY SITUATION

Acknowledgement: W P L Carter for MIR values
CONCLUSIONS ABOUT REACTIVITY SCALES

• can represent a huge amount of atmospheric chemistry in a single number

• can see that OH-reactivity is not the major term determining reactivity

• other determining factors included organic NO\textsubscript{y} formation, formation of photochemically-labile molecules, formation of unreactive molecules, competition between pathways

• new chemistry, eg. for aromatics, can drastically change reactivities
MULTI-DAY OZONE FORMATION AND THE REACTIVITIES OF THE OLEFINS

All completely reacted on 1st day

17 olefins

European conditions
FIRST DAY AND SECOND DAY OZONE PRODUCTION WITH THE OLEFINS

• Conclude that all olefins have some ozone production on the second day and that it is highly species dependent

• Second day ozone production occurs even with the almost complete decay (>99%) of the parent olefin on the first day

• There are routes in the Master Chemical Mechanism that allow a VOC to continue making ozone on the second day despite its almost complete decay on the first day
DEGRADATION OF TERMINAL OLEFINs

OH + 1-pentene = HCHO + C₄H₉CHO + HO₂

OH + C₄H₉CHO ➞ ➞ ➞ C₃H₇CHO
OH + C₃H₇CHO ➞ ➞ ➞ C₂H₅CHO
OH + C₂H₅CHO ➞ ➞ ➞ CH₃CHO
OH + CH₃CHO ➞ ➞ ➞ HCHO

Aldehydes and ketones are longer-lived than olefins and some may survive past the end of the first day.

Formaldehyde is often the end of the decay chain and its production is delayed towards the end of the first day.
PEROXYACYLNITRATES - PANs

• important set of temporary reservoir species for NO\textsubscript{y}

• thermally unstable with a lifetime of many hours

\[
\begin{align*}
\text{OH} + \text{RCHO} & \Rightarrow \text{RCOO}_2 \\
\text{RCOO}_2 + \text{NO}_2 & \Leftrightarrow \text{RCOO}_2\text{NO}_2 \\
\text{RCOO}_2 + \text{NO} & \Rightarrow \text{NO}_2 + \text{RCO}_2
\end{align*}
\]

• MCM v3.1 contains 207 individual PAN-type species

• peroxyacetylnitrate PAN is usually present in the highest concentration
SECOND DAY OZONE PRODUCTION vs OVERNIGHT PANs FOR OLEFINs
CONCLUSIONS ON MULTI-DAY REACTIVITY

• All highly reactive organic compounds have some multi-day ozone formation potential

• Some of the routes are impossible to represent in simplified chemical mechanisms

• PAN formation is an important route and this can be represented in simplified mechanisms
PERTURBING THE SPECIATION MATRIX

Emission source categories

Organic species

Incremental reactivity scale

Incremental source reactivity
INCREMENTAL REACTIVITY IR
OF A VOC EMISSION SOURCE

This is the increase in ozone $\Delta O_3$ in ppb divided by the fractional increase in the emissions from that source category:

$$IR = \frac{\Delta O_3}{\Delta VOC \cdot VOC}$$

Incremental reactivities depend on the environmental conditions and are not geophysical quantities.
SENSITIVITY EXPERIMENTS

An additional emission was added in turn from each of the 248 VOC emission source categories across Europe.

The extra emission amounted to a 7.3% increase in VOC emissions.

The speciation of the extra emission was given the same species profile as the emission source category.

The increase in emission was applied everywhere across Europe.
## INCREMENTAL REACTIVITIES
### – TOP 12 SOURCE CATEGORIES

<table>
<thead>
<tr>
<th>Source Category</th>
<th>Incremental Reactivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical waste incineration</td>
<td>53.8</td>
</tr>
<tr>
<td>Blast furnaces_Coke-oven gas</td>
<td>49.5</td>
</tr>
<tr>
<td>Iron &amp; steel (Flaring)_Coke-oven gas</td>
<td>49.0</td>
</tr>
<tr>
<td>Iron &amp; steel industry_Coke-oven gas</td>
<td>48.9</td>
</tr>
<tr>
<td>Other industrial combustion_Coke-oven gas</td>
<td>48.9</td>
</tr>
<tr>
<td>Industrial coatings (drum)</td>
<td>47.5</td>
</tr>
<tr>
<td>Printing (metal decorating)</td>
<td>47.1</td>
</tr>
<tr>
<td>Printing (heatset web offset)</td>
<td>47.0</td>
</tr>
<tr>
<td>Industrial coatings (marine)</td>
<td>46.5</td>
</tr>
<tr>
<td>Railways (Freight)_Gas oil</td>
<td>46.2</td>
</tr>
<tr>
<td>Road transport (rigid HGVs)_DERV</td>
<td>46.2</td>
</tr>
<tr>
<td>Other industrial (off-road)_Gas oil</td>
<td>46.0</td>
</tr>
</tbody>
</table>

Expressed relative to ethylene = 100
CONTRIBUTION TO OZONE FORMATION

Ozone formation from a particular source category

= Incremental Reactivity x Fractional contribution to total VOC emissions

Sum of all 248 source category contributions to ozone formation

= 31 ppb

out of the peak ozone concentration of 87.8 ppb
### CONTRIBUTION TO OZONE FORMATION IN 2000 - TOP 15 SOURCE CATEGORIES

<table>
<thead>
<tr>
<th>Source Category</th>
<th>% emissions</th>
<th>incremental reactivity</th>
<th>ozone ppb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Road transport (cars without catalysts) _Petrol</td>
<td>11.524</td>
<td>41.387</td>
<td>4.769</td>
</tr>
<tr>
<td>Road transport (cars with catalysts) _Petrol</td>
<td>5.264</td>
<td>41.578</td>
<td>2.189</td>
</tr>
<tr>
<td>Onshore loading of crude oil</td>
<td>5.098</td>
<td>31.532</td>
<td>1.608</td>
</tr>
<tr>
<td>Chemical industry</td>
<td>5.364</td>
<td>28.337</td>
<td>1.520</td>
</tr>
<tr>
<td>Offshore loading of crude oil</td>
<td>3.739</td>
<td>31.026</td>
<td>1.160</td>
</tr>
<tr>
<td>Spirit manufacture (maturation)</td>
<td>3.401</td>
<td>30.890</td>
<td>1.051</td>
</tr>
<tr>
<td>Refineries (process fugitives)</td>
<td>2.091</td>
<td>41.291</td>
<td>0.863</td>
</tr>
<tr>
<td>Petrol stations (vehicle refuelling with unleaded petrol)</td>
<td>2.709</td>
<td>31.327</td>
<td>0.849</td>
</tr>
<tr>
<td>Other solvent use</td>
<td>3.370</td>
<td>20.229</td>
<td>0.682</td>
</tr>
<tr>
<td>Gas leakage</td>
<td>4.648</td>
<td>13.527</td>
<td>0.629</td>
</tr>
<tr>
<td>Decorative paint (trade decorative)</td>
<td>1.811</td>
<td>31.395</td>
<td>0.569</td>
</tr>
<tr>
<td>Industrial coatings (metal &amp; plastic)</td>
<td>1.627</td>
<td>34.835</td>
<td>0.567</td>
</tr>
<tr>
<td>Aerosols (cosmetics and toiletries)</td>
<td>1.883</td>
<td>28.638</td>
<td>0.539</td>
</tr>
<tr>
<td>Decorative paint (retail decorative)</td>
<td>1.669</td>
<td>31.313</td>
<td>0.523</td>
</tr>
<tr>
<td>Industrial adhesives</td>
<td>1.822</td>
<td>28.569</td>
<td>0.520</td>
</tr>
</tbody>
</table>
CONCLUSIONS

• The detailed representation of the atmospheric degradation pathways for organic compounds can be handled in near-explicit chemical mechanisms such as the MCM.

• Reactivity scales represent a means of reducing all the detailed mechanistic information into a single number for each organic compound.

• There are policy implications particularly for the formation and long-range transport of ozone in the detailed representation of the degradation pathways for organic compounds.