Assessing anthropogenic impact on secondary pollutant formation in the South Eastern US via airborne formaldehyde measurements


UW-Madison, JCET UMBC, NASA GSFC, UMD, Harvard, CIRES, CU Boulder, NOAA ESRL, NOAA GFDL, UW-Seattle, Princeton, Caltech, Hendrix College, UW-Seattle, University of Oslo, Georgia Tech

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NASA-ISAF (HCHO) Instrument

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SENEX 2013
Southeast Nexus

NOAA WP-3D aircraft

NSF GRFP

Jen Kaiser
Why Formaldehyde?

HCHO tracks photochemical evolution of VOCs.

1a) Yield related to VOC type
1b) Formation rate related to reactive carbon processing rate
2) HCHO is an important radical source

From Jen Kaiser
Formaldehyde (HCHO)

30 – 50% of isoprene-derived carbon will become HCHO at some point
Anthropogenic Influence

Many forms of anthropogenic influence:

• Land-use change (VOC, NH$_3$, N$_2$O emissions, ...)
• Emissions: NH$_3$, SO$_2$, VOCs, NO$_x$, ... 

Identification of
(a) Impact of NO$_x$ emissions on VOC processing
(b) VOC emission type
(c) Investigation of aerosol glyoxal sink
   (Jingy Li, Jinqiu Mao)
SENEX (= SouthEast NEXus) Flights

- Summer 2013
- Wide range of VOC (isoprene) and NO$_x$
I. $\text{NO}_x$ influence on HCHO
I. \( \text{NO}_x \) influence on HCHO

Group and fit by log(\( \text{NO}_x \))
“Isoprene Sensitivity” effectively represents the response of HCHO to a change in isoprene emissions.
“Background” represents HCHO that cannot be directly linked to isoprene emissions (too aged or other precursors)
**NO*\textsubscript{x} influence on HCHO:** Comparison with Different Model Mechanisms

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Species</th>
<th>Reactions</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CB05</td>
<td>51</td>
<td>156</td>
<td>Yarwood et al. (2005)</td>
</tr>
<tr>
<td>CB6r2</td>
<td>56</td>
<td>216</td>
<td>Ruiz and Yarwood (2013)</td>
</tr>
<tr>
<td>MCMv3.2*</td>
<td>447</td>
<td>1428</td>
<td>Saunders et al. (2003)</td>
</tr>
<tr>
<td>MCMv3.3.1*</td>
<td>610</td>
<td>1974</td>
<td>Jenkin et al. (2015)</td>
</tr>
</tbody>
</table>

*Isoprene subset

**CB: Carbon Bond Mechanism**
- Condensed
- Commonly used for air quality simulations

**MCM: Master Chemical Mechanism**
- Explicit
- Benchmark mechanism
Box Model Simulations

University of Washington Chemical Model (Wolfe and Thornton, 2011)

• Diel steady-state
• Constrained to aircraft observations of C$_5$H$_8$, NO, NO$_2$, CO, CH$_4$, O$_3$, PAN, CH$_3$OH
• Physical losses represented by a 24-hour lifetime
• Assumes clear sky conditions
• Four simulations
  – Differ only in choice of gas-phase mechanism

CB05  MCMv3.2
CB6r2  MCMv3.3.1
Model-Measurement Comparison

Linear regression analysis:

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Slope</th>
<th>Int.</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CB05</td>
<td>0.65</td>
<td>0.15</td>
<td>0.63</td>
</tr>
<tr>
<td>CB6r2</td>
<td>0.74</td>
<td>0.01</td>
<td>0.67</td>
</tr>
<tr>
<td>MCMv3.2</td>
<td>0.79</td>
<td>-0.01</td>
<td>0.64</td>
</tr>
<tr>
<td>MCMv3.3.1</td>
<td>0.88</td>
<td>-0.11</td>
<td>0.65</td>
</tr>
</tbody>
</table>
Chemical Dependence of HCHO Concentration on NO\textsubscript{x} Conditions

- Mechanisms maintain shape of dependence (slope)
- Mechanisms underestimate HCHO concentrations (intercept)

Equal N per bin
N = 100
Take-Away Points

- HCHO variability driven by both emissions and chemistry
- Up-to-date mechanisms represent isoprene-HCHO relationship well but background HCHO not captured well
- Most of the NO\textsubscript{x}-driven increase in HCHO reflects faster VOC oxidation

For more details: Wolfe et al., ACP (2016)
II. Formaldehyde and Glyoxal as Indicator of VOC Speciation

- Relative yields of glyoxal and HCHO differ between classes of VOC
- Similar atmospheric lifetimes
- Ratio related to local VOC species
- Measurable by satellite
- Aerosol important sink for glyoxal
Observations of $R_{GF}$ have led to conflicting conclusions.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Method</th>
<th>Biogenic $R_{GF}$ (%)</th>
<th>Anthropogenic $R_{GF}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vrekousiss et al. (2010)</td>
<td>Satellite</td>
<td>&gt;4.5</td>
<td>&lt;4.5</td>
</tr>
<tr>
<td>DiGangi et al. (2012)</td>
<td>LIF$^a$/LIP$^b$; review</td>
<td>&lt;2</td>
<td>&gt;2.5</td>
</tr>
<tr>
<td>MacDonald et al. (2012)</td>
<td>DOAS$^c$;</td>
<td>20-40</td>
<td>--</td>
</tr>
<tr>
<td>Li et al. (2014)</td>
<td>DOAS; model</td>
<td>0.2-17 (Depends on NO$_x$, OH, ...)</td>
<td></td>
</tr>
<tr>
<td>Miller et al. (2014)</td>
<td>Satellite</td>
<td>&lt;4 (isoprene)</td>
<td>~4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>&gt;4 (terpenes)</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Laser Induced Fluorescence (HCHO)

$^b$Laser Induced Phosphorescence (CHOCHO)

$^c$Differential Optical Absorption Spectroscopy
Satellite and in situ \( R_{GF} \) in better agreement

- Better agreement between platforms
- Outliers in flight based averaged out in satellite
- Flight-based provides VOC measurements

Low $R_{GF}$ over the Ozarks and near gas flares.

Glyoxal (molec/cm$^2$)

Formaldehyde (molec/cm$^2$)

Formaldehyde (ppb)

Glyoxal (ppb)
High $R_{GF}$ is associated with monoterpenes.
Urban plum: \( \text{NO}_x \) and Anthropogenic VOCs
$R_{GF}$ in a city outflow

VOC speciation changing
$R_{GF}$ in a city outflow

- VOC speciation changing
- $\text{RO}_2$ fate changing
- $[\text{OH}]$ changing
$R_{GF}$ in a city outflow

- VOC speciation changing
- $\text{RO}_2$ fate changing
- $[\text{OH}]$ changing
- $R_{GF}$ consistent!

$R_{GF}$ is only a tracer of dominant VOC species.
Trends are matched by satellite retrievals.

Quick, neighborhood-level $R_{GF}$ in the near future!
Anthropogenic Influence on Glyoxal and Implications for SOA production

Overprediction of gas-phase glyoxal in model = SOA

GFRL Atmospheric General Circulation Model AM3
Leeds Master Chemical Mechanism MCM v3.3.1

Jingqiu Mao, Jingyi Li
**NO$_x$ Influence on HCHO Production in Different Mechanisms**

**HCHO yield (ppbv) from isoprene**

- **Isomerization**
- $\beta$-ISOPO2+NO
- ISOPO2+HO$_2$
- $\delta$-ISOPO2+NO

**Influence on HCHO Production in Different Mechanisms**

**Box model:**
- 60 ppbv O$_3$
- 1 ppbv ISOP

**Good agreement!**

![Graph showing HCHO yield from isoprene in different mechanisms with AM3B and MCM v3.3.1 models.]
NO$_x$ Influence on Glyoxal Production in Different Mechanisms

**Glyoxal yield** (ppbv) from isoprene

- **Isomerization**: β-ISOPO2+NO
- **ISOPO2+HO$_2$**: δ-ISOPO2+NO

Significant discrepancy of yield and NO$_x$ dependence
Mean Vertical Profiles During SENEX

Heterogeneous loss of dicarbonyls (irreversible) => SOA

<table>
<thead>
<tr>
<th>$\gamma_{glyx}$ ($\times 10^{-3}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8-7.3</td>
<td>Liggio et al., 2005</td>
</tr>
<tr>
<td>3.7</td>
<td>Volkamer et al., 2007</td>
</tr>
<tr>
<td>0-0.8 (day)</td>
<td>Washenfelder et al., 2011</td>
</tr>
<tr>
<td>3.3</td>
<td>Waxman et al. 2013</td>
</tr>
<tr>
<td>$\sim 1.0$ (OA)</td>
<td>V. Faye McNeill, 2015</td>
</tr>
</tbody>
</table>

* From dry aerosols
Comparison with Observations

- NO$_x$ dependence of HCHO and glyoxal are similar
  - HCHO is underestimated
  - AM3B could reproduce NO$_x$-glyoxal
- AM3B overestimates $R_{GF}$ at NO$_x$ < 0.5 ppbv
- AM3M (MCM v3.3.1) underestimates glyoxal and $R_{GF}$ across NO$_x$ levels
Glyoxal SOA

Boundary layer average during June-July of 2013

- Irreversible uptake by aerosols & clouds
  0.5-1.0 μg m⁻³ (10-20% of total SOA)

Profound discrepancies between different mechanisms with this approach
Publications from Work Under This Grant

Published Manuscripts

- Wolfe: Formaldehyde production from isoprene oxidation across NOx regimes ACP 2016
- Kaiser: Reassessing the ratio of glyoxal to formaldehyde as an indicator of hydrocarbon precursor speciation ACP 2015
- De Gouw: Airborne Measurements of the Atmospheric Emissions from a Fuel Ethanol Refinery

Submitted Manuscripts

- Li: Observational Constraints on Glyoxal Production from Isoprene Oxidation and Its Contribution to Organic Aerosol Over the Southeast United States GRL

Manuscripts in Preparation

- Marvin: Investigating Differences in Isoprene Oxidation Chemistry Between Gas-Phase Mechanisms Using a Constrained Chemical Box Model
- Additional ones in early stages