The saga of tropospheric ozone

Daniel J. Jacob
Vasco McCoy Family Professor of Atmospheric Chemistry and Environmental Engineering
Harvard University
Ozone is of central interest to atmospheric chemistry

In stratosphere: UV shield
\[ O_2 + \text{hv} \rightarrow O + O \]
\[ O + O_2 + M \rightarrow O_3 + M \]

In upper troposphere: greenhouse gas

In lower/middle troposphere: source of OH
\[ O_3 + \text{hv} \rightarrow O_2 + O^{(1D)} \]
\[ O^{(1D)} + H_2O \rightarrow 2OH \]

At surface: toxic air pollutant

The main atmospheric oxidant
Ozone: the early history

1839: Schonbein discovers a smell from electrolysis of water, calls it ozone (Greek: to smell)

1865: Soret establishes that ozone is $O_3$

1913: Fabry discovers atmospheric ozone at high altitude by observing solar absorption spectrum

1927: Gotz infers vertical distribution of ozone by observing solar radiation near the horizon: peak at 25 km

1930: Dobson maps global distribution of ozone in stratosphere

1930: Chapman proposes mechanism driven by photolysis of $O_2$

$$O_2 + h\nu \rightarrow O + O \quad \lambda < 240\text{nm}$$

$$O + O_2 + M \rightarrow O_3 + M$$

Mechanism operates only above ~25 km altitude

1934: Regener measures ozone vertical profile up to 34 km from hydrogen balloon
Atmospheric chemistry is mainly driven by photo-assisted reaction chains

**Initiation:**

\[
\text{non-radical} + hv \rightarrow \text{radical} + \text{radical} \quad \text{photolysis}
\]

**Propagation:**

\[
\text{radical} + \text{non-radical} \rightarrow \text{non-radical} + \text{radical} \quad \text{bimolecular reaction (generally redox)}
\]

\[\ldots\]

**Termination:**

\[
\text{radical} + \text{radical} \rightarrow \text{non-radical} + \text{non-radical} \quad \text{bimolecular reaction (generally redox)}
\]

\[
\text{radical} + \text{radical} + M \rightarrow \text{non-radical} + M \quad \text{3-body reaction}
\]
Penetration of UV radiation in troposphere
is suppressed by absorption by $O_2$ and $O_3$

Until the 1950s it was thought that there could be no active photochemistry in troposphere.
Haagen-Smit (1953) identifies ozone produced in air from car exhaust as the harmful component in Los Angeles smog. Shows in the lab that ozone is produced by volatile organic compounds (VOCs) and NO\textsubscript{x} in presence of sunlight.

Postulated mechanism:

\[
\begin{align*}
\text{NO}_2 + h\nu &\rightarrow \text{NO} + \text{O} \quad \lambda < 450 \text{ nm} \\
\text{VOC} + \cdot &\rightarrow \text{O}_2 + \ldots \\
\text{HO}_2 + \text{HO}_2 &\rightarrow \cdot + \text{O}_3 \\
\text{HO}_2 + \text{HO}_2 &\rightarrow \text{H}_2\text{O}_2 + \text{O}_2 
\end{align*}
\]
Urban smog aside, troposphere until 1970s was thought to be inert except for slow oxidation by $O_2$.

"The chemistry of the troposphere is mainly that of a large number of atmospheric constituents and of their reactions with molecular oxygen...Methane and CO are chemically quite inert in the troposphere"


Carbon monoxide (CO): product of incomplete fuel combustion

Will CO from increasing vehicles accumulate to produce a global pollution cloud?
Discovery of OH radical production in troposphere (Levy, 1971)

\[ \text{Photolysis at sea level is controlled by photons in 300-320 nm range} \]

\[ k = \int_{0}^{\infty} q_{X}(\lambda)\sigma_{X}(\lambda)\varphi_{\lambda} d\lambda \]

\[ \text{O}_3 + h\nu \rightarrow \text{O}_2 + \text{O}^{(1D)} \]

\[ \text{O}^{(1D)} + \text{H}_2\text{O} \rightarrow 2\text{OH} \]

Ozone layer

310 nm flux

some flux remains

surface

Chip Levy
Tropospheric OH enables fast oxidation of non-radicals

Example: oxidation of CO to CO₂

\[
\text{CO} + \text{O}_2 \rightarrow \text{CO}_2 + \text{O} \quad \text{(Endothermic (requires heat): will not happen in atmosphere)}
\]

Ozone is a stronger oxidant but is not a radical so reaction is too slow

\[
\text{CO} + \text{O}_3 \rightarrow \text{CO}_2 + \text{O}_2 \quad \text{(Exothermic (releases heat)) but still negligibly slow in atmosphere)}
\]

But oxidation of CO by OH is fast:

\[
\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}
\]

Oxidation by OH is further promoted if H abstraction can take place

\[
\text{RH} + \text{OH} \rightarrow \text{R} + \text{H}_2\text{O}
\]

hydrocarbon

OH is the PacMan of the atmosphere: it oxidizes anything that can be oxidized, with particular fondness for abstracting H atoms

Tropospheric [OH] ~ 1x10⁶ molecules cm⁻³ → 2-month CO lifetime → 9-year CH₄ lifetime
Demerjian et al. [1973] used discovery of OH to explain the chain formation of ozone in urban smog.

\[ \text{VOC} + \text{OH} \rightarrow \text{HO}_2 + \text{products} \]
\[ \text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2 \]
\[ \text{NO}_2 + hv \rightarrow \text{NO} + \text{O}_3 \]
Until the 1980s, it was thought that global tropospheric ozone was mainly of stratospheric origin – but that doesn’t work.

A large tropospheric source of ozone is needed:
1. to balance the chemical loss of ozone
2. to avoid titration of OH by CO and CH₄ emissions

\[
\begin{align*}
    \text{CO} + \text{OH} & \text{ } \stackrel{O_2}{\longrightarrow} \text{CO}_2 + \text{HO}_2 \\
    \text{HO}_2 + \text{NO} & \rightarrow \text{OH} + \text{NO}_2 \\
    \text{NO}_2 + h\nu & \stackrel{O_2}{\longrightarrow} \text{NO} + \text{O}_3
\end{align*}
\]

\[
\begin{align*}
    \text{CH}_4 + \text{OH} & \text{ } \stackrel{O_2}{\longrightarrow} \text{CH}_3\text{O}_2 + \text{H}_2\text{O} \\
    \text{CH}_3\text{O}_2 + \text{NO} & \rightarrow \text{CH}_3\text{O} + \text{NO}_2 \\
    \text{NO}_2 + h\nu & \stackrel{O_2}{\longrightarrow} \text{NO} + \text{O}_3
\end{align*}
\]

But where would the NO\textsubscript{x} come from?

NO\textsubscript{x} has a lifetime of a few hours against oxidation to HNO\textsubscript{3}, so should only be present near combustion source regions.
Discovery of NO$_x$ in remote troposphere by aircraft in late 1980s

Observations over South Atlantic (NASA TRACE-A): sufficient ozone production to offset loss

- Implies that chemical production is main source of ozone in global troposphere, stratospheric input is small in comparison
- Lightning NO$_x$ drives ozone maximum in upper troposphere

Jacob et al. [1996]
We now know that $\text{NO}_x$ is present throughout troposphere and fuels ozone production globally.

Sources: fuel combustion, open fires, lightning, soils

Tropospheric $\text{NO}_2$ columns measured by TROPOMI satellite (Apr-Sep 2018)

Organic nitrate reservoirs allow transport of $\text{NO}_x$ on global scale
Current chemical transport models reproduce major features of tropospheric ozone
Mean 500 hPa ozone in JJA 2013

Hu et al. [2018.]

IPCC global budget averages across models (Tg a⁻¹)

<table>
<thead>
<tr>
<th></th>
<th>Chemical production in troposphere</th>
<th>Chemical loss in troposphere</th>
<th>Transport from stratosphere</th>
<th>Deposition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4600±400</td>
<td>4200 ±400</td>
<td>500 ±100</td>
<td>900 ± 100</td>
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</tbody>
</table>

Tropospheric ozone lifetime: 24 ±4 days

Hu et al. [2018.]
...but we still cannot explain long-term ozone trends

1. Why does historical record show no increase until 1980?
2. Why is global tropospheric ozone presently increasing, when NO\textsubscript{x} emissions are thought to have plateaued?

TOAR [2020]; Kazuyuki et al. [2020]
Ozonesondes over East Asia show very high ozone through depth of troposphere that cannot be captured by the GEOS-Chem model

Mean ozonesonde data during KORUS-AQ campaign, May 1 – June 10, 2016

- Underestimate of 10-25 ppb in free troposphere
- Observed ozone exceeds 70 ppb air quality standard throughout the column
- Lack of correlation with CO shows that this is a background rather than a regional pollution export problem

Nadia Colombi, in prep.
GEOS-Chem didn’t use to have that underestimate problem…but observed ozone has increased while GEOS-Chem has not

1997-2017 ozonesonde trends at Pacific Rim sites

- Sonde data show ozone increase in past decades not captured by the model
- Recent developments in GEOS-Chem (halogen chemistry, NO$_x$ loss in clouds, aromatic chemistry…) have led to decreases in model ozone

Xiao Lu, in prep.
Importance and mystery of tropospheric halogen chemistry

- Halocarbons
- Sea-salt aerosol (SSA)
- Halogen radicals
- Reservoirs
- NOx, ozone, mercury sinks

- Industry
- Fires
- Volcanoes

- Stratosphere
- Troposphere

- hv, OH
- ozone sink

- HOI, I₂
- Biosphere
- Sea-salt aerosol (SSA)

Wang et al. [2021]
Halogen (X) chemistry is an important tropospheric ozone sink in GEOS-Chem

Dominant pathways:

\[ X + O_3 \rightarrow XO + O_2 \]
\[ XO + HO_2 \rightarrow HOX + O_2 \]
\[ HOX + hv \rightarrow X + OH \]  
\( (X \equiv \text{Br, I}) \)

\[ XO + NO_2 + M \rightarrow XNO_3 + M \]
\[ XNO_3 + H_2O \rightarrow HNO_3 + HOX \]  
\( (X \equiv \text{Br, Cl}) \)

- Halogen chemistry decreases tropospheric ozone by \( \sim 10 \) ppb and global OH by 4%.
- Halogen chemistry is a major contributor to model ozone underestimate – though model is too low in northern hemisphere even without halogens.

Wang et al. [2021]
Evaluation of model tropospheric BrO is limited by inconsistency of observations

GEOS-Chem BrO: tropospheric mean 0.19 ppt

BrO from aircraft campaigns over Pacific and Atlantic: observations are close to detection limit

Wang et al. [2021]
GEOS-Chem underestimates NO over remote oceans as observed in ATom campaigns.

- Model NO is 3x too low in lower/middle troposphere, especially in winter.

Viral Shah, in prep.
Fast photolysis of aerosol nitrate ($J_{NO3}$) as missing source of NO$_x$ suggested by observations of HONO over the oceans this largely fixes the GEOS-Chem NO simulation in ATom

Atlantic
[Ye et al., 2016]
Cape Verde
[Andersen et al., in prep]

Standard models

\[
\begin{align*}
\text{HONO} + hv & \rightarrow \text{NO} + \text{OH} \\
\text{HONO} + \text{OH} & \rightarrow \text{NO} + \text{H}_2\text{O} + \text{O}
\end{align*}
\]

Viral Shah, in prep.
Updated model including nitrate photolysis and suppressing sea salt aerosol debromination corrects the GEOS-Chem ozone underestimate.

Ozone at 500 hPa

...but this is unlikely to be the final word

Viral Shah, in prep.
Evidence of NO\textsubscript{x} emission decrease from OMI satellite NO\textsubscript{2} data

Russell et al. [2012]
Evidence of NO$_x$ emission decrease from OMI satellite NO$_2$ data

30% decrease in NO$_x$ emissions from 2005 to 2011

Russell et al. [2012]
US NO\textsubscript{x} emissions have continued to decrease according to EPA…
but OMI tropospheric NO\textsubscript{2} column observations suggest otherwise!

EPA National Emission Inventory (NEI): 53\% sustained decrease of NO\textsubscript{x} emissions over 2005-2017
*EPA, 2018*

OMI NO\textsubscript{2} columns over CONUS, 2005-2015: flat after 2009
*Jiang et al., PNAS 2018*
OMI annual NO$_2$ trends over CONUS, 2005-2017
Importance of NO\textsubscript{x} background for interpreting tropospheric NO\textsubscript{2} satellite measurements

![Diagram showing the importance of NO\textsubscript{x} background for interpreting tropospheric NO\textsubscript{2} satellite measurements. The diagram includes a sun, a satellite, and a graph showing detection sensitivity vs. altitude. The tropopause and NO\textsubscript{2} slant column are also illustrated.]
US NO$_x$ emissions are now so low that OMI mostly sees background.

OMI NO$_2$ sensitivity vs. altitude

- Boundary layer below 2 km accounts for only 20-35% of tropospheric NO$_2$ column as seen by OMI.
- Need understanding of tropospheric background to properly interpret NO$_2$ observations from space.

Travis et al., ACP 2016
Some take-aways

- Tropospheric ozone is well understood at a basic level as controlled by a balance between photochemical production from VOCs and NO$_x$ and photochemical loss.

- However, current models fail to reproduce observed long-term trends, suggesting some problems with fundamental understanding.

- Tropospheric halogen chemistry and background NO$_x$ chemistry may be key to advancing understanding.

- Background NO$_x$ is also important for the interpretation of satellite NO$_2$ data.