Source and change of tropospheric ozone in China and Pacific Rim

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at
Nanjing University of Information Science and Technology
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GOOD vs. BAD OZONE

Nitrogen oxide radicals; $\text{NO}_x = \text{NO} + \text{NO}_2$

Sources: combustion, soils, lightning

Volatile organic compounds (VOCs)

Methane
Sources: wetlands, livestock, natural gas…

Reactive VOCs
Sources: vegetation, combustion

Carbon monoxide
Source: combustion

Tropospheric ozone precursors

Good (UV shield)

Bad (greenhouse gas)

Good (OH source)

Bad (smog)
An important greenhouse gas, especially in the upper troposphere

IPCC (2001) RADIATIVE FORCING ESTIMATE:

\[ \Delta F_{O_3} = 0.35 \pm 0.15 \text{ W m}^{-2} \]
Ozone / Hospital Admissions
(Burnett, et al 2001)

Respiratory Hospital Admissions Anomalies
(adjusted)

O₃ (ppbv) difference from mean value
(5-day average filtered Max 1-hour ppb)
Threat for vegetation
Is ozone pollution affecting crop yields in China?
(W. L. Chameides et al., 1999)

- **Economic:**
  - $1-2 billion lost annually in the U.S. from ozone damage to agriculture and commercial forestry alone.
    - To put this in perspective, PA’s total crop production for 2006 was approximately $1.7 billion
  - $5 billion in some other countries such as China

http://www.ucar.edu/learn/1_7_1.htm
Ozone plays a pivotal role in the tropospheric chemistry: origin of all oxidants such as OH and H$_2$O$_2$ affecting the chemical composition and oxidizing capacity of the atmosphere.

Atmospheric Chemistry is controlled by atmospheric oxidants

“The Earth’s Oxidizing Capacity”

M. Thiemens
Sources of ozone in troposphere
• a dynamic combination of natural (stratospheric) and anthropogenic (from made-made precursors) origin.

Saya, Hainan, spring 2004
Tropospheric ozone chemistry

Initiation:
R1: \( \text{O}_3 + \text{hv} \rightarrow \text{O}^{(1D)} + \text{O}_2 \)
R2: \( \text{O}^{(1D)} + \text{H}_2\text{O} \rightarrow 2\text{OH} \)

Chain propagation: Multipliers
R3: \( \text{CO} + \text{OH} + \text{O}_2 \rightarrow \text{HO}_2 + \text{CO}_2 \) \( m \)
R4a: \( \text{HO}_2 + \text{NO} \rightarrow \text{NO}_2 + \text{OH} \) \( m_1 \)
R4b: \( \text{HO}_2 + \text{O}_3 \rightarrow \text{OH} + 2\text{O}_2 \) \( m_2 \)
R5: \( \text{NO}_2 + \text{O}_2 + \text{hv} \rightarrow \text{NO} + \text{O}_3 \) \( m_1 \) \( m = m_1 + m_2 \)

Termination:
R6: \( \text{OH} + \text{NO}_2 + \text{M} \rightarrow \text{HNO}_3 + \text{M} \)
R7: \( \text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \)

Net (R1 – R5):
R8: \( \text{O}_3 + \text{H}_2\text{O} + m\text{CO} + (2m_1-m_2-1)\text{O}_2 \rightarrow m\text{CO}_2 + 2\text{OH} + (m_1-m_2)\text{O}_3 \)

Net Production of \( \text{O}_3 \): \( m_1 > m_2 + 1 \)
O\(_3\) neutral: \( m_1 = m_2 + 1 \)
Net destruction of \( \text{O}_3 \): \( m_1 \leq m_2 \)
Tropospheric ozone production cycle

Image: Anja Kaiser. From www.atomsphere.mpg.de/enid/1442
Photochemical ozone production

- photolysis of ozone is most significant source of OH

- atmospheric oxidation of hydrocarbons, CO and CH$_4$ (in descending order) initiated by OH radical
  - production of peroxy radicals (HO$_2$, RO$_2$) which interact with O$_3$-NO-NO$_2$ cycle to photo-chemically produce ozone
  - produce carbonyl compounds (aldehydes and ketones) which undergo further oxidation
  - recycling of OH

- termination by formation of nitric acid (OH + NO$_2$ $\equiv$ HNO$_3$) or peroxides (H$_2$O$_2$, ROOH)
Nonlinear ozone chemistry upon NO\textsubscript{x}

- NO\textsubscript{x} concentrations almost always low enough that ozone production is NO\textsubscript{x} limited ([NO\textsubscript{x}] > ~20 pptv)

- for [NO\textsubscript{x}] < ~20 pptv, chemistry results in net ozone destruction: no NO\textsubscript{x} to turn-over the NO-NO\textsubscript{2} cycle

\[
\text{O}_3 + \text{hv} \equiv \text{O}^{(1D)} + \text{O}_2
\]

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

- Also \HO_2\cdot + \text{O}_3 \equiv \text{OH}\cdot + 2 \text{O}_2

- important in tropical marine boundary layer
Estimates global NO$_x$ emissions for early 1990s (Tg-N/year).

<table>
<thead>
<tr>
<th>Source</th>
<th>Emissions (Tg-N/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Technological</td>
<td>23 - 27</td>
</tr>
<tr>
<td>Aircraft</td>
<td>0.5</td>
</tr>
<tr>
<td>Biomass burning</td>
<td>7.0 - 8.0</td>
</tr>
<tr>
<td>Soils</td>
<td>5.0 - 12.0</td>
</tr>
<tr>
<td>Lightning</td>
<td>3.0 - 20.0</td>
</tr>
</tbody>
</table>

- Biomass burning includes savannah burning, tropical deforestation, temperate wildfires and agricultural waste burning

- Lifetime from ~ 6 hours in planetary boundary layer (PBL) to several days to a week in the upper troposphere (UT)

- From 10s ppbv in urban areas to 10s pptv in remote regions (UT and remote MBL), give rise to different chemical regimes and control local ozone chemistry
Global tropospheric residual ozone

Tropospheric ozone column from satellite

Data from asd-www.larc.nasa.gov/TOR/data.html (Fishman et al., 2003).
## Surface O₃ levels in various regimes

<table>
<thead>
<tr>
<th>Description</th>
<th>O₃ Level(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural background (pre-industrial):</td>
<td>10-20 ppb</td>
</tr>
<tr>
<td>Remote locations in the Northern Hemisphere:</td>
<td>20-40 ppb (varying by season and latitude)</td>
</tr>
<tr>
<td>Rural areas during region-wide pollution events</td>
<td>80-100 ppb</td>
</tr>
<tr>
<td>Peak O₃ in urban areas during pollution events</td>
<td>120-200 ppb</td>
</tr>
<tr>
<td>Maximum urban O₃ (Los Angeles, Mexico City)</td>
<td>490 ppb</td>
</tr>
<tr>
<td>Stratospheric ozone layer</td>
<td>15000 ppb</td>
</tr>
<tr>
<td>USEPA health standard for ozone</td>
<td>85 ppb, 8 hour exposure</td>
</tr>
<tr>
<td>HKAQO</td>
<td>122 ppb</td>
</tr>
</tbody>
</table>
Scientific and interesting questions

• In Europe and N. America, increases of photochemical ozone produced from pollution has resulted in change of seasonal cycle of tropospheric ozone, and thus oxidizing capacity of the atmosphere.

• What happens in Asia? How this will impact on the regional air quality, atmospheric chemistry and eco-climate system?

• To understand the issues, we HAVE TO separate natural ozone and anthropogenic ozone from pollution to tropospheric ozone budget, especially the seasonal maximum.

• Challenges: very limited systematic and long-term ozone measurements in Asia and there is still no a good method.
Source of spring-summer tropospheric ozone maximum in Asia
Debate on sources of ozone maximum

Dynamic processes: strat-trop exchanges, such as tropopause folding

Chemical processes: formation from industrial and urban pollution

Seasonal cycle of $\text{O}_3$ at different pressure levels (eight different stations of northern hemisphere) (Logan, 1999).
Debate on sources of summer ozone maximum

- natural strat. ozone (Ding et al.)
- long-range transport from Eurasia (Zhu et al.)
- transport of from east China (Akimoto)
- combination of both (Zheng et al.)

![Graph showing ozone (ppbv) and CO (ppbv) from 2001 to 2009 at Waliguan Observatory](image)
NASA’s Aircraft Mission- Global Tropospheric Experiment (GTE) Program

• The Transport and Chemical Evolution over the Pacific (TRACE-P) in March/April 2001

• Objectives to determine:
  • chemical composition of the Asian outflow over the western Pacific in spring in order to understand and quantify the export of chemically and radiatively important gases and aerosols, and their precursors, from the Asian continent

  • chemical evolution of the Asian outflow over the western Pacific in spring and to understand the ensemble of processes that control the evolution, focusing on tropospheric O3 and aerosols.
NASA/TRACE-P Aircraft Mission to the Pacific Rim (March-April 2001)

Quantifying the export of Asian pollution

Satellite data:
MOPITT (CO)
TOMS (ozone)
SEAWIFS,
TOMS (aerosols)

3-D chemical transport model forecasts

DC-8 and P-3 aircraft

Flight tracks were designed to optimize model testing and satellite validation  
Jacob et al., 2003
Ozonesonde experiment programs

- Since 1993 and 1994;
- NASA TRACE-P: spring 2001;
- NASDA PEACE-A: winter 2002;
- TAPTO: spring 2004;
- TAPTO: spring 2005

Locations:
- Linan, 30.30°N, 119.75°E
- Hilo and Mauna Loa Observatory, 18.21°N, 110.31°E, and others.
Tropospheric ozone over Asia

Hong Kong (22.4°N) (1994-2007)

Hong Kong (22.4°N) (2000-2001)
Sapporo, Japan (43°N) (2000-2001)

Kagoshima, Japan (32°N) (2000-2001)
Change of ozone profiles

Winter: 2002 - (Jan-Feb)
Spring: 2005 - (April-May)

Spring (April-May)

Spring:
2001 - (March-April)
2004 - (April-May)

(a) Beijing and Xining
Winter

(b) Hong Kong
Spring

(c) Tengchong and Kunming
Lin’an

Lin’an 2001
Tengchong
Kunming
Lin’an 2004
Lin’an-red
Solid-2001
Dash-dotted-2004
Tengchong
Black-2005
Kunming
Blue-2001

Beijing-red
Solid-2005
Dash-dotted-2002
Xining-black
Solid-2005
Dash-dotted-2002

Black-2000 (n=9)
Red-2001 (n=7)
Blue-2003 (n=7)
Cyer-2004 (n=21)
Purple-2005 (n=6)
Green-average
Characteristics of ozone profiles in south and north transport pathways

Spring 2004

2004
Black-Tengchong
Red-Sanya
Blue-Hong Kong
Purple-Linan
Green-Taipei

Spring 2005

2005
Black-Altay
Red-Xining
Blue-Beijing
Purple-Longfengshan
Green-Taipei
SE Asian biomass burning and ozone enhancements over the Pacific

The seasonal distribution of the ozone enhancement cases and the vertical distribution of local ozone peaks over Hong Kong from 1993 to 1999.

Chan et al., 2001, 2003
Biomass burning activity in SE Asia

Seasonal distributions of fire hot spots

SE Asia (-10° to 30° N and 60° to 150° E).

Source: ESA
Typical transport patterns of ozone-rich air masses following the transport pathways of upper westerly wind from the fire hot spot regions in SE Asia.

L.Y. Chan et al., 2000
TRACE-P biomass burning plume
TRACE-P biomass burning plume
Feb. 22-27, 2001

- Aircraft observations during outbound trans-Pacific TRACE-P flights observed elevated levels of CO (and $O_3$)

Jacob et al., 2003
### MOPITT OBSERVATIONS OF A TRANS PACIFIC PLUME

**Total column CO**

<table>
<thead>
<tr>
<th>Date</th>
<th>MOPITT</th>
<th>GEOS-CHEM x Avgker</th>
<th>GEOS-CHEM (12 GMT)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feb 23</td>
<td><img src="image1" alt="MOPITT Feb 23" /></td>
<td><img src="image2" alt="GEOS-CHEM x Avgker Feb 23" /></td>
<td><img src="image3" alt="GEOS-CHEM (12 GMT) Feb 23" /></td>
</tr>
<tr>
<td>Feb 24</td>
<td><img src="image4" alt="MOPITT Feb 24" /></td>
<td><img src="image5" alt="GEOS-CHEM x Avgker Feb 24" /></td>
<td><img src="image6" alt="GEOS-CHEM (12 GMT) Feb 24" /></td>
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<td>Feb 25</td>
<td><img src="image7" alt="MOPITT Feb 25" /></td>
<td><img src="image8" alt="GEOS-CHEM x Avgker Feb 25" /></td>
<td><img src="image9" alt="GEOS-CHEM (12 GMT) Feb 25" /></td>
</tr>
<tr>
<td>Feb 26</td>
<td><img src="image10" alt="MOPITT Feb 26" /></td>
<td><img src="image11" alt="GEOS-CHEM x Avgker Feb 26" /></td>
<td><img src="image12" alt="GEOS-CHEM (12 GMT) Feb 26" /></td>
</tr>
<tr>
<td>Feb 27</td>
<td><img src="image13" alt="MOPITT Feb 27" /></td>
<td><img src="image14" alt="GEOS-CHEM x Avgker Feb 27" /></td>
<td><img src="image15" alt="GEOS-CHEM (12 GMT) Feb 27" /></td>
</tr>
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</table>

- **Asian pollution exported via cold front**
- **Plume encounters a blocking H Pressure System and splits**
- **Elevated CO reaches North America Southern branch at low latitudes produces O₃**
Origin: Warm Conveyor Belt over Asia

Evolution: Split by blocking high pressure
Scientific questions: Impact of Asian pollution over Pacific and N. America

- Since 1990s, Jaffe, Yienger and others suggested that the observed oxidant, trace gas and aerosol compositions increases in eastern Pacific and North America are due to transboundary transport of pollutants from Asia.

- Jacob et al. pointed out that the surface ozone increases in America are results of cross-Pacific transport of ozone of anthropogenic ozone from Asia.

- Oltmans et al. however reported that ozone increases at Mauna Loa Observatory in Pacific during springtime when transport of pollutants from Asia is more significant is insignificant. On the contrary, most apparent increases occur during the fall and winter of 1980-2000 due to large scale change in air mass flow pattern in the Pacific.
Ozone enhanced by Stratosphere-Troposphere Exchange
How to distinguish natural and anthropogenic ozone?
Chan et al., Tellus, 2003
Scientific hypothesis:

- **Natural ozone due to stratospheric-tropospheric exchange process** is one of the candidates that mix with anthropogenic ozone and pollution and being transported to the downwind Pacific and America and resulted in ozone increases there.

- **Will the recovery of stratospheric ozone layer cause increases of tropospheric ozone due to frequent STE processes? Will such natural ozone reaches surface and impacts on air quality?**

- **How to distinguish this natural ozone and to quantify this natural ozone at surface?**
New evidence and isotope mass independent fractionation method for assessing stratospheric air at surface
**FIGURE 1.14** Diagram showing that the asymmetric $C_{s}$ ozone molecule has a greater number of rotational states superimposed on its vibrational levels, resulting in greater stability in the $O_{3}^*$ intermediate.
Chemical interaction of O₃ and CO₂

- a source of mass independent fractionation of stable oxygen isotopes in CO₂

- significant sources of δ¹⁷O and δ¹⁸O in CO₂ at stratosphere and mesosphere
SOURCE OF ANOMALOUS CARBON DIOXIDE

\[ ^{18}\text{O}(1\text{D}) + \text{CO}_2 \longrightarrow \text{CO}_3^* \longrightarrow \]

\[ ^{16}\text{O}(3\text{P}) + \text{CO}_2 \]

Thus, the oxygen isotopic anomaly in carbon dioxide reflects ozone photochemical activity. Coupled to trace species measurements, this is a new, highly sensitive means to study stratospheric and mesospheric chemistry.

Also effective measure of stratosphere-troposphere mixing

M. Thiemens
New evidence from $\delta^{18}O_{\text{CO}_2}$ — contribution from stratosphere at surface

Liang et al., GRL, 2007
Relationship between $\Delta^{17}O_{CO2}$ and stratospheric air tracers ($\Delta^{17}O_{CO2} = \delta^{17}O - 0.516 \times \delta^{18}O$)

NASA - ER-2 High Altitude Airborne Science Aircraft

**Figure 3.** $\Delta^{17}O_{CO2}$ vs N$_2$O mixing ratio from the ER-2 and rocket [Thiemens et al., 1995b].

**Figure 4.** O$_3$ mixing ratios vs $\Delta^{17}O_{CO2}$ from the ER-2. (Source: Boering et al., 2004, GRL)
Can the simultaneous measurements of $\Delta^{17}\text{O} (\text{CO}_2)$, $^{35}\text{SO}_2$, $^{35}\text{SO}_4^{2-}$ and $\text{O}_3$ constrain the dynamic of STE process and its impacts?

Considering the high altitude of Tibetan Plateau (with an average of 4000m a.s.l.), it would be easier to catch the signature of STE there. Such study is being conducted in Nam Co Station (4730m a.s.l.). Results are going to come out in the following months.
Trends of tropospheric ozone and precursors
TROPOSPHERIC NO$_2$ MEASUREMENTS FROM SPACE
map the distribution of NO$_x$ emissions

OMI satellite instrument (13x24 km$^2$ resolution)

October 2004

Boersma et al. [JGR, submitted]
Recent trends of tropospheric ozone

Ozone background trend over California in spring
10-15 ppbv increase over past 20 years

Trend: 0.5-0.8 ppbv yr⁻¹

Jaffe et al. [2003]
Rising background ozone in Europe

- Hohenpeissenberg/Payerne
- Mace Head, 1987-2004, [Simmonds et al., 2004]

Naja et al. [2003]
Recent trends of ozone over Japan

Background $O_3$ over Japan is Rising

Why is Japanese $O_3$ rising?
- Emissions in Japan are almost stabilized
- Rising $NO_x$/CO/NMVOCs emissions over East Asia?

National Institute for Environmental Studies
Linan, Yangtze River Delta  

Xu et al., 2009

Taipei

Chou et al., 2006
Present background ozone is sizable increment towards violation of U.S. air quality standards.
Recent trends of ozone in China

\[ y = 1.5x + 23.5 \]

\[ R^2 = 0.7 \]

(winter monsoon period: October-April; early morning 01-05 am data)

Chan et al., OSE, 2004
Recent trends in Pearl River Delta

- Increases in NOx in China is especially significant due to growth in vehicle and traffic
- Substantial changes in hydrocarbons
Impacts of ozone increases on atmospheric environmental quality

Time series of RV, concentrations of SO$_2$ and O$_3$ in HK
## Impacts of ozone increases on atmosphere

Multiple linear regression equations of RV (%) and pollutant conc. (μg m⁻³)

<table>
<thead>
<tr>
<th>Regression Model</th>
<th>Independent Variables</th>
<th>Equation¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (Hong Kong 1993 – 2008)</td>
<td>O₃, SO₂, NOₓ, NO₂, PM₁₀</td>
<td>[RV] = 0.28 [SO₂] + 0.27 [NO₂] + 0.15 [O₃] – 15.80</td>
</tr>
<tr>
<td>2 (Macao 1999 - 2007)</td>
<td>O₃, SO₂, NO₂, PM₁₀</td>
<td>[RV] = 0.33 [PM₁₀] – 5.70</td>
</tr>
<tr>
<td>3 (Foshan 2001 - 2008)</td>
<td>SO₂, NO₂, PM₁₀</td>
<td>[RV] = 0.14 [NO₂] + 0.50 [PM₁₀] - 21.24</td>
</tr>
</tbody>
</table>

### Hong Kong

<table>
<thead>
<tr>
<th>Regression Model</th>
<th>Period</th>
<th>Independent Variables</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model 1</td>
<td>1993 – 2008</td>
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</tr>
<tr>
<td>Model 2</td>
<td>1984 – 2008</td>
<td>O₃, SO₂, NOₓ, NO₂</td>
<td>[RV] = 0.26 [SO₂] + 0.13 [NO₂] + 0.25 [O₃] – 12.21</td>
</tr>
<tr>
<td>Model 3</td>
<td>1993 – 2008</td>
<td>O₃, SO₂, NOₓ, NO₂</td>
<td>[RV] = 0.29 [SO₂] + 0.33 [NO₂] + 0.17 [O₃] – 16.87</td>
</tr>
<tr>
<td>Model 4</td>
<td>1984 – 1992</td>
<td>O₃, SO₂, NOₓ, NO₂</td>
<td>[RV] = 0.11 [NOₓ] – 0.09 [NO₂] – 1.12</td>
</tr>
</tbody>
</table>
Schematic diagram of ozone impact on sulfate formation and visibility degradation

Formation of $O_3$ + $SO_2$

Emissions of Ozone Precursors:
$NO_x$ (NO & $NO_2$), VOCs, CO, etc.

Secondary Sulfate

Impacts on Visibility, Public Health, Climate, etc.

$SO_2 (g) + OH^* + M \rightarrow HOSO_2^* + M$
$HOSO_2^* + O_2 (g) \rightarrow HO_2^* + SO_3 (g)$
$SO_3 (g) + H_2O (l) + M \rightarrow H_2SO_4 (g) + M$
$HSO_3^- (aq) + H_2O (aq) \leftrightarrow SO_2OHH^+ (aq) + H_2O (l)$
$O_3 (aq) + SO_3^{2-} (aq) \rightarrow O_2 (g) + SO_4^{2-} (aq)$

Chan et al., Air Pollution, 2011
What other impacts can be?

• ozone in the BL has a lifetime of ~ 2 weeks;
• transported of increased ozone to tropical SE Asia from east Asian coast is possible;
• what will be the impacts on air quality degradation and crop yield?