Topic 7
Atmospheric processes

Atmospheric chemistry
Air quality
Climate change
Synopsis

• Physical processes in the atmosphere – $T, p,$ transport
• Emissions of organic compounds and nitrogen oxides.
• Atmospheric chemistry: oxidation of organic compounds. Influence of NOx
• Air quality: ozone, particulate matter, nitrogen dioxide. Local, regional and hemispheric scales.
• Climate change: radiative forcing: carbon dioxide, methane, nitrous oxide, ozone, CFCs. Aerosols and clouds. Changes in albedo.
• How well do we understand atmospheric chemistry and the oxidation of organic compounds?
Structure of the atmosphere
atmospheric transport
Temperature and pressure variations in the atmosphere

Barometric equation
\[ p = p_0 \exp(-z/H_s) \]
\[ H_s = k_b T/mg \]
Atmospheric transport

• Random motion – mixing
  – Molecular diffusion is slow in the troposphere, diffusion coefficient \( D \sim 2 \times 10^{-5} \text{ m}^2 \text{ s}^{-1} \)
  – Average distance travelled in one dimension in time \( t \) is \( \sim \sqrt{2Dt} \).
  – In the troposphere, eddy diffusion is more important:
    – \( K_z \sim 20 \text{ m}^2 \text{ s}^{-1} \) Molecular diffusion more important at very high altitudes, low p. Takes ~ month for vertical mixing by eddy diffusion (~10 km). Implications for short and long-lived species.

• Directed motion
  – Advection – winds, e.g. plume from power station.
  – Occurs on
    • Local (e.g. offshore winds)
    • Regional (weather events)
    • Global (Hadley circulation)
Winds due to weather patterns

As air moves from high to low pressure on the surface of the rotating Earth, it is deflected by the Coriolis force.
Global circulation - Hadley Cells

Intertropical conversion zone (ITCZ) - rapid vertical transport near the equator.
Emissions of organic compounds and NOx
Global budgets - sources and sinks
Global budget for methane (Tg CH₄ yr⁻¹)

- **Sources:**
  - Natural: 160
  - Anthropogenic: 375
  - **Total:** 535

  **Natural Sources:**
  - wetlands, termites, oceans...

  **Anthropogenic Sources:**
  - natural gas, coal mines, enteric fermentation, rice paddies,

- **Sinks:**
  - Trop. Oxidation by OH: 445
  - Transfer to stratosphere: 40
  - Uptake by soils: 30
  - **Total:** 515

  These rates are very uncertain
HISTORICAL TRENDS IN METHANE

Historical methane trend

Recent methane trend
# Global Budget of CO

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<th>Sources</th>
<th>Range of estimates (Tg CO yr(^{-1}))</th>
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<td>Fossil fuel combustion/industry</td>
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<td>Oxidation of other hydrocarbons</td>
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<td>Soil uptake</td>
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Emissions of non methane volatile organic compounds (VOCs)

**Anthropogenic:**
- fuel production and distribution 17; fuel consumption 49; road transport 36; chemical industry 2; solvents 20; waste burning 8, other 10. Total 142 Tg yr\(^{-1}\)

**Biogenic:**
- isoprene 503; monoterpenes 127; other reactive VOCs 260, unreactive VOCs 260; Total 1150 Tg yr\(^{-1}\)
Removal of organic compounds from the atmosphere by reaction with OH

- Atmospheric lifetime = $1/\{k[\text{OH}]\} = 1/\{1\times10^6k\}$ s. What does it mean?
- Rate coefficients at 298 K/10^{-12} cm^3 molecule^{-1} s^{-1}
  - CH₄: 7x10^{-3}; CO: 0.24; isoprene: 110; ethane: 0.25
- Approximate lifetimes for OH = 1 x 10^6 molecule cm^{-3}
  - CH₄: 5 yr; CO: 7 weeks; isoprene: 3 h; ethane: 7 weeks
- Atmospheric distribution depends on lifetime. NH is major source of anthropogenic pollutants. CH₄ is distributed globally with only a slight NH/SH difference. Isoprene is found only close to its (very extensive) sources.
- The *oxidising capacity* of the atmosphere refers to its capacity to remove VOCs and depends on [OH] (and the concentrations of other oxidants - O₃, NO₃)
GLOBAL DISTRIBUTION OF METHANE

NOAA/CMDL surface air measurements

- Seasonal dependence - higher in winter than summer (maximum in NH correlates with minimum in SH).
- NH concentrations > SH - main sources are in NH; slow transport across ITCZ.
Atmospheric oxidation of organic compounds
THE OH RADICAL: MAIN TROPOSPHERIC OXIDANT

What are its main global sources and sinks?

Primary source:

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

\[ \text{O}^{(1D)} + \text{M} \rightarrow \text{O} + \text{M} \]  \hspace{1cm} (2)

\[ \text{O}^{(1D)} + \text{H}_2\text{O} \rightarrow 2\text{OH} \]  \hspace{1cm} (3)

Sink: oxidation of reduced species

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

\[ \text{CH}_4 + \text{OH} \rightarrow \text{CH}_3 + \text{H}_2\text{O} \]

**GLOBAL MEAN [OH] \sim 1.0 \times 10^6 \text{ molecules cm}^{-3}**
Methane oxidation. (Effectively a very short radical chain)

Initiation by OH formation from ozone photolysis

Propagation:

\[
\begin{align*}
CH_4 + OH \ ( +O_2 ) & \rightarrow CH_3O_2 + H_2O \quad *** \\
CH_3O_2 + NO & \rightarrow CH_3O + NO_2 \\
CH_3O + O_2 & \rightarrow HO_2 + HCHO \\
HO_2 + NO & \rightarrow OH + NO_2
\end{align*}
\]

Secondary radical formation

\[
\begin{align*}
HCHO + OH \ ( +O_2 ) & \rightarrow HO_2 + CO + H_2O \\
HCHO + h\nu & \rightarrow H_2 + CO \\
HCHO + h\nu \ ( +2O_2 ) & \rightarrow 2HO_2 + CO
\end{align*}
\]

Termination

\[
\begin{align*}
OH + NO_2 & \rightarrow HNO_3 \\
HO_2 + HO_2 & \rightarrow H_2O_2 + O_2 \\
CH_3O_2 + HO_2 & \rightarrow CH_3OOH + O_2
\end{align*}
\]

**** \( k(CH_3 + O_2) \sim 10^{-12} \text{ cm}^3\text{molecule}^{-1} \text{ s}^{-1} \)
General oxidation scheme for VOCs

\[ O_3 + h\nu \rightarrow O_1^D + O_2 \]
\[ O_1^D + H_2O \rightarrow 2OH \]
\[ OH + RH (+O_2) \rightarrow RO_2 + H_2O \]
\[ RO_2 + NO \rightarrow NO_2 + RO \]
\[ RO \rightarrow HO_2 (+R'CHO) \]
\[ HO_2 + NO \rightarrow OH + NO_2 \]

\[ NO_2 + h\nu \rightarrow NO + O; O + O_2 \rightarrow O_3 \]

Secondary chemistry from R’CHO photolysis
 Termination as before - NB the termination route depends on the NO\textsubscript{x}: VOC ratio

**OVERALL**

\[ NO_x + VOC + sunlight \rightarrow \text{ozone} \]

The same reactions can also lead to formation of secondary organic aerosol (SOA)
Free radical propagated oxidation cycle

Chain reaction:
- Radical initiation, e.g. OH production from $O_3$
- Propagation
- Termination: $OH + NO_2$
  $HO_2/RO_2 + HO2/RO2$

Dependence on:
- $NO_x$
- VOC
- Light

VOC

$O_3 + h\nu \rightarrow O^{1}D + O_2$
$O^{1}D + H_2O \rightarrow 2OH$
$O^{1}D + N_2, O_2 \rightarrow O^{3}P$
$O^{3}P + O_2 \rightarrow O_3$

$NO_2 + h\nu \rightarrow NO + O$
$O + O_2 (+M) \rightarrow O_3 (+M)$

Ozone formation from conversion of NO to NO$_2$
Other oxidising species / initiators of VOC oxidation

\[ \text{NO}_3 \]

\[ \text{NO}_2 + O_3 \rightarrow \text{NO}_3 + O_2 \]
\[ \text{NO}_2 + \text{NO}_3 + M \rightarrow \text{N}_2\text{O}_5 \]

\( \text{NO}_3 \) is rapidly lost in the day by photolysis and reaction with NO (\( \rightarrow \text{NO}_2 \)), so that its daytime concentration is low. It is an important night time oxidant. It adds to alkenes to form nitroalkyl radicals which form peroxy radicals in the usual way and also abstracts H from the higher alkanes, aldehydes etc.

\[ \text{O}_3 \]

Ozone reacts with alkenes to form a carbonyl + an energised Criegee biradical. The latter can be stabilised or decompose. One important reaction product is OH: \( \text{O}_3 \) reactions with alkenes can act as a source of OH, even at night.

\textbf{Photolysis}
Why should we worry about ground level ozone?

• The human health impacts of ozone derive from its irritant properties and its induction of an inflammatory response in the lung.

• It is not clear whether or not it has a threshold for causing health effects.

• The WHO guideline is 50 ppb, measured as the daily maximum of a running 8-hour mean ozone concentration. The European Union (EU) - less stringent target of a daily maximum of a running 8-hour mean of 60 ppb, not to be exceeded more than 25 times a year, averaged over three years. from 31st December 2010. The US has just introduced an objective value of 75 ppb.

• Concentrations are highest during summer episodes, but exceedances of AQ objectives can occur throughout the year. (See discussion on NH background ozone)

• Ozone also has adverse effects on crop yields, on tree growth and on the composition of natural plant communities and on materials.
Global budget for tropospheric NOx: Formation and coupling

- NOx is central to tropospheric ozone formation. What are its global sources and sinks?

- **Global sources (Tg N yr$^{-1}$):**

  Fossil fuel combustion  21;  Biomass burning:  12
  Soils  6  Lightning  3
  Ammonia oxidation  3  Aircraft  0.5
  Transport from stratosphere  0.1

- **Coupling (rapid - ~ 1 minute in the day)**

  \[
  \text{NO} + O_3 \rightarrow NO_2 + O_2 \\
  NO_2 + \text{Light} \rightarrow NO + O; O + O_2 + M \rightarrow O_3 + M
  \]

  Also  \[
  \text{HO}_2 + \text{NO} \rightarrow NO_2 + OH
  \]
Global budget for tropospheric NOx: Loss and coupling

- **Loss**

  \[ \text{OH} + \text{NO}_2 + \text{M} \rightarrow \text{HNO}_3 + \text{M} \]

  Rainout of HNO3.

  Conversion into other forms of oxidised nitrogen, e.g. organic nitrates

- Lifetime of NO\(_x\) is about 1 day. NO\(_x\) is a key component in ozone formation. It is emitted mainly from anthropogenic sources, in populated regions. Can it be transported to regions where it is not strongly emitted?
PEROXYACETYLNITRATE (PAN) AS RESERVOIR FOR LONG-RANGE TRANSPORT OF NO\textsubscript{x}

\[ \text{PAN} = \text{CH}_3\text{C(\text{O})O}_2\text{NO}_2 \]
Reductions in NOx emissions from industrial combustion plant in Europe
Sector sources of NOx and their reductions in the UK

Recent road transport data for the UK.
Links between policy actions for $O_3$ reduction and chemical mechanisms

- **Initiation**: OH formed from ozone photolysis at a rate $P_{OH} (= 2k_3[H_2O]J_1[O_3]/\{k_2[M] + k_3[H_2O]\})$

- **Propagation**

  \[
  \begin{align*}
  \text{OH} + \text{RH} (+\text{O}_2) & \rightarrow \text{RO}_2 + \text{H}_2\text{O} \quad \text{(R4)} \\
  \text{RO}_2 + \text{NO} & \rightarrow \text{RO} + \text{NO}_2 \quad \text{(R5)} \\
  \text{RO} + \text{O}_2 & \rightarrow \text{R'}\text{CHO} + \text{HO}_2 \quad \text{(R6)} \\
  \text{HO}_2 + \text{NO} & \rightarrow \text{OH} + \text{NO}_2 \quad \text{(R7)} \\
  
  \end{align*}
  \]

- **Termination**

  \[
  \begin{align*}
  \text{HO}_2 + \text{HO}_2 & \rightarrow \text{H}_2\text{O}_2 \quad \text{(R8)} \\
  \text{OH} + \text{NO}_2 + \text{M} & \rightarrow \text{HNO}_3 + \text{M} \quad \text{(R9)} \\
  
  \end{align*}
  \]

- **Ozone formation**

  $O_3$ is formed by NO$_2$ photolysis with a rate equal to the sum of the rates of reactions 5 and 7 ($= v_5 + v_7$)
NOx and VOC control of ozone formation

- Under polluted conditions, chain propagation is fast, so $v_4 = v_5 = v_6 = v_7$
- $P_{O3} = v_5 + v_7 = 2v_7 = 2k_7[HO_2][NO]$  \( A \)
- Also $v_4 = v_7$ \( \therefore [OH] = k_7[HO_2][NO]/\{k_4[RH]\} \)  \( B \)
- Steady state for radicals: rate of termination = rate of initiation, ie $P_{OH} = v_8 + v_9$

1. **Low NOx:** $v_8 \gg v_9$  
   $P_{OH} = 2k_8[HO_2]^2$;  
   $[HO_2] = \sqrt{\frac{P_{OH}}{2k_8}}$
   Sub in A: $P_{O3} = 2k_7[NO] \sqrt{\frac{P_{OH}}{2k_8}}$.  
   $P_{O3} \propto [NO]$, independent $[RH]$  \( \text{NOx limited} \)

2. **High NOx:** $v_8 \ll v_9$  
   $[OH] = P_{OH}/(k_9[NO_2][M])$
   Sub in B: $[HO_2] = P_{OH}k_4[RH]/\{k_7k_9[NO][NO_2][M]\}$
   Sub in A: $P_{O3} = 2k_4[RH]/\{k_9[NO_2][M]\}$
   $P_{O3} \propto [NO_2]^{-1}; [RH]$  \( \text{VOC limited} \)
DEPENDENCE OF OZONE PRODUCTION ON NO\(_x\) AND HYDROCARBONS

\[ P(O_3) = \frac{2k_4 P_{HOx} [RH]}{k_9 [NO_2] [M]} \]

“NOx- saturated” or “VOC-limited” regime

\[ P(O_3) = 2k_7 \left( \frac{P_{HOx}}{k_8} \right)^{1/2} [NO] \]

“NOx-limited” regime
OZONE CONCENTRATIONS vs. NO\textsubscript{x} AND VOC EMISSIONS

Air pollution model calculation for a typical urban airshed

**Ozone isopleths**
Global budget for ozone (Tg O₃ yr⁻¹)

- **Chemical production**
  - $\text{HO}_2 + \text{NO}$
  - $\text{CH}_3\text{O}_2 + \text{NO}$
  - $\text{RO}_2 + \text{NO}$
  - 3000 – 4600
  - 70%
  - 20%
  - 10%

- **Transport from stratosphere**
  - 400 – 1100

- **Chemical loss**
  - $\text{O}^1\text{D} + \text{H}_2\text{O}$
  - $\text{HO}_2 + \text{O}_3$
  - $\text{OH} + \text{O}_3$
  - others
  - 3000 – 4200
  - 40%
  - 40%
  - 10%
  - 10%

- **Dry deposition**
  - 500 – 1500
Global budget of ozone

**Stratosphere**

**Troposphere**

**Stratosphere/Troposphere Exchange** 540 Tg y⁻¹

**Chemical Production** 4500 Tg y⁻¹

**Chemical Loss** 4100 Tg y⁻¹

**Emissions**

- NMHCs, CO, CH₄
- Sunlight
- NO
- NO₂
- OH

**Deposition** 1000 Tg y⁻¹

**OH**

**HO₂, RO₂**

**CO, O₃**

**H₂O, OH**

**Tropopause ~8-15 km**
Geographical determinants of ozone in W. Europe
What is happening to background ozone - a selection of results

- Ozone in range 5 - 16 ppb, Montsouris Observatory in Paris 1876 - 1910
- $O_3$ at Arosa, Switzerland, during the 1950s give mixing ratios of ~18 ppb with doubling over next 30 years.
- Ozone sondes (26 - 59 N). Increase in 1970s; no clear trend 1980 to 1996
- Ozone sonde at Hohenpeissenberg (alpine location in southern Germany; 1966 - present day). mid-troposphere layer - large increases 1960s - 1980s; with smaller increases and even declines thereafter
- Surface ozone, 17 background stations up to mid-1990s - no clear and consistent trend even in northern latitudes
- Background ozone has increased by up to 5 ppb per decade over the last 20 to 30 years, according to measurements at sea level and on mountain tops that are less influenced by European sources
Annual mean ozone at Mace Head, Western Ireland (screened)

Figure 3.3 Annual mean background ozone concentrations for filtered air masses at Mace Head, Ireland, as determined by Derwent et al. (2007a).
What is happening in the US?

(i) Trends in ozone at Trinidad Head vs altitude 1998-2007
(ii) Monthly average daytime ozone mixing ratios, Trinidad Head, 2002 - 2007 vs earlier analyses which suggest increasing background ozone
Background ozone is primarily determined by NOx, CH₄ and CO concentrations, which provide the best policy opportunity for control.

Next slide:
IIASA: Planned global legislation for road vehicles
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<tr>
<td>Taipei, China US Tier 1</td>
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<td>US Tier 1</td>
<td>US Tier 2 for diesel</td>
<td>Euro 3</td>
<td>Euro 4</td>
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<tr>
<td>Thailand Euro 1</td>
<td></td>
<td>Euro 1</td>
<td>Euro 2</td>
<td>Euro 3</td>
<td>Euro 4</td>
<td></td>
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<tr>
<td>Viet Nam</td>
<td></td>
<td>Euro 1</td>
<td>Euro 2</td>
<td>Euro 3</td>
<td>Euro 4</td>
<td></td>
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</tbody>
</table>

Notes:
- Italics – under discussion
- a – gasoline
- b – diesel
- c – Entire country
- d – Delhi, Chennai, Mumbai, Kolkata, Bangalore, Hyderabad, Agra, Surat, Pune, Kanpur, Ahmedabad, Sholapur, Lucknow; Other cities in India are in Euro 2
- e – Beijing and Guangzhou (as of 01 September 2006) have adopted Euro 3 standards; Shanghai has requested the approval of the State Council for implementation of Euro 3
- f – Euro 4 for gasoline vehicles and California ULEV standards for diesel vehicles
- g – Gasoline vehicles under consideration
Revised NOx and CO emissions projections (contrast IPCC 4th Assessment Report)
$\text{CH}_4$ emissions projections - little change from IPCC 4AR

This work: range A2-B1
This work B2
Original IPCC SRES B2

Europe
Former Soviet Union
North America
Asia
Rest of world
World total
Original SRES B2
Regional Air Quality
World Health Organisation, Air Quality Guidelines, 2005 (apply world-wide)

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>8-hour mean</th>
<th>Annual mean</th>
<th>24-hour mean</th>
<th>1-hour mean</th>
<th>10-minute mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ozone ($O_3$)</td>
<td>100 µg/m³</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PM$_{2.5}$</td>
<td>10 µg/m³</td>
<td>-</td>
<td>25 µg/m³</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PM$_{10}$</td>
<td>20 µg/m³</td>
<td>-</td>
<td>50 µg/m³</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>NO$_2$</td>
<td>40 µg/m³</td>
<td>-</td>
<td>-</td>
<td>200 µg/m³</td>
<td>-</td>
</tr>
<tr>
<td>SO$_2$</td>
<td>20 µg/m³</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>500 µg/m³</td>
</tr>
</tbody>
</table>

- The WHO Air quality guidelines represent the most widely agreed and up-to-date assessment of health effects of air pollution, recommending targets for air quality at which the health risks are significantly reduced. The Guidelines indicate that by reducing particulate matter (PM10) pollution from 70 to 20 micrograms per cubic metre, we can cut air quality related deaths by around 15%.
Air Quality Standards in the US
http://www.epa.gov/air/criteria.html

National Ambient Air Quality Standards (NAAQS)

The Clean Air Act, which was last amended in 1990, requires EPA to set National Ambient Air Quality Standards (40 CFR part 50) for pollutants considered harmful to public health and the environment. The Clean Air Act identifies two types of national ambient air quality standards. Primary standards provide public health protection, including protecting the health of "sensitive" populations such as asthmatics, children, and the elderly. Secondary standards provide public welfare protection, including protection against decreased visibility and damage to animals, crops, vegetation, and buildings.

EPA has set National Ambient Air Quality Standards for six principal pollutants, which are called "criteria" pollutants. They are listed below. Units of measure for the standards are parts per million (ppm) by volume, parts per billion (ppb) by volume, and micrograms per cubic meter of air (µg/m³).

### Pollutant

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Primary/Secondary</th>
<th>Averaging Time</th>
<th>Level</th>
<th>Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon Monoxide</td>
<td>primary</td>
<td>8-hour</td>
<td>9 ppm</td>
<td>Not to be exceeded more than one per year</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1-hour</td>
<td>15 ppm</td>
<td></td>
</tr>
<tr>
<td>Lead</td>
<td>primary and secondary</td>
<td>Rolling 3 month average</td>
<td>0.15 µg/m³</td>
<td>Not to be exceeded</td>
</tr>
<tr>
<td>Nitrogen Dioxide</td>
<td>primary</td>
<td>1-hour</td>
<td>100 ppb</td>
<td>98th percentile, averaged over 3 years</td>
</tr>
<tr>
<td></td>
<td>primary and secondary</td>
<td>Annual</td>
<td>53 ppb</td>
<td>Annual Mean</td>
</tr>
<tr>
<td>Ozone</td>
<td>primary and secondary</td>
<td>8-hour</td>
<td>0.075 ppm</td>
<td>Annual fourth-highest daily maximum 8-hr concentration, averaged over 3 years</td>
</tr>
<tr>
<td></td>
<td></td>
<td>annual</td>
<td>12 µg/m³</td>
<td>annual mean, averaged over 3 years</td>
</tr>
<tr>
<td></td>
<td></td>
<td>secondary</td>
<td>15 µg/m³</td>
<td>averaged over 3 years</td>
</tr>
<tr>
<td></td>
<td></td>
<td>24-hour</td>
<td>35 µg/m³</td>
<td>98th percentile, averaged over 3 years</td>
</tr>
<tr>
<td>Sulfur Dioxide</td>
<td>primary</td>
<td>1-hour</td>
<td>75 ppb</td>
<td>99th percentile of 1-hour daily maximum concentrations, averaged over 2 years</td>
</tr>
<tr>
<td></td>
<td>secondary</td>
<td>3-hour</td>
<td>0.5 ppm</td>
<td>Not to be exceeded more than one per year</td>
</tr>
</tbody>
</table>

as of October 2011

(1) Final rule signed October 15, 2008. The 1978 lead standard (1.5 µg/m³ as a quarterly average) remains in effect until one year after an area is designated for the 2008 standard, except that in areas designated nonattainment for the 1978, the 1978 standard remains in effect until implementation plans to attain or maintain the 2008 standard are approved.

(2) The official level of the annual SO2 standard is 0.033 ppm, equal to 33 ppb, which is shown here for the purpose of clearer comparison to the 1-hour standard.

(3) Final rule signed March 12, 2008. The 1997 ozone standard (0.08 ppm, annual fourth-highest daily maximum 8-hour concentration, averaged over 3 years) and related implementation rules remain in place. In 1997, EPA revoked the 1-hour ozone standard (0.12 ppm, not to be exceeded more than once per year) in all areas, although some areas have continued obligations under that standard ("anti-backsliding"). The 1-hour ozone standard is attained when the expected number of days per calendar year with maximum hourly average concentrations above 0.12 ppm is less than or equal to 1.

(4) Final rule signed June 2, 2010. The 1971 annual and 24-hour SO2 standards were revoked in that same rulemaking. However, these standards remain in effect until one year after an area is designated for the 2010 standard, except in areas designated nonattainment for the 1971 standards, where the 1971 standards remain in effect until implementation plans to attain or maintain the 2010 standard are approved.

See historical tables of NAAQS standards

- Carbon Monoxide
- Lead
- Nitrogen Dioxide
Use of satellite measurements of HCHO columns to infer emissions and sources of non-methane VOCs (NMVOCs) in China and to assess the impact on ozone formation.

Fu et al, J Geophys Res 2007, 112, D06312
Relating HCHO Columns to VOC Emissions (Palmer)

\[ E_{\text{ISOP}} = \frac{k_{\text{HCHO}} \Omega_{\text{HCHO}}}{k_{\text{ISOP}} \text{Yield}_{\text{ISOP} \rightarrow \text{HCHO}}} \]

Distance downwind

100 km

VOC source

Isoprene
\(~0.5\) 2-3 hrs

\(\alpha\)-pinene
\(~0.3\) 3-4 days

\(\beta\) pinene
\(~0.25\) 3-4 days

MBO
\(~0.4\) 3-4 days

Ultimate Yield \(Y\) (per C)  Approx. Time to \(Y\)
BIOGENIC ISOPRENE IS THE MAIN SOURCE OF HCHO IN U.S. IN SUMMER

GOME footprint
320X40 km$^2$

GEIA isoprene emissions

GEOS-CHEM HCHO

GOME HCHO

HCHO columns – July 1996

[10$^{12}$ atoms C cm$^{-2}$ s$^{-1}$]

[10$^{16}$ molec cm$^{-2}$]
Annual mean reactive NMVOC emissions from east and south Asia.  
(top) Bottom-up inventories  
(bottom) Emissions inferred from GOME HCHO on the basis of the regression analysis  
Colour scale at the left indicates anthropogenic and biomass burning, and the color scale on the right indicates biogenic and total sources.
Satellite hot spot counts (ATSR = Along track scanning radiometer)

Evidence for large agricultural biomass burning in the North China Plain in June.

(a) ATSR hot spots over China for May-July 1997;
(b) ATSR monthly hot spot counts time series over the North China Plain (yellow box) for 1997-2003;
(c) spatial extent and timing of winter wheat harvest in China, based on data from Ministry of Agriculture of China [2007].
Monthly mean afternoon (1300 to 1700 LT) surface ozone concentrations simulated by a global model (GEOS-Chem) using bottom-up inventories for NMVOCs) in (a) March, (b) June, (c) September, and (d) December 2001.

Difference in modeled monthly mean afternoon (1300 to 1700 LT) surface ozone concentrations using GOME-inferred reactive NMVOC emission versus the bottom-up inventories for (a) March, (b) June, (c) September, and (d) December 2001.
Particulate matter
PM10 and PM2.5
World Bank data: most polluted cities as measured by particulate matter concentration

Most Polluted World Cities by PM\textsuperscript{[33]}

<table>
<thead>
<tr>
<th>Particulate matter, μg/m\textsuperscript{3} (2004 and 2011)</th>
<th>City</th>
</tr>
</thead>
<tbody>
<tr>
<td>508</td>
<td>Skopje, Macedonia</td>
</tr>
<tr>
<td>279</td>
<td>Korfu, Greece</td>
</tr>
<tr>
<td>169</td>
<td>Cairo, Egypt</td>
</tr>
<tr>
<td>150</td>
<td>Delhi, India</td>
</tr>
<tr>
<td>128</td>
<td>Kolkata, India (Calcutta)</td>
</tr>
<tr>
<td>125</td>
<td>Tianjin, China</td>
</tr>
<tr>
<td>123</td>
<td>Chongqing, China</td>
</tr>
<tr>
<td>109</td>
<td>Kanpur, India</td>
</tr>
<tr>
<td>109</td>
<td>Lucknow, India</td>
</tr>
<tr>
<td>104</td>
<td>Jakarta, Indonesia</td>
</tr>
<tr>
<td>101</td>
<td>Shenyang, China</td>
</tr>
</tbody>
</table>


Reminder: WHO AQ guidelines
PM\textsubscript{2.5} 10 μg/m\textsuperscript{3} annual mean; 25 μg/m\textsuperscript{3} 24-hour mean
PM\textsubscript{10} 20 μg/m\textsuperscript{3} annual mean; 50 μg/m\textsuperscript{3} 24-hour mean
Analysis of PM$_{10}$ from 196 sites in UK in 2003

AQEG report on Particulate Matter:

While PM$_{10}$ is higher at roadside sites, it is clear that there are regional contributions, that come, at least in part, from secondary PM.
Schematic illustration of relative contributions to PM concentrations in $\mu g \, m^{-3}$ for road side sites in an east-west row of grid squares (right to left) across London (based on estimates for 1996).
Functionalization reduces volatility, fragmentation can generate more-volatile species - less likely to partition to the OA. Branching ratio ($\beta$) between these pathways is critical.
NO$_2$ over China observed by satellite

SCIAMACHY tropospheric NO$_2$ vertical columns averaged between December 2003 and November 2004 for selected industrial regions


Region 6 is that referred to as 'East Central China'
The mean annual NO$_2$ column amount normalized to that in 1996 for the geographical regions USA, Central East Coast USA, Western Europe, Poland, Japan, East Central China, and Hong Kong, which are defined in Fig. 2. The error bars represent the estimated uncertainty (s.d.) for an individual year, the values over China being larger as a result of the poorer knowledge and therefore larger uncertainty of the aerosol loading and its changes.
Satellite measurements of NO$_2$ over East Central China

A plot of the monthly mean of the three-day composite of the tropospheric NO$_2$ vertical column versus time is presented for the area defined by latitudes 30° N to 40° N and longitudes 110° E to 123° E. Both GOME data (open symbols) and SCIAMACHY measurements (filled symbols) are shown. SCIAMACHY nadir measurements started in August 2002, but limited data are available prior to 2003. Shaded areas represent the standard deviation estimated for the monthly mean three-day composite, and take into account the variability of the measurements resulting from changes in NO$_2$ and data gaps arising from cloud cover and any missing observations.
Climate change and chemistry
Radiative Forcing

- **Radiative forcing**: the change in the net radiation balance at the tropopause caused by a particular external factor in the absence of any climate feedbacks.

- These forcing mechanisms can be caused by:
  - change in the atmospheric constituents such as the increase in greenhouse gases (GHGs)
  - aerosols due to anthropogenic activity,
  - changes in other components of the Earth/atmosphere system such as changes in the surface albedo (the fraction of incoming radiation that is reflected). Albedo changes are caused, e.g., by changes in vegetation (e.g. burn scars or agriculture).
Mechanisms of the radiative forcing due to greenhouse gases and of the direct radiative forcings due to aerosols
Global-average radiative forcing (RF) estimates and ranges in 2005 (relative to 1750) for anthropogenic GHGs and other important agents and mechanisms.
Carbon dioxide and methane mixing ratios versus time (NOAA Climate Monitoring and Diagnostics Laboratory http://www.cmdl.noaa.gov/ccgg/insitu.html)
Other GHGs

- **N₂O** mixing ratios show an increase from a pre-industrial value of around 270 ppb (Prather et al., 2001) to 318 – 319 ppb in early 2004.

- **CFC-11, CFC-12, CFC-13, HCFC-22, and CCl₄** concentrations increased from a pre-industrial value of zero to 268 ppt, 533 ppt, 4 ppt, 132 ppt, and 102 ppt respectively (1998 concentrations) - leads to radiative forcings of 0.07 W m⁻², 0.17 W m⁻², 0.03 W m⁻², 0.03 W m⁻² and 0.01 W m⁻².

- **Ozone**: approximate doubling of concentrations between the pre-industrial and present day.
Schematic description of an ocean atmosphere general circulation model
Evolution of models

Off-line model development

Strengthening colours denote improvements in models
Carbon cycle

Diagram showing the carbon cycle with processes such as vegetation, fire, soil, fossil fuel, surface water, and deep water. The diagram also includes a legend for the speed of exchange processes: very fast (less than 1 year), fast (1 to 10 years), slow (10 to 100 years), very slow (more than 100 years).
Processes in an atmospheric chemistry model

Gas-phase chemistry:
- $\text{NO}_2 + \text{hv} (+\text{O}_2) \rightarrow \text{O}_3$
- $\text{O}_3 + \text{NO} \rightarrow \text{NO}_2 + \text{O}_2$
- $\text{HO} + \text{NO}_2 \rightarrow \text{HNO}_3$

Meteorological transport

Emissions
- $\text{NO}_x$
- Hydrocarbons

Cloud processes:
- Aqueous chemistry: $\text{H}_2\text{O}_2 + \text{SO}_2 \rightarrow \text{H}_2\text{SO}_4$

Transport

Wet deposition

Dry deposition

Environment

Biogenic compounds
Predicted global temperature rise for different scenarios
Surface O3 (ppbv) 1990s

IIASA_BAU 1990s Surface O$_3$/ppbv
Change in surface O3, CLE 2020s-1990s
No climate change

IIASA CLE 2020s-1990s Surface O₃/ppbv

+2 to 4 ppbv over N. Atlantic/Pacific
A large fraction is due to ship NOx

>+10 ppbv India
**ΔO₃ from climate change**

**2020s CLEcc-2020s CLE**

Warmer temperatures & higher humidities increase O₃ destruction over the oceans.

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

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

\[
\text{O}^{1} \text{D} + \text{N}_2, \text{O}_2 \rightarrow \text{O}^{3}\text{P}
\]

But also a role from increases in isoprene emissions from vegetation & changes in lightning NOx.

\[
\text{OH} + \text{RH}(+\text{O}_2) \rightarrow \text{RO}_2 + \text{H}_2\text{O}
\]

\[
\text{RO}_2 + \text{NO} \rightarrow \text{RO} + \text{NO}_2
\]

\[
\text{NO}_2 + h\nu(+\text{O}_2) \rightarrow \text{NO} + \text{O}_3
\]
Atmospheric oxidation of methane

---

- **CH4 removed mainly by reaction with OH**
- **Yield of OH and loss of O3 depends on humidity**

- **Low NOx route**: Ozone destruction (background atmos)
- **High NOx route**: Ozone formation (polluted atmos)

---

**Reaction Equations**:

- \( O_1^D + H_2O \rightarrow 2OH \)
- \( O_1^D + N_2O_2 \rightarrow O_3\)
PAN is a reservoir compound for nitrogen oxides and provides a mechanism for their transport, especially in the upper troposphere. It provides a means of carrying nitrogen oxides from polluted to less polluted regions. It is a major player in the intercontinental transport of pollutants.
Emission of biomass smoke from Portugal in August 2003: effects on local albedo
Chemical mechanisms and their evaluation
General description of a chemical mechanism

**Initiation reactions**
- **Photolysis**
  - carbonyls, ROOH, RC(O)OOH and RONO₂

**Reactions of intermediates**
- **OXY: RO**
  - O₂ reaction
  - decomposition
  - isomerisation

- **PEROXY: RO₂**
  - NO, NO₇, NO₃, HO₂, RO₂

**NO₃ reaction**
- alkenes, dienes, aldehydes and ethers

**O₃ reaction**
- alkenes, dienes, and unsaturated oxygenated products

**Excited Criegee [RC(OO)R']⁺**
- stabilisation
- decomposition

**Oxygenated products**
- carbonyls, ROOH, ROH, RC(O)OOH, RC(O)OH, RONO₂, PANs, multifunctional and CO

**Stabilised Criegee RC(OO)R'**
- reaction with H₂O, NO, NO₂, CO and SO₂
The Master Chemical Mechanism

VERSION 3.2  What's new?

MCMv3.1 Archive site

Welcome to the MCM website

The Master Chemical Mechanism (MCM) is a near-explicit chemical mechanism which describes the detailed gas-phase chemical processes involved in the tropospheric degradation of a series of primary emitted volatile organic compounds (VOCs). Currently, the degradation of methane and 142 non-methane VOCs is represented.
1st page of isoprene mechanism

\[ \text{NO}_3 + \text{C}_5\text{H}_8 \rightarrow 3.15 \times 10^{-12} \exp(-450/\text{TEMP}) \rightarrow \text{NISOPO}_2 \]

\[ \text{O}_3 + \text{C}_5\text{H}_8 \rightarrow 1.03 \times 10^{-14} \exp(-1995/\text{TEMP}) \times 0.3 \rightarrow \text{CH}_2\text{OO}_2 \text{E} + \text{MACR} \]

\[ \text{O}_3 + \text{C}_5\text{H}_8 \rightarrow 1.03 \times 10^{-14} \exp(-1995/\text{TEMP}) \times 0.2 \rightarrow \text{CH}_2\text{OO}_2 \text{E} + \text{MVK} \]
Mechanism subset for marked species

Each product species is linked to the point in the subset where that species reacts. Select "Goto MCM" next to the first occurrence of each reactant to browse the MCM from that point.

<table>
<thead>
<tr>
<th>Goto MCM</th>
<th>Reaction</th>
<th>Rate Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO3 + C5H8 → NISOPQ2</td>
<td>3.15D-12*EXP(-450/TEMP)</td>
<td></td>
</tr>
<tr>
<td>O3 + C5H8 → CH2OQE + MACR</td>
<td>1.03D-14*EXP(-1995/TEMP)*0.3</td>
<td></td>
</tr>
<tr>
<td>O3 + C5H8 → CH2OQE + MVK</td>
<td>1.03D-14*EXP(-1995/TEMP)*0.2</td>
<td></td>
</tr>
<tr>
<td>O3 + C5H8 → HCHO + MACROOA</td>
<td>1.03D-14*EXP(-1995/TEMP)*0.3</td>
<td></td>
</tr>
<tr>
<td>O3 + C5H8 → HCHO + NVKOOA</td>
<td>1.03D-14*EXP(-1995/TEMP)*0.2</td>
<td></td>
</tr>
<tr>
<td>OH + C5H8 → ISOPAO2</td>
<td>2.7D-11*EXP(390/TEMP)*0.148</td>
<td></td>
</tr>
<tr>
<td>OH + C5H8 → ISOPBO2</td>
<td>2.7D-11*EXP(390/TEMP)*0.444</td>
<td></td>
</tr>
<tr>
<td>OH + C5H8 → ISOPCO2</td>
<td>2.7D-11*EXP(390/TEMP)*0.102</td>
<td></td>
</tr>
<tr>
<td>OH + C5H8 → ISOPDO2</td>
<td>2.7D-11*EXP(390/TEMP)*0.306</td>
<td></td>
</tr>
<tr>
<td>NISOPQ2 + HO2 → NISOPQOH</td>
<td>KRO2HO2*0.706</td>
<td></td>
</tr>
<tr>
<td>NISOPQ2 + NO → NISOPNO3</td>
<td>KRO2NO*0.052</td>
<td></td>
</tr>
<tr>
<td>NISOPQ2 + NO → NISOPQ + NO2</td>
<td>KRO2NO*0.948</td>
<td></td>
</tr>
</tbody>
</table>
Atmospheric chambers and their application in mechanism evaluation
Large outdoor chamber
Valencia, Spain 200m³
Photochemical Reactor

Volume: 200 m³
Surface material: 127 µm Teflon film, transparent to sunlight
Ground: temperature controlled aluminum plates covered with teflon
Wind protection: automatic closing cover

Optical path for DOAS (1152 m)
Optical path for FTIR (634 m)
SAPHIR chamber Juelich, Germany
Cooling coils – T down to 230 K
Variable pressure 10 - 1000 Torr

Highly intrumented reactor for Atmospheric Chemistry (HIRAC)

FAGE Laser induced fluorescence for detection of OH, HO₂

GC for hydrocarbons, oxygenates ...

NO, NO₂, O₃, CO detectors

ATMOSPHERIC CHEMISTRY AND PHYSICS 7 (20): 5371-5390 2007
Statistical and uncertainty analyses of chamber measurements and models

Comparison of ethene measurements and simulations

$2\sigma$ measurement uncertainty (grey bands)

$2\sigma$ uncertainties from Monte-Carlo simulations (error bars) J. Zador, et al., Atmospheric Environment, 2005, 39, 2805-2817
Model measurement comparisons and uncertainties

O₃ [ppb] vs. Time [h]

HCHO [ppb] vs. Time [h]
Uncertainty contributions, ethene, low and high NOx
Toluene Oxidation Routes in MCMv3.2

Little ring opening along phenol route
Successive addition of OH, NO\textsubscript{3}. Leads to formation of nitrophenols

Yields for different channels determined through chamber experiments
e.g. Volkamer et al. at EUPHORE using DOAS. Epoxy oxy product only observed – not fully quantified. Yield completes mass balance. Initial rate coefficients from pulsed photolysis.
Comparison of MCM3.1 to Toluene Chamber Experiment (27/09/01)

Conclusions:
- Ozone overpredicted but OH is too low. Need early OH source that doesn’t produce $O_3$
- $NO_2$ is not formed or removed rapidly enough
- Co-products of glyoxal/Me glyoxal not detected in sufficient concn
Photo-oxidation of $\alpha$-pinene / NO$_X$: gas-phase simulation

$[\alpha$-pinene]$_0 = 97$ ppb; $[\text{NO}]_0 = 9.7$ ppb; $[\text{NO}_2]_0 = 0.85$ ppb

Jenkin - OSOA project

27-Sep-00 Chamber A
How well do we understand the general structure of oxidation mechanisms

Missing radical sources
Examples of recent observations suggesting that new sources of OH are needed.
Conclusions from Gabriel analyses

“To explain the observed isoprene concentrations, the effective rate constant for the reaction of isoprene with OH be reduced by about 50% compared with the lower bound of the range recommended by IUPAC. A reasonable explanation for this lower effective rate constant could be the segregation of isoprene and OH in the mixed layer.”
Measurement of OH reactivity: Leeds OH reactivity (lifetime) instrument

Flow-tube reactor with the atmosphere as the reagent

Sampled Atmosphere

From Flowmeter: Air / N2 + H2O

Ambient OH is removed in sample line

90°-bend

Teflon Flow Tube

OH Injector

Hg Lamp

OH made in injector

OH decays

OH is measured by FAGE

Anemometer

Fan

PMT

Laser

Fluorescence cell

Translator to move injector

Also Brune, Juelich, Tokyo.
Semi-log decay of OH

\[ [\text{OH}] = [\text{OH}]_0 \exp \left( -k' \text{OH} \, t \right) \]. Obtain \( k \text{OH} \) from semi-log plot.

Change \( t \) by moving injector position.

\[ k'_\text{OH} = \sum_i k_i [\text{VOC}]_i \]

\[ = \frac{1}{\tau_{\text{OH}}} \]

Physical loss (zero air)

\[ k' = 1.88 \pm 0.09 \text{ s}^{-1} \]

Field measurements

\[ 12.46 \pm 0.15 \text{ s}^{-1} \]

\[ 18.59 \pm 0.21 \text{ s}^{-1} \]
Combine measurement of OH reactivity with measurement of $[\text{OH}]$, $[\text{HO}_2]$ and concentrations of OH sources (ozone, HONO….). Check budget balance.
• Pearl River Delta, 3 – 30 July 2006 Photochemistry study with measurements of HOx in China (PRIDE-PRD 2006) ~ 60 km outside of Guangzhou City (23.5°N)
• Forschungszentrum Jülich, Peking University, Beijing, RCEC, Taiwan University of Tokyo
• Science. 2009; >324:1702-1704.

OH lifetime measurements:
Measure \( \tau = 1/k_{OH} \)
Where \( k_{OH} \) is the pseudo 1\textsuperscript{st} order rate for loss of OH
Rate of loss of OH = \( k_{OH}[OH] \)

Mean Diurnal Profiles

OH peak values
2 x 10\(^7\) molecules / cm\(^2\)
~ 0.8 pptv

High photochemical activity!

\( OH \) peak values
\( HO_2 \) peak values
~ 80 pptv

Isoprene and its oxid\( n \) products important in pm.
• Radical budget closed in morning - OH recycling is very efficient.
• No closure in afternoon. Since HO$_2$, NO and OH loss are directly measured, observation indicates additional source of OH
HO\textsubscript{x} radical regeneration in the oxidation of isoprene
Peeters et al., PCCP 2009

\[ \frac{k_{\text{HO}_2}}{10^{-12} \cdot \text{cm}^3 \cdot \text{s}^{-1}} \]

\[ k_{\text{HO}_2} = 0.3 \]

\[ k_{\text{HO}_2} = 15.0 \cdot \text{s}^{-1} \]

\[ k_{\text{HO}_2} = 1.5 \]

\[ k_{\text{HO}_2} = 7.0 \cdot \text{s}^{-1} \]

\[ k_{\text{HO}_2} = 1.5 \]

\[ k_{\text{HO}_2} = 2.1 \cdot \text{s}^{-1} \]

Pristine tropical forest (303 K)
5x10\textsuperscript{8} NO, 10\textsuperscript{9} HO\textsubscript{2}, 10\textsuperscript{9} RO\textsubscript{2}

\[ k = 0.025 \cdot \text{s}^{-1} \]

\[ k \geq 0.004 \cdot \text{s}^{-1} \]

\[ k \geq 1 \cdot \text{s}^{-1} \]

\[ \text{Products} \]

\[ \text{Products} \]

\[ \text{OH + CH}_2\text{O} \]

\[ + \text{methylvinylketone} \]

\[ \text{Products} \]

\[ \text{Products} \]

\[ \text{OH + OOH} \]

\[ \text{O}_2 \]

\[ \text{HO}_2 \]

\[ \text{OOH} \]

Fig. 1 Reaction scheme for OH and HO\textsubscript{2} radical formation following 1-OH addition to isoprene (60\%), in pristine forest BL conditions, at 303 K. Note: to obtain the pseudo-first-order \( k'_{\text{HO}_2} \), in these conditions, multiply the \( k_{\text{HO}_2} \) values listed by 5x10\textsuperscript{18} \text{cm}^{-3}. \]
Other possible sources of OH

- The main requirement is to form OH without going through HO₂, since that route is quantified through the measurement of [HO₂] and N
- Unrecognised photolysis routes to OH
- RO₂ → QOOH → OH + produc the ‘combustion route’, via we C-H and O-H bonds, c.f. reactions in ethers and acetylene.
- RC(O)O₂ + HO₂ → OH
- Both mechanisms less efficient at high NOₓ
OH + $C_2H_2$

Reaction occurs to form an adduct $HOC_2H_2$ in which the radical is cis (CC) or trans to the OH.

Addition of $O_2$ then generates respectively a per oxy radical that dissociates rapidly to form different products depending on the stereochemistry.
Is the reaction of vibrationally excited species significant in the atmosphere?

Science, 337, 1066 (2012)
The future?
How will global energy markets evolve to 2035?
(International Energy Agency)

• Energy-related CO₂ emissions increase by 20%, consistent with a long-term rise in the average global temperature.
• 90% of projected growth from non-OECD economies, 30% from China
• The share of fossil fuels in global primary energy consumption falls slightly from 81% in 2010 to 75% in 2035
• On planned policies, rising fossil energy use will lead to irreversible and potentially catastrophic climate change
• China, responsible for nearly half of global coal use in 2009, holds the key to the future of the coal market with an ambitious 12th Five-Year Plan for 2011-2015 to reduce energy and carbon intensity through enhanced energy efficiency and diversifying the energy mix.
Reading
Some more general reading in addition to the specific references given in the lectures

- **General kinetics:** Pilling and Seakins, Reaction Kinetics.
- **Atmospheric Chemistry:** R P Wayne, Chemistry of Atmospheres
- **IPCC:** 4th Assessment Report, 2007. 5th AR. 2013/2014