Final Review
AOSC 433/633 & CHEM 433/633

Ross Salawitch

Class Web Site: http://www.atmos.umd.edu/~rjs/class/spr2013

9 May 2013

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Final Exam

– Wednesday, 15 May, 10:30 am to 12:30 pm
– This room
– Format similar to prior exams
  – Please bring a calculator
– “Virtual conversation”
– Closed book, no notes
– Backbone of course remains the lectures

– Entire course will be covered on the final exam
– Tim & Allison will be present to answer questions …
  please ask if you think a question requires clarification
Of the “nine ways to cool the planet” discussed in the IEEE article, which of these seems most appealing to you? Briefly state why.
Radiative Forcing of Climate, 1750 to 2005

Radiative Forcing of Climate is Change in Energy reaching the lower atmosphere (surface to tropopause) as GHGs rise. “Back Radiation” is most important term.
Connection Between GHG Abundance and Surface T

How much does $\Delta F$ change when $CO_2$ changes?

$$\Delta F \approx 5.35 \text{ W/m}^2 \ln \left( \frac{CO_2^{\text{Final}}}{CO_2^{\text{Initial}}} \right)$$

Changes in $\Delta F$ can be caused by changes in chemical composition (GHGs), aerosol loading, as well as surface albedo, $H_2O$, & cloud feedback

$$\Delta T = \lambda_{BB} (1 + f) (\Delta F_{CO_2} + \Delta F_{CH_4+N_2O} + \Delta F_{ALBEDO} + \Delta F_{AEROSOLS})$$

where $\lambda_{BB} = 0.3 \text{ K / W m}^{-2}$,

and $f =$ represents total feedbacks due to surface albedo, $H_2O$, & clouds

GWP – Global Warming Potential

$$\text{GWP (CH}_4) = \int_{\text{time initial}}^{\text{time final}} a_{\text{CH}_4} \times \text{[CH}_4(t)] \, dt$$

$$\int_{\text{time initial}}^{\text{time final}} a_{CO_2} \times \text{[CO}_2(t)] \, dt$$

where:

$a_{\text{CH}_4} =$ Radiative Efficiency (W m$^{-2}$ ppb$^{-1}$) due to an increase in CH$_4$

$a_{CO_2} =$ Radiative Efficiency (W m$^{-2}$ ppb$^{-1}$) due to an increase in CO$_2$

CH$_4(t) =$ time-dependent response to an instantaneous release of a pulse of CH$_4$

CO$_2(t) =$ time-dependent response to an instantaneous release of a pulse of CO$_2$
GWP – Global Warming Potential

SAR: Second Assessment Report (issued in 1995)

Table TS.2. Lifetimes, radiative efficiencies and direct (except for CH₄) global warming potentials (GWP) relative to CO₂ (Table 2.14)

<table>
<thead>
<tr>
<th>Industrial Designation or Common Name (years)</th>
<th>Chemical Formula</th>
<th>Lifetime (years)</th>
<th>Radiative Efficiency (W m⁻² ppb⁻¹)</th>
<th>SARI (100-yr)</th>
<th>Global Warming Potential for Given Time Horizon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon dioxide</td>
<td>CO₂</td>
<td>See below¹</td>
<td>1.4x10⁻⁵</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Methane²</td>
<td>CH₄</td>
<td>12</td>
<td>3.7x10⁻⁴</td>
<td>21</td>
<td>72, 25, 7.6</td>
</tr>
<tr>
<td>Nitrous oxide</td>
<td>N₂O</td>
<td>114</td>
<td>3.03x10⁻²</td>
<td>310</td>
<td>289, 258, 153</td>
</tr>
</tbody>
</table>

Notes:

¹ SAR refers to the IPCC Second Assessment Report (1995) used for reporting under the UNFCCC.

² The CO₂ response function used in this report is based on the revised version of the Bern Carbon cycle model used in Chapter 10 of this report (Bern2.5CC, Joos et al. 2001) using a background CO₂ concentration value of 378 ppm. The decay of a pulse of CO₂ with time t is given by

\[ a_0 + \sum_{i=1}^{3} a_i e^{-b_i t} \]

where \( a_0 = 0.217, a_2 = 0.250, a_3 = 0.250, a_4 = 0.186, b_0 = 122.9 \text{ years}, b_2 = 18.51 \text{ years}, \) and \( b_4 = 1.186 \text{ years}, \) for \( t < 1,000 \text{ years}.\)

³ The radiative efficiency of CO₂ is calculated using the IPCC (1990) simplified expression as revised in the TAR, with an updated background concentration value of 378 ppm and a perturbation of +1 ppm (see Section 2.10.2).

⁴ The perturbation lifetime for CH₄ is 12 years as in the TAR (see also Section 7.4). The GWP for CH₄ includes indirect effects from enhancements of ozone and stratospheric water vapour (see Section 2.10).

Time constant of 172.9 years dominates

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Sea Level Rise: Projection for 7 meter rise

http://www.geo.arizona.edu/dgesl/index.html

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Sea Level Rise: Future Uncertain

Greenland's ice sheet: Climate change outlook gets a little more dire

If temperatures reach 1.6 degrees C above preindustrial levels, the iconic ice sheet will probably tip toward irreversible loss. With climate change, temperatures have already risen 0.8 degrees C.

By Pete Spotts, Staff writer / March 13, 2012

Robinson et al., Nature Climate Change, 2012 modeling study

Schrama and Wouters, JGR, 2011

Evolution of the average mass in Gt in Greenland from the Gravity Recovery and Climate Experiment (GRACE)

What about the polar bears?

Average Monthly Arctic Sea Ice Extent
September 1979 - 2012

What about the polar bears?

Polar bear census data:

<table>
<thead>
<tr>
<th>Location</th>
<th>Polar Bear Population Status</th>
<th>Risk of Future Decline</th>
<th>Location</th>
<th>Polar Bear Population Status</th>
<th>Risk of Future Decline</th>
</tr>
</thead>
<tbody>
<tr>
<td>East Greenland</td>
<td>Data deficient</td>
<td>No estimate</td>
<td>Norwegian Bay</td>
<td>Not reduced</td>
<td>Higher</td>
</tr>
<tr>
<td>Barents Sea</td>
<td>Data deficient</td>
<td>No estimate</td>
<td>Lancaster Sound</td>
<td>Not reduced</td>
<td>Higher</td>
</tr>
<tr>
<td>Kara Sea</td>
<td>Data deficient</td>
<td>No estimate</td>
<td>M’Clintock Channel</td>
<td>Severely reduced</td>
<td>Very Low</td>
</tr>
<tr>
<td>Laptev Sea</td>
<td>Data deficient</td>
<td>No estimate</td>
<td>Gulf of Boothia</td>
<td>Not reduced</td>
<td>Lower</td>
</tr>
<tr>
<td>Chukchi Sea</td>
<td>Data deficient</td>
<td>No estimate</td>
<td>Foxe Basin</td>
<td>Not reduced</td>
<td>Lower</td>
</tr>
<tr>
<td>Southern Beaufort Sea</td>
<td>Reduced</td>
<td>No estimate</td>
<td>Western Hudson Bay</td>
<td>Reduced</td>
<td>Very High</td>
</tr>
<tr>
<td>Northern Beaufort Sea</td>
<td>Not reduced</td>
<td>No estimate</td>
<td>Southern Hudson Bay</td>
<td>Not reduced</td>
<td>Lower</td>
</tr>
<tr>
<td>Viscount Melville</td>
<td>Severely reduced</td>
<td>Very Low</td>
<td>Kane Basin</td>
<td>Reduced</td>
<td>Very High</td>
</tr>
<tr>
<td>Norwegian Bay</td>
<td>Not reduced</td>
<td>Higher</td>
<td>Baffin Bay</td>
<td>Reduced</td>
<td>Very High</td>
</tr>
</tbody>
</table>

Tables on this website updated frequently:
http://pbsg.npolar.no/en/status/status-table.html

The Ozone Hole may have shielded the Antarctic from warming

Simulated and observed changes in surface temperature (K) and winds from 1969 to 2000, averaged over December to May.

Antarctic Ice Mass Slowly Declining

Shepherd et al., Science, 2012

Associated Sea level rise = 1.1 cm / 12 yr = 0.001 m / year

Sea Level Rise: Future Uncertain

Chill out? Greenland glaciers' acceleration to slow, study says

For the past ten years, skyscraper-sized icebergs have cracked off glaciers in Greenland and tumbled into the sea at an ever-quickening rate in response to global warming, raising concerns about runaway ice loss and rising seas. The good news? The rate of acceleration will slow, according to a new study.

The slowdown is related to the physics and geography that govern glacier movement, not a forecast that the rise in global temperatures will halt anytime soon. Indeed, the ice sheets will continue to melt and push up sea levels around the world, just not as quickly as feared, the study's lead author said.

The earlier work extrapolated the rate of acceleration seen since the late 1990s out to 2100, explained Faezeh Nick, a glaciologist at The University Center in Svalbard, Norway.

But scientists now know that glaciers respond to warming in complex ways, especially those that end at the sea. These moving tongues of ice, known as outlet glaciers, accelerate in bursts — dumping tons of ice into the ocean — but then the pace slackens. "It doesn't go lower than it was before, but it doesn't stay at the top" rate, Nick told NBC News.

http://science.nbcnews.com/news/2013/05/08/18126209-chill-out-greenland-glaciers-acceleration-to-slow-study-says

based on Nick et al., Nature, 9 May 2013
Ozone Depletion and Halocarbons

Table Q7-1. Atmospheric Lifetimes and Ozone Depletion Potentials of some halogen source & HFC substitute gases.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Atmospheric Lifetime (years)</th>
<th>Ozone Depletion Potential (ODP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorine gases</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CFC-11</td>
<td>45</td>
<td>1</td>
</tr>
<tr>
<td>CFC-12</td>
<td>100</td>
<td>0.82</td>
</tr>
<tr>
<td>CFC-113</td>
<td>85</td>
<td>0.82</td>
</tr>
<tr>
<td>Carbon tetrachloride (CCl4)</td>
<td>26</td>
<td>0.82</td>
</tr>
<tr>
<td>HFCs</td>
<td>1–17</td>
<td>0.01–0.12</td>
</tr>
<tr>
<td>Methyl chloroform (CH3Cl)</td>
<td>5</td>
<td>0.16</td>
</tr>
<tr>
<td>Methyl chloride (CH3Cl)</td>
<td>1</td>
<td>0.02</td>
</tr>
<tr>
<td>Bromine gases</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Halon-1301</td>
<td>65</td>
<td>15.9</td>
</tr>
<tr>
<td>Halon-1211</td>
<td>16</td>
<td>7.9</td>
</tr>
<tr>
<td>Methyl bromide (CH2Br)</td>
<td>0.8</td>
<td>0.66</td>
</tr>
<tr>
<td>Hydrofluorocarbons (HFCs)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HFC-134a</td>
<td>13.4</td>
<td>0</td>
</tr>
<tr>
<td>HFC-23</td>
<td>222</td>
<td>0</td>
</tr>
</tbody>
</table>

ODP (species "i") = \( \frac{\text{global loss of } O_3 \text{ due to unit mass emission of } "i"}{\text{global loss of } O_3 \text{ due to unit mass emission of CFC-11}} \approx \left( \alpha n_{\text{Br}} + n_{\text{Cl}} \right) \frac{\tau_i}{\tau_{\text{CFC-11}}} \frac{MW_{\text{CFC-11}}}{MW_i} \frac{1}{3} \)

where:
- \( \tau \) is the global atmospheric lifetime
- \( MW \) is the molecular weight
- \( n \) is the number of chlorine or bromine atoms
- \( \alpha \) is the effectiveness of ozone loss by bromine relative to ozone loss by chlorine

\[ \alpha = 60 \]

Halons (anthropogenic halocarbons containing bromine) much worse for ozone than CFCs (anthropogenic halocarbons containing chlorine)

HFCs (anthropogenic halocarbons containing only fluorine, carbon, and hydrogen) and thus pose no threat to the ozone layer
Heterogeneous Chemistry, Mid-Latitude vs Polar Regions

a) What type of aerosol particles are present in the mid-latitude stratosphere?

b) What chemical reaction occurs on the aerosol particles present in the mid-latitude stratosphere? (we call this a “heterogeneous reaction” since it involves a reaction of gases on a particle).

c) What is the effect on ClO of the “heterogeneous” reaction from part b)?

d) What type of particles are present in the polar stratosphere during winter?

e) What is the effect of these particles on the chemical composition of the polar stratosphere (chemical reactions occurring on the surface of these particles convert species such as _____ and _____ to more reactive species such as _____ and _____)?

f) Why does the heterogeneous reaction of part e) occur only at high-latitudes during winter (to receive full credit, we’d like for you to draw upon material presented in Lecture 11 in your reply)?
Polar Ozone Loss: Antarctica

Total Ozone Over Halley Bay, Antarctica (76°S)
Average for October

Much of this “leveling off” is indeed due to the “leveling off” of halogens.

The Stratosphere Cools as the Surface Warms!

Annual Mean Trend
1980-2005, 70°N-70°S

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Link Between Ozone-Depleting Substances (ODS) and Climate Change

Most ozone depleting substances have a significant “GWP”

Twenty Questions and Answers About The Ozone Layer: 2010 Update (WMO, 2010)
**Tropospheric Ozone Production**

\[
\text{CO + OH } \rightarrow \text{CO}_2 + \text{H} \\
\text{H + O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M} \\
\text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2 \\
\text{NO}_2 + \text{hv} \rightarrow \text{NO} + \text{O} \\
\text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M}
\]

Net: \( \text{CO + 2 O}_2 \rightarrow \text{CO}_2 + \text{O}_3 \)

"Chain Mechanism" for production of ozone

Initiation: \( \text{O}_3 \) photolysis giving \( \text{O}^{(1D)} \), followed by \( \text{H}_2\text{O} + \text{O}^{(1D)} \rightarrow 2\text{OH} \) as well as emission of \( \text{CO} \) & \( \text{NO}_x \) from combustion of fossil fuels

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

Propagation: \( \text{HO}_2 + \text{NO} \)

Ozone Production “limited” by \( k[\text{HO}_2][\text{NO}] \) (propagation term)

High \( \text{NO}_x \) (NO+NO\(_2\)) forces termination via production of HNO\(_3\).

In this case, as \( \text{NO}_x \) rises, OH and \( \text{HO}_2 \) (HO\(_x\)) fall

\( \Rightarrow \) what happens to \( \text{O}_3 \) production?
Tropospheric Ozone Production

\[ CO + OH \rightarrow CO_2 + H \]
\[ H + O_2 + M \rightarrow HO_2 + M \]
\[ HO_2 + NO \rightarrow OH + NO_2 \]
\[ NO_2 + hv \rightarrow NO + O \]
\[ O + O_2 + M \rightarrow O_3 + M \]

Net: \[ CO + 2 O_2 \rightarrow CO_2 + O_3 \]

**Ozone Production “limited” by \([HO_2][NO]\) (propagation term)**

High \( NO_x \) (\( NO + NO_2 \)) forces termination via production of \( HNO_3 \).

In this case, as \( NO_x \) rises, \( OH \) and \( HO_2 \) (\( HO_x \)) fall

\[ \Rightarrow \text{what happens to } O_3 \text{ production?} \]

Illustrative calculation of the dependence of \( O_3 \) production on \([NO]\)

This curve has key policy implications!

Tropospheric Ozone Production versus \( NO_x \) and VOCs

**Ridge: local maximum for \( O_3 \) that separates the \( NO_x \)-limited regime from and VOC limited regime**

An important discovery in the past decade is that the focus on hydrocarbon emission controls to combat \( O_3 \) pollution may have been partly misdirected. Measurements and model calculations now show that \( O_3 \) production over most of the United States is primarily \( NO_x \) limited, not hydrocarbon limited. The early models were in error in part because they underestimated emissions of hydrocarbons from automobiles, and in part because they did not account for natural emission of biogenic hydrocarbons from trees and crops.

*Jacob, Chapter 12, Introduction to Atmospheric Chemistry, 1999*

Figure: [http://www-personal.umich.edu/~sillman/ozone.htm](http://www-personal.umich.edu/~sillman/ozone.htm)
Significant Improvements in *Local* Air Quality since early 1980s

![Graph showing improvements in local air quality](http://www.mde.state.md.us/programs/Air/AirQualityMonitoring/Pages/HistoricalData.aspx)

Subtropical Jet

**Subtropical Jet**: area where poleward descending branch of the Hadley Circulation meets the equatorward descending of the Ferrel Cell (see Lecture 3)

Semi-permanent area of high pressure, fair weather, low rainfall: *conditions conducive to high ozone*

![Image of Subtropical Jet](http://www.ux1.eiu.edu/~cffps/1400/FIG07_014A.jpg)
Climate Change and Air Pollution

Poleward expansion of the sub-tropical jet:
- Surface ozone highs occur along Subtropical Jet
- Number of days Subtropical Jet within 150 miles of Baltimore has increased by ~50% between 1979 and 2003, due to “frontal movement”
- Driving force: weakening of the equator to pole temperature gradient, caused by more rapid warming at high latitudes compared to tropics

Seidel et al., Nature Geoscience, 2008

- Computer models predict increase in severity and duration of pollution episodes over Midwest, Mid-Atlantic, and Northeast U.S. in 2050, even for constant emissions

Market Force #1: Cost of Cost of Fossil Fuel ↑

Market Force #2: Cost of Electricity from Renewables ↓

2011 US Average Cost of Electricity: ~11.8 cents per kw-hour

Wind turbines: ~50 kW/acre → 81,000 m²/MW
http://www.greenenergyexplained.com/2008/01/wind-energy.html

Hydroelectric: enormous impact upstream of reservoir

• Sugar Cane: 650 gal/acre  
  http://www.earth-policy.org/Books/PB2/PB2ch10 ss7.htm
  650 gal/acre × 3785.1 cm³/gal × 0.789 g/cm³ × 29.7 kJ/g = 5.8×10⁷ kJ/acre
  5.8×10⁷ kJ/acre/year = 1.83 kW/acre = 2,211,393 m²/MW   !!!

• Corn: 350 gal/acre → 4,106,872 m²/MW   YIKES   !!!!
Our Favorite Air Pollutants

<table>
<thead>
<tr>
<th>Species</th>
<th>Source</th>
<th>Consequence</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td></td>
<td>Increases surface radiative forcing, leading to climate change</td>
</tr>
<tr>
<td>CH₄</td>
<td></td>
<td>Same as above + stratospheric ozone depletion</td>
</tr>
<tr>
<td>N₂O</td>
<td></td>
<td>NOx</td>
</tr>
<tr>
<td>SO₂</td>
<td></td>
<td>Soot</td>
</tr>
<tr>
<td>Soot</td>
<td></td>
<td>CFCs</td>
</tr>
<tr>
<td>CFCs</td>
<td></td>
<td>Halons</td>
</tr>
<tr>
<td>Halons</td>
<td></td>
<td>CH₃Br</td>
</tr>
<tr>
<td>CH₃Br</td>
<td></td>
<td>HCFCs</td>
</tr>
</tbody>
</table>

Final Statements

It is difficult for people living now, who have become accustomed to the steady exponential growth in the consumption of energy from fossil fuels, to realize how transitory the fossil fuel epoch will eventually prove to be when it is viewed over a longer span of human history

M. King Hubbert, Scientific American, 1971
as quoted in foreword of When Oil Peaked by Kenneth S. Deffeyes

We believe that the development of renewable energy will be to students of your generation what the electronics & computer industry were to students of our generation: an opportunity for great innovation, entrepreneurial development, societal benefit, and also a very comfortable lifestyle for those who lead the “green revolution”

Ross Salawitch & Tim Canty