Assignments

upload to ELMS – NO Hardcopy (save the trees)
Reading: Wolfson – Chapter 2-3

Energy Audit assignment – see elms for instructions
Clickers = all but three of you have them (Bottoms, Littleford, Matsa)

**Tragedy of the Commons**

- Garrett Hardin 1968
  - Article is on ELMS
- A commons is an open space available to all
- Hypothetical case of 10 dairy farmers using the land
  - In hard times everyone has a few cows and there is plenty of grass for all
  - As things improve we assume the that eventually we get 20 cows each (total 200 cows) and we have reached the carrying capacity of the land
G. Hardin – 1998

- "A 'managed commons' describes either socialism or the privatism of free enterprise. Either one may work; either one may fail: 'The devil is in the details.' But with an unmanaged commons, you can forget about the devil: As overuse of resources reduces carrying capacity, ruin is inevitable."

Fishing Industry as the T.o.C

- Fisheries are similar to Hardin's pasture in that increased fishing pressure has caused certain stocks of fish to become over fished to a point that threatens the survival of the fishery.
- All the conditions described by Hardin are met in this case:
  - an unrestricted number of users, unfettered by any limits on their access extract an increasing share of a resource until natural resources are severely depleted.
  - Fishers tend to have little incentive to practice conservation, for they know that if they do not catch the available fish, someone else probably will.
Cod Fishing on the Grand Banks

- After his voyage in 1497, John Cabot’s crew reported that “the sea there is full of fish that can be taken not only with nets but with fishing-baskets”.
- Around 1600 English fishing captains still reported cod shoals “so thick by the shore that we hardly have been able to row a boat through them.”
- In 1951 factory fishing began with new super-trawlers – 280 feet long and 2,600 gross tons.

Collapse of the Cod Fishery

![Graph showing fish landings in tons over time from 1860 to 2000. The graph peaks around 1880 and then declines sharply in 1992. Source: Millennium Ecosystem Assessment.]
Collapse of the Cod Fishery

- The cod catch peaked in 1968 at 810,000 tons, approximately three times more than the maximum yearly catch achieved before the super-trawlers.
- Approximately 8 million tons of cod were caught between 1647 and 1750, a period encompassing 25 to 40 cod generations. The factory trawlers took the same amount in 15 years.
- The industry collapsed entirely in the early 1990s owing to overfishing and debatably, greed, lack of foresight and poor local administration.
- By 1993 six cod populations had collapsed, forcing a belated moratorium on fishing. Spawning biomass had decreased by at least 75% in all stocks, by 90% in three of the six stocks, and by 99% in the case of 'northern' cod, previously the largest cod fishery in the world.
- After a 10 year moratorium on fishing the cod had still not returned.

My Neighbor and the Tragedy of the Commons

- I live on a small court.
- Everyone rakes their leaves in the fall.
  - Everyone that is, but George.
- George reasons: Since everyone else rakes their leaves, if I do nothing, mine will blow away spreading over everywhere and I will have very few leaves in my yard.
- Of course, if we all did that then all yards would be full of leaves and eventually all the grass will die.
So what should we do about George?
1. Speak to George nicely and hope he responds
2. Talk to the homeowner’s association
3. Clean up George’s leaves ourselves
4. Kick his ass

TANSTAAFL

- There ain’t no such thing as a free lunch
  - Every thing has a cost
    - This cost may not be obvious at first
  - Ozone
  - Industrialization
    - Pollution
    - Energy usage
  - Cell phones
    - Bad driving
  - Nuclear Energy
    - Waste
    - Proliferation
Electromagnetic Spectrum

Can something be “whiter than white”?  
1. Yes  
2. No
Ozone is?

1. A major component of Smog
2. Poisonous
3. Good only in the upper atmosphere
4. All of the above
5. None of the above

Ozone - an interesting example of a global problem

- Ozone (O₃) is a triatomic molecule, consisting of three oxygen atoms. Ozone in the upper atmosphere filters potentially damaging ultraviolet light from reaching the Earth's surface.
- Low level ozone (or tropospheric ozone) is regarded as a pollutant by the World Health Organization with harmful effects on the respiratory systems of animals.
- Sulfuric Acid (acid rain) can be produced from ozone, starting either from elemental sulfur or from sulfur dioxide:
  $$ S + H_2O + O_3 \rightarrow H_2SO_4 $$
The Atmosphere

- We live in the Troposphere (0 – 6/20KM)
  - Weather is in the troposphere
  - It contains 46% of the atmosphere's mass and almost all of its water vapor
- How high do airplanes fly?
  - 37,000’
  - 5,280’/mile
  - ~7 miles high

Life and UV Radiation

- DNA molecules have resonances at 265 nm
- Proteins have resonances at 275–285 nm
- UV at or below these wavelengths is absorbed, breaking molecules and damaging cells
  - UV at 254 nm is used to sterilize equipment
- UV is absorbed by a few meters of water; life initially was found only in the ocean
- Marine plants produced $O_2$, which accumulated in atmosphere; $O_2$ absorbs UV-C (<280 nm)
- $O_3$ produced from $O_2$; $O_3$ absorbs most UV-B (280–320 nm), making terrestrial life possible
Ozone, Oxygen and Life

Impacts of Increased UV

Humans:
- more melanoma and other skin cancers
- more eye cataracts, photosensitivity
- more sunburn, premature aging
- weakened immune systems; more infection

Other Life:
- Cataracts in mammals, increased mortality/morbidity in animals with UV-sensitive skin
- reduced plant yields (1% for each 1% decrease O₃)
- damage to ocean ecosystems

Damage to plastics, other materials
Do you know someone who had skin cancer?

1. Yes
2. No
**Skin Cancer**

- More than 1 million new cases of skin cancer will be diagnosed in the United States this year.
- 1 in 5 Americans will develop some form of skin cancer during their lifetime.
- There will be about 110,000 new cases of melanoma in 2009.
- In 2009, at current rates, a person has a one in 33 chance of developing melanoma (both in situ and invasive). The risk of developing invasive melanoma is one in 63.
- Melanoma is the second most common cancer in women aged 20-29.
- One American dies of melanoma almost every hour (every 65 minutes).
Ozone Depleting Substances

- Chlorofluorocarbons (CFCs)
  - contain: Cl, F, C
  - long-lived, non-toxic, non-corrosive, and non-flammable
  - Great as propellants
  - in 1960s used in refrigerators, air conditioners, spray cans, solvents, foams
- The Problem was they were found to migrate to the upper atmosphere where they would break down and catalyze the destruction of Ozone.
- TANSTAAFL
Threats to the Ozone Layer: SST

- SSTs fly in stratosphere where air is thin to minimize drag at high velocities, emit NO, H₂O
- In 1970s, calculations showed 500 SSTs flying 8 h/d at 20 km, emitting 15 g NO/kg fuel would produce 20% decrease in O₃ in Northern Hemisphere
  - new calculations: 7% decrease in O₃, 14% increase in skin cancers
  - 300 SSTs flying at 22.5 km emitting 12 g/kg, 3% decrease in O₃, 6% increase skin cancer, 100,000 additional cancers/y, of which 5,000 would be fatal
In 1973 Chemists Frank Sherwood Rowland and Mario Molina, at the University of California, Irvine, began studying the impacts of CFCs in the earth's atmosphere. They discovered that CFC molecules were stable enough to remain in the atmosphere until they got up into the middle of the stratosphere where they would finally (after an average of 50-100 years) be broken down by ultraviolet radiation releasing a chlorine atom.
History Continued

- Rowland and Molina then proposed in June 1974 that these chlorine atoms might be expected to cause the breakdown of large amounts of ozone (O3) in the stratosphere.
- Their argument was based upon an analogy to contemporary work by Paul J. Crutzen and Harold Johnston, which had shown that nitric oxide (NO) (like from the SST) could catalyze the destruction of ozone.

- Crutzen, Molina and Rowland were later awarded the 1995 Nobel Prize for Chemistry for their work on this problem.

The Ozone Cycle

1. Oxygen molecules are photolyzed, yielding 2 oxygen atoms (SLOW).

2. Ozone and oxygen atoms are continuously being interconverted as solar UV breaks ozone and the oxygen atom reacts with another oxygen molecule (FAST).

3. Ozone is lost by a reaction of the oxygen atom or the ozone molecule with each other, or some other trace gas such as chlorine (SLOW).
History Continued

- But the Rowland-Molina hypothesis was strongly disputed by representatives of the aerosol and halocarbon industries.
- The Chair of the Board of DuPont was quoted as saying that ozone depletion theory is:
  - "a science fiction tale...a load of rubbish...utter nonsense".
- Robert Abplanalp, the President of Precision Valve Corporation (and inventor of the first practical aerosol spray can valve), wrote to the Chancellor of UC Irvine to complain about Rowland's public statements.

History Continued

- After publishing their pivotal paper in June 1974, Rowland and Molina testified at a hearing before the U.S. House of Representatives in December, 1974.
  - As a result significant funding was made available to study various aspects of the problem and to confirm the initial findings.
  - In 1976 the U.S. National Academy of Sciences (NAS) released a report that confirmed the scientific credibility of the ozone depletion hypothesis. NAS continued to publish assessments of related science for the next decade.
History Continued

- Then, in 1985, British Antarctic Survey scientists Farman, Gardiner and Shanklin shocked the scientific community when they published results of a study showing an ozone "hole" in the journal Nature – showing a decline in polar ozone far larger than anyone had anticipated.

- That same year, 20 nations, including most of the major CFC producers, signed the Vienna Convention which established a framework for negotiating international regulations on ozone-depleting substances.
History Continued

- But the CFC industry did not give up that easily. As late as 1986, the Alliance for Responsible CFC Policy (an association representing the CFC industry founded by DuPont) was still arguing that the science was too uncertain to justify any action.
- In 1987, DuPont testified before the US Congress that
  
  "we believe that there is no immediate crisis that demands unilateral regulation"

Ozone Chronology

1928 CFCs invented at DuPont
1930 pure oxygen chemistry explained
1950 OH chemistry explained
1957 Dobson stations established
1970s NO\textsubscript{x} chemistry; SSTs, nuclear explosions
1974 Rowland-Molina paper, Cl chemistry
NRDC petitions CPSC to ban aerosols
1974–76 congressional hearings, boycott, Oregon and New York bans, NAS report
1977 ozone amendment to CAA banning aerosols; US hosts first international meeting
Ozone Chronology

1978     US bans nonessential aerosols
         (Canada, Norway, and Sweden)
1979     Germany hosts second UNEP meeting
1981     UNEP council recommends convention
         Reagan/Gorsuch/Hodel; DuPont discontinues
         research on CFCs alternatives
1982-85  working group meetings
1985     Vienna Convention
         British scientists publish Antarctic data
1987     Montreal Protocol: 50% reduction
         CFCs below 1986 by 2000)

NASA Video
Ozone Hole

- Largest Antarctic ozone hole ever recorded (Sept. 2006)

2011 Southern Hemisphere Ozone Hole Area
NOAA SBUV/2
Current Year Compared Against Past 10 Years

Updated through Sep 13, 2011
Estimated Ozone Depletion

- If emissions of CFCs continued at the 1974–86 rate of \( \approx 1 \) Mt/y (CFC-11 equivalent)...
- ...calculations indicated 15–20% decrease in \( O_3 \) stock...
- ...30–40% increase in skin cancer (of which 2.5–5% of which are fatal)
- 500,000 to 700,000 additional cancers
- 15,000 to 35,000 additional cancer deaths
- most in northern hemisphere, 20% in US

- HOW DO YOU KNOW THIS?
Incidence of Skin Cancer v. UV-B

NASA Estimates of what would have happened without Montreal Protocols

[Graph showing age-adjusted incidence of non-melanoma skin cancer (per 100,000/year) vs. UV-B radiation index, with regression lines and equations: y = 0.012x, R² = 0.80 for white males; y = 0.018x, R² = 0.75 for white females.]

[Images showing ozone concentration for North America in 1974, 1994, 2009, and 2016, with color gradients indicating levels of ozone.]
Ozone Hole

- Largest Antarctic ozone hole ever recorded (Sept. 2006)

Ozone - Polar

- $O_3$

Lowest value of ozone measured each year in the ozone hole. Global average ozone is about 300 Dobson units. Before 1980 ozone less than 200 Dobson units was rarely seen.
Antarctic Ozone Hole

- As winter arrives, a vortex of winds develops around the pole and isolates the polar stratosphere. When temperatures drop below -78°C (-109°F), thin clouds form of ice, nitric acid, and sulphuric acid mixtures. Chemical reactions on the surfaces of ice crystals in the clouds release active forms of CFCs. When sunlight arrives ozone depletion begins, and the ozone "hole" appears.

- Ozone is destroyed through catalytic cycles involving reactive nitrogen (NO₃), Cl and Br and hydrogen species (HO₃).
- In the upper atmosphere, chlorine is found in "reservoirs," in combination with nitrogen compounds.
- The CFCs, which were stable in the lower atmosphere, break apart under the action of sunlight and release chlorine to the "reservoir molecules," where chlorine (or bromine) is inactivated.
- In winter and spring, ozone destruction is mostly due to Cl and Br because at low temperatures, the reservoir molecules don’t reform after they break apart.
There is a lag time between emissions reduction and polar chlorine concentration because it takes some years for the lower atmospheric chlorofluorocarbons to reach the stratosphere and be broken up through action of ultraviolet solar radiation.

The best estimate for the lifetime of CFC-11, for example, is about 50 years.

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**Destruction of Ozone**

- **Nitrous Oxide**
  - \( \text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 \)
  - \( \text{NO}_2 + \text{O} \rightarrow \text{NO} + \text{O}_2 \)
  - \( \text{NO}_2 + \text{O}_3 \rightarrow \text{NO} + \text{O}_2 \)
  - Clearly, the net effect of this cycle is to eliminate ozone: \( 2\text{O}_3 \) becomes \( 3\text{O}_2 \).
  - Note that this cycle will continue until (somehow) the NO is removed. NO acts as a catalyst to destroy ozone.

- **Chlorine**
  - \( \text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2 \)
  - \( \text{ClO} + \text{O} \rightarrow \text{Cl} + \text{O}_2 \).
  - The net result of this reaction is \( \text{O}_3 + \text{O} \rightarrow 2\text{O}_2 \). As with the NO cycle, chlorine will continue its destruction until (somehow) it is removed from the stratosphere.
Ozone Production and Protection in the Upper Atm.

- \( O_2 + \text{solar energy of wavelength less than 242 nm} \rightarrow 2O, \)
- \( O + O_2 \rightarrow O_3, \)
- \( O + O_3 \rightarrow 2O_2, \)
- \( O_3 + \text{solar energy of wavelength less than 336 nm} \rightarrow O^* + O_2. \)
- UV below 336nm doesn’t get through
  - UVA 400 nm - 320 nm
  - UVB 320 nm - 290 nm
  - UVC 290 nm - 100 nm

Catalytic Destruction of \( O_3 \) by Cl from CFCs

\[
\begin{align*}
\text{CFCl}_3 & \xrightarrow{UV-B,C} Cl + \text{fragment} \\
Cl + O_3 & \rightarrow ClO + O_2 \\
ClO + O & \rightarrow Cl + O_2 \quad \text{(repeated many times)}
\end{align*}
\]
Fully Halogenated Compounds

<table>
<thead>
<tr>
<th>Chlorofluorocarbons</th>
<th>τ</th>
<th>ODP</th>
<th>GWP</th>
<th>Uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>CFC-11 (CFCl₃)</td>
<td>50</td>
<td>1.0</td>
<td>4000</td>
<td>B/R</td>
</tr>
<tr>
<td>CFC-12 (CF₂Cl₂)</td>
<td>100</td>
<td>0.8</td>
<td>8500</td>
<td>AC/B</td>
</tr>
<tr>
<td>CFC-113 (C₂F₃Cl₃)</td>
<td>85</td>
<td>0.9</td>
<td>5000</td>
<td>S</td>
</tr>
<tr>
<td>CFC-114 (C₂F₄Cl₂)</td>
<td>300</td>
<td>0.85</td>
<td>9300</td>
<td>S</td>
</tr>
<tr>
<td>CFC-115 (C₂F₅Cl)</td>
<td>1700</td>
<td>0.4</td>
<td>9300</td>
<td>S/R</td>
</tr>
</tbody>
</table>

AC: air conditioning  
B: blowing foam  
F: fire extinguisher  
R: refrigerant  
S: solvent

CFC Use

1974: 970 kt
- Refrigerant: 16%
- Cleaning Agents: 8%
- Blowing Agents: 5%
- Other: 2%
- Propellants: 98%

1986: 1130 kt
- Refrigerant: 23%
- Cleaning Agents: 21%
- Blowing Agents: 28%
- Other: 2%

1991: 680 kt
- Refrigerant: 32%
- Cleaning Agents: 18%
- Blowing Agents: 26%
- Other: 3%
- Propellants: 3%
CFC Production and Concentrations

What have we learned from this?