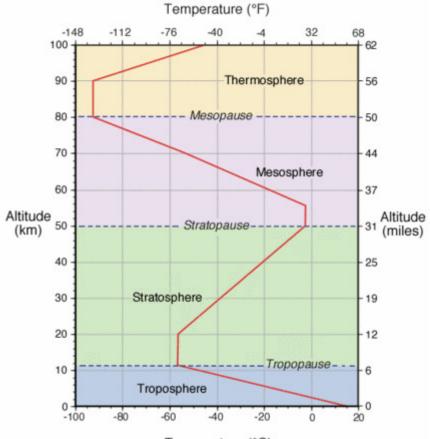
Ch. 20 Notes - The Atmosphere: Climate, Climate Change and Ozone Depletion

20.1 Notes

- I. Atmosphere and Weather
 - A. Atmospheric Structure (FYI: 1.61 km = 1 mi)



Temperature (°C)

1) troposphere

- a) lowest layer: 4-12 miles (6-19 km) above the surface
- b) densest layer; air is well-mixed
- c) temperature decreases with altitude
- d) contains most of the water vapor and *weather*
- e) **tropopause**—top of the troposphere

2) stratosphere

- a) second layer: to ~40 miles (64 km) above the earth's surface
- b) much less dense than the troposphere
- c) contains the protective *ozone* (O_3) *layer*
- d) temperature increases with altitude
- e) **stratopause**—top of the stratosphere
- 3) mesosphere
 - a) coldest layer
 - b) temperature decreases with altitude
 - c) **mesopause**—top of the mesosphere

Because it lies between the maximum altitude for most aircraft and the minimum altitude for most spacecraft, this region of the atmosphere is only directly accessible through the use of sounding (elevator research) rockets. As a result, the region is one of the most poorly understood in the atmosphere.

4) thermosphere

- a) hottest layer
- b) temperature increases with altitude
- c) ionosphere-ion layer; contribute to auroras
- 5) exosphere
 - a) beyond Earth's atmosphere; merges with interplanetary gases
 - b) primarily low-density H₂ and He
- B. Composition of Earth's atmospheric gases

 $(ppm = parts \ per \ million = mg/L \ for \ air \ and \ water = mg/kg \ for \ soil)$

(from Thad Godish's Air Quality)

ATMOSPHERIC C	CONSTITUENTS:	CONSTANT CONCENTRATIONS
CONSTITUENT	FORMULA	CONCENTRATION (ppm)
Nitrogen	N_2	780,840.00
Oxygen	O_2	209,460.00
Argon	Ar	9340.00
Neon	Ne	18.18
Helium	He	5.24
Krypton	Kr	1.14
Hydrogen	H_2	0.50
Xenon	Xe	0.09

ATMOSPHERIC CONSTITU	UENTS: VARIABI	LE CONCENTRATIONS
CONSTITUENT	FORMULA	CONCENTRATION (ppm)
Water vapor	H_2O	0.1 – 30,000.00
Carbon dioxide	CO_2	350.00
Methane	CH_4	1.67
Nitrous oxide	N_2O	0.30
Carbon monoxide	CO	0.19
Ozone	O_3	0.04
Ammonia	NH_3	0.004
Nitrogen dioxide	NO_2	0.001
Sulfur dioxide	SO_2	0.001
Nitric oxide	NO	0.0005
Hydrogen sulfide	H_2S	0.00005

C. Weather

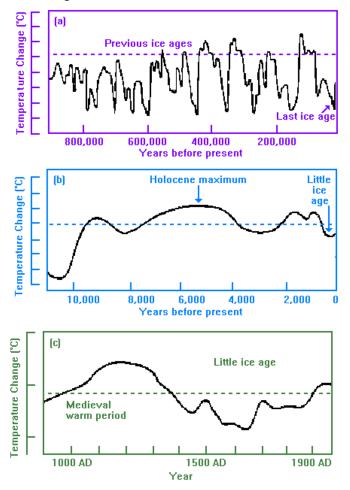
- 1) **weather**—*daily variations* in temperature, precipitation, wind, pressure, etc.
- 2) **climate**—*long-term weather patterns* of an area
 - tropical, polar, middle-latitude climates
- 3) **convection currents** making up *Hadley cells*: warm air rises, cooler air sinks

- 4) meteorology—the study of the atmosphere and its changes
- 5) *air masses—large bodies of air with the same temperature and moisture*
 - a) maritime polar—(mP)—moist and cool air mass
 - b) *maritime tropical*—(mT)—*moist* and *warm* air mass
 - c) *continental polar*—(cP)—*dry* and *cool* air mass
 - d) continental tropical—(cT)—dry and warm air mass
 - e) continental arctic—(cA)—very dry and cold Arctic air mass
- 6) **fronts**—air mass boundaries
 - a) regions of change
 - b) can be cold, warm, stationary, or occluded
- 7) **monsoons**—*climatic systems anywhere in which the moisture increases dramatically in the warm season*
- 8) **jet stream**—*current of fast moving air found in the upper levels of the atmosphere*

20.2 Notes

- II. Climate
 - A. Climates in the Past

From nasa.gov



1) Milankovitch cycles—time periods of oscillations

- 2) How do we know about past climate?
- a) "The *geological record* of carved mountain valleys, scratched bedrock, and glacial debris and moraines gives evidence of the past several million years.
- b) Cores have been removed from the *ice* at Vostok Station in Antarctica. The longest cores are about 2000 meters, sampling layers of ice deposited as early as 160,000 years ago. The *ice trapped bubbles of air when it froze. The ratio of oxygen isotopes in this air indicates the average air temperature at the time the bubble was trapped in ice. The bubbles also trap atmospheric greenhouse gases that can be measured.*
- c) *Tree rings* provide a record of the weather back 3,000 years in some cases, and hundreds of years in many areas.
- d) *Fossil plants and the distribution of pollen* show that vegetation has changed, consistent with changing climate.
- e) The *historical record* speaks to us for some 2,000 years and there have been real quantitative measurements since about 1850.
- f) Pollen from plants, buried in shallow deposits of earth, indicate the distribution of vegetation since the last glaciation, about 20,000 years ago."

3) **Ice Ages**—"intervals of time when large areas of the surface of the earth are covered with ice sheets (large continental glaciers)

from http://www.museum.state.il.us/exhibits/ice_ages/when_ice_ages.html

- a) describes long, generally cool intervals of Earth history (tens to hundreds of millions of years) during which glaciers advanced and receded
- b) shorter time periods (tens of thousands of years) during which glaciers were near their maximum extent ('glaciations')
- c) the term 'Ice Age' is sometimes used to refer to the last major glaciation that occurred in North America and Eurasia. When used in this way, the first letters of both words are often capitalized."



Four Geologic Times of Glaciations

B. Ocean and Atmosphere

1) oceans' importance

From MIT: "Understanding the circulation and CO_2 biogeochemistry of the oceans is key to our ability to predict and assess the future evolution of climate."

- a) role in hydrologic cycle
- b) *regulation of heat and moisture*
- c) ocean currents move heat as well as water (convection currents, horizontal currents)
- d) oceanic physical and biogeochemical processes are major regulators of natural atmospheric carbon dioxide (as well as being an important sink of fossil fuel CO₂)
- e) high specific heat of water (4.184 J/g°C): heats up and cools downs slowly

(see specific heat practice problems)

2) The Oceanic Conveyor System

a) definition—*a global system that continually exchanges water, heat, and salt among all the oceans and between the surface layer and the deep water*

b) warm, poleward flowing surface currents cool as they lose heat to the air and water

c) through *thermohaline convection* at high latitudes, the resulting cold, relatively salty near-surface water sinks into the deep ocean, then flows slowly toward the equator in the deep current

From MIT:

"Two regions in the North Atlantic, to the north and to the south of Iceland, are at present the locations in which most of this sinking occurs. The resulting deep current of cold, salty (i.e., dense) water flows southward, then around the southern tip of Africa, across the southern Indian Ocean, passes east of Australia, and ultimately *into the North Pacific, where it upwells to the surface*.

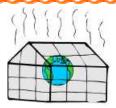
Surface water from the North Pacific moves south, passing between Asia and Australia, around southern Africa (this time heading west), and then across the South Atlantic, finally *connecting to the Gulf Stream to flow north* once more.

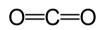
For most of this journey, the surface water is heated by the Sun and collects fresh water from river outflow to become progressively more buoyant. Only when it starts up the Gulf Stream does loss of heat to the air and evaporation lead to increasing density and lack of buoyancy.

The oceanic conveyor appears to susceptible to '*mode switching*', that is, it can exist in more than one configuration."

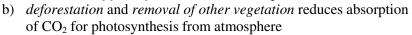
20.3 Notes

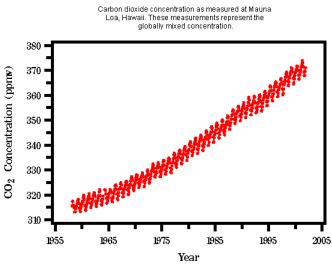
- *human-made* = **anthropogenic**
- from biological processes = biogenic
- *from geochemical activity* = **geogenic**
- III. Global Climate Change
 - A. The Earth as a Greenhouse
 - 1) warming processes
 - a) greenhouse effect—heating up of the earth's atmosphere
 - first recognized in 1827
 - incoming solar radiation is absorbed by the earth's surface
 - infrared radiation or IR is radiated out from the ground as heat
 - *IR is absorbed and back-radiated by greenhouse gases and is trapped in the troposphere*
 - b) greenhouse gases (GHG)—any gases contributing to this effect2) global cooling
 - a) **nlanetary albedo**
 - a) **planetary albedo**—*reflection of solar radiation from low-level clouds back into space*
 - (high-level clouds contribute to the greenhouse effect)
 - b) *volcanism*—contributes particulates and aerosols
 - c) anthropogenic (human-made) sulfate $(SO_4)^{2-}$ aerosols
 - B. Carbon Dioxide (CO₂): Major Greenhouse Gas
 - 1) causes of increased atmospheric CO_2





a) combustion of fossil fuels increases atmospheric CO₂





Source: Dave Keeling and Tim Whorf (Scripps Institution of Oceanography)

- 2) Review of the CARBON CYCLE
- C in CO₂ in atmosphere and in water is moved to C in glucose by **PHOTOSYNTHESIS** by producers. $6CO_2 + 6H_2O + energy \rightarrow C_6H_{12}O_6 + 6O_2$
- C in glucose is moved to C in CO₂ by CELL RESPIRATION: C₆H₁₂O₆ + 6O₂ \rightarrow 6CO₂ + 6H₂O + energy
- C in glucose is moved to C in organic molecules by synthesis reactions in living things.
- C in organic molecules is moved to C in CO₂ by combustion.
- C in organic molecules in organisms is moved to C in fossil fuels over millions of years by pressure, heat, and bacterial action.
- C in limestone (CaCO₃) is released slowly to C in CO₂ when exposed to oxygen and/or water.
- Largest reservoir of carbon: sedimentary rocks (limestone)
- Second largest reservoir of carbon: top 300 m of ocean (dissolved CO₂), living things in ocean.
- In water:
 - $CO_2 + H_2O \rightarrow HCO_3^{-1}$ (bicarbonate ions) + CO_3^{2-1} (carbonate ions)

 $Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3$ (calcium carbonate) in shells/skeletons of aquatic organisms $CaCO_3 \rightarrow$ buried, long period of time, pressure \rightarrow limestone

B. Other Greenhouse Gases

1) water vapor: $H_2O(g)$

From <u>http://lwf.ncdc.noaa.gov/oa/climate/gases.html#wv</u> : *"Water vapor is the most abundant greenhouse gas in the atmosphere...* However, changes in its concentration is also considered to be a result of climate <u>feedbacks</u> related to the warming of the atmosphere rather than a direct result of industrialization. The feedback loop in which water is involved is critically important to projecting future climate change, but as yet is still fairly poorly measured and understood."

- 2) *methane: CH*⁴
 a) the simp
 b) "lifetime
 - a) the simplest *hydrocarbon* (*structure containing H and C*)
 - b) "lifetime" in the atmosphere is relatively brief (10-12 years)



Η

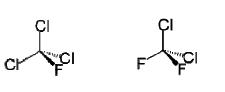
- c) sources of methane
 - *fermentation—cell respiration by partial breakdown of glucose*
 - "swamp gas" in wetlands
 - livestock
 - landfills
 - natural gas production
 - manure
 - coal mining
 - paddy rice farming
 - covered vented landfill emissions
 - newer style fully vented septic systems
- 3) nitrous oxide (AKA dinitrogen monoxide): N₂O

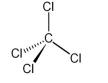
$$N \equiv N^+ - O^- \quad \text{and} \quad N^- = N^+ = O$$

- a) N_2O is a resonance structure ("flipping" of bonds)
- b) sources of nitrous oxide
 - agriculture
 - combustion of biomass
 - combustion of fossil fuels (lower conc.)
 - anaerobic denitrification
 - acts as a greenhouse gas and contributes to ozone depletion
- 4) CFCs and other halocarbons (halons) anthropogenic emissions only
 - a) **CFC = chlorofluorocarbon** (hydrocarbon halogenated specifically with Cl and F)
 - b) 10,000 times more efficient than CO₂ in absorbing IR radiation
 - c) uses: refrigerants, industrial solvents, fire suppressants
 - d) types of CFCs
- CCl₃F: trichlorofluoromethane, CFC-11, Freon-11, or R-11
- CCl₂F₂: dichlorodifluoromethane, CFC-12, Freon-12, or R-12
- *CCl₄: carbon tetrachloride or tetrachloromethane*
- CCl₂FCClF₂: 1,1,2-Trichloro-1,2,2-trifluoroethane, CFC-113, F-113, R-113

e) hydrochlorofluorocarbons (HCFCs):

• *CHClF*₂: *chlorodifluoromethane*, *difluoromonochloromethane*, *HCFC*-22, *Freon*-22, *Halocarbon* R22, *or* R-22





 CCl_4



CFC-11

CFC-12

CFC-113

HCFC-22

CONCENTRATIONS OF CFCs and halocarbons

<u>Gas</u> (1998)	Amount by volume
CFC-11	268 ppt (parts per trillion)
CFC-12	533 ppt
Carbon tetrachloride (CCl ₄)	102 ppt
CFC-113	84 ppt
HCFC-22	69 ppt

5) other gases <u>http://lwf.ncdc.noaa.gov/oa/climate/gases.html#wv</u> a) *carbon monoxide (CO)*

"Carbon monoxide (CO) is not considered a direct greenhouse gas, mostly because it does not absorb terrestrial thermal IR energy strongly enough. However, CO is able to modulate the production of methane and tropospheric ozone."

b) Volatile Organic Compounds (VOCs)

"Volatile Organic Compounds (VOCs) also have a small direct impact as greenhouse gases, as well being involved in chemical processes which modulate ozone production. VOCs include nonmethane hydrocarbons (NMHC), and oxygenated NMHCs (eg. alcohols and organic acids), and their largest source is natural emissions from vegetation. However, there are some anthropogenic sources such as vehicle emissions, fuel production and biomass burning. Though measurement of VOCs is extremely difficult, it is expected that most anthropogenic emissions of these compounds have increased in recent decades."

c) long-lived synthesized gases

- CF₄ (carbon tetrafluoride)
- SF_6 (sulfur hexafluoride)
- SF₅CF₃ (trifluoromethyl sulfur pentafluoride)
- perfluorocarbons (PFCs; fluorinated hydrocarbons)

C. Amount of Warming and its Probable Effects

- 1) contributions of modeling
 - a) GCMs—general circulation model or global climatic models
- *Simple general circulation model (SGCM)*, a minimal GCM studying atmospheric processes; not suitable for future climate projections
- *Atmospheric GCMs (AGCMs)* model the atmosphere and typically contain a land-surface model as well; and impose sea surface temperatures
- *Oceanic GCMs (OGCMs)* model the ocean with fluxes from the atmosphere imposed; may or may not contain a sea ice model
- Coupled atmosphere-ocean GCMs (AOGCMs) combine AGCMs and AOCGMs.
 - 2) U.S. National Assessment
 - a) search by region
 - b) sectors: Agriculture, Water, Health, Forests, Coastal Areas & Marine Resources
 - c) U.S. Climate Action Reports (CAR): periodically since 1989

Executive Summary Excerpts:

Changes in the ozone layer

• Springtime Antarctic ozone depletion due to halogens has been large throughout the last decade.

• In some recent cold Arctic winters during the last decade, maximum total column ozone losses due to halogens have reached 30%.

Changes in uv radiation

• Additional measurements continue to confirm that decreases in ozone column amounts lead to increases in UV radiation.

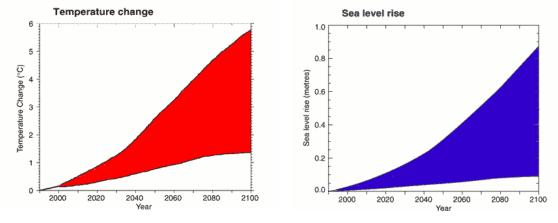
The ozone layer and climate change

- The understanding of the impact of ozone depletion on climate change has been strengthened.
- Other atmospheric changes influence both the ozone layer and the climate system.
- New research has begun to explore the coupling between climate change and the recovery of the ozone layer.
 - 3) Global Impacts of Future Warming
 - a) regional climate changes
 - *affect agriculture*
 - affect rainfall and droughts
 - affect oceanic circulation
 - more exaggerated in the poles than at the equator
 - b) weather changes
 - *more intense El Niño events—warm*, nutrient-poor ocean currents in the equatorial Pacific Ocean
 - ENSO El Niño Southern Oscillation
 - o occurs yearly in December
 - o affects climate
 - o affects fishing industry

(La Niña—*cold* ocean currents in the equatorial Pacific Ocean)

- warmer and wetter European winters
- increased yearly U.S. rainfall; increased heavy storms
- c) rising sea level ~ 2 mm/year
 - glacier and ice field melting
 - thermal expansion





D. Actions on Climate Change

1) **IPCC** from <u>http://www.ipcc.ch/</u>

"Intergovernmental Panel on Climate Change (IPCC) was established in 1988 by two United Nations organizations, the World Meteorological Organization (WMO) and the United Nations Environment Programme (UNEP) to assess the 'risk of human-induced climate change'."

- a) The IPCC has three working groups (WGs) and a task force
 - WGI: Scientific aspects of climate
 - WGII: Vulnerability, consequences, and options
 - WGIII: Limitation and mitigation options
 - Task Force: National Greenhouse Gas Inventories Program
- b) Assessment reports (AR) done periodically
- c) Reports researched and written by hundreds of experts
- d) Fifth assessment report being written now
- e) Summaries of the 2007 (fourth assessment) report:

ATMOSPHERIC CHANGES

- "Carbon dioxide, methane, and nitrous oxide have increased markedly as a result of human activities since 1750 and now far exceed pre-industrial values.
- The amount of carbon dioxide in the atmosphere in 2005 (379 ppm) exceeds by far the natural range of the last 650,000 years (180 to 300 ppm).
- The amount of methane in the atmosphere in 2005 (1774 ppb) exceeds by far the natural range of the last 650,000 years (320 to 790 ppb).
- The primary source of the increase in carbon dioxide is fossil fuel use, but land-use changes also make a contribution.
- The primary source of the increase in methane is very likely to be a combination of human agricultural activities and fossil fuel use. How much each contributes is not well determined.

WARMING

- Eleven of the twelve years in the period (1995-2006) rank among the top 12 warmest years in the instrumental record (since 1850, towards the end of the Little Ice Age).
- Warming in the last 100 years has caused about a 0.74 °C increase in global average temperature. This is up from the 0.6 °C increase in the 100 years prior to the Third Assessment Report.
- Observations since 1961 show that the ocean has been absorbing more than 80% of the heat added to the climate system, and that ocean temperatures have increased to depths of at least 3000 m (9800 ft).
- Average Arctic temperatures increased at almost twice the global average rate in the past 100 years.
- It is likely that greenhouse gases would have caused more warming than we have observed if not for the cooling effects of volcanic and human-caused aerosols.
- Average Northern Hemisphere temperatures during the second half of the 20th century were very likely higher than during any other 50-year period in the last 500 years and likely the highest in at least the past 1300 years (a time near the beginning of the Little Ice Age).

ICE, SNOW, RAIN, OCEANS

- Mountain glaciers and snow cover have declined on average in both hemispheres.
- Losses from the land-based ice sheets of Greenland and Antarctica have very likely (> 90%) contributed to sea level rise between 1993 and 2003.

- Ocean warming causes seawater to expand, which contributes to sea level rising.
- Sea level rose at an average rate of about 1.8 mm/year during the years 1961-2003. The rise in sea level during 1993-2003 was at an average rate of 3.1 mm/year. It is not clear whether this is a long-term trend or just variability.
- Antarctic sea ice shows no significant overall trend, consistent with a lack of warming in that region.

2) United Nations Framework Convention on Climate Change

(UNFCCC) – document signed at the UNCED (United Nations Conference on Environment And Development) conference in Rio in 1992

3) **Kyoto Protocol** (December 1997)

a) background info.

From http://unfccc.int/kyoto protocol/items/2830.php :

"The Kyoto Protocol is an international agreement linked to the United Nations Framework Convention on Climate Change (FCCC). The major feature of the Kyoto Protocol is that it sets binding targets for industrialized countries and the European community for reducing greenhouse gas (GHG) emissions. These targets amount to an average of 5% against 1990 levels over the five-year period 2008-2012. The major distinction between the Protocol and the Convention is that while the Convention *encouraged* industrialized countries to stabilize GHG emissions, the Protocol *commits* them to do so."

b) implementation

From http://unfccc.int/kyoto_protocol/items/2830.php and www.about.com

- Kyoto Protocol countries must meet their targets primarily through national measures
 - o restrict companies, etc. emitting the most pollutants
 - o reduce emissions from vehicles
 - promote and use renewable, alternative energy sources
- three market-based mechanisms to assist in other ways:
 - o emissions trading the 'carbon market'
 - *clean development mechanism* (CDM)

... "allows a country to implement an emission-reduction project in developing countries, which can earn saleable *certified emission reduction (CER) credits*, each equivalent to one ton of CO_2 counted towards meeting Kyoto targets" *joint implementation* (JI)

joint implementation (JI)
 ... "allows a country to implement an emission-reduction or emission-removal project in other countries, which can earn saleable *emission reduction units* (*ERUs*), each equivalent to one ton of CO₂ counted towards meeting Kyoto targets"

c) An updated Kyoto protocol

- U.S., Canada, Russia, and Japan will not sign a new agreement. They object that developing countries are not required to make targeted emission cuts.
- <u>http://www.breakingnews.com/topic/kyoto-protocol</u> December 2012: "Almost 200 nations extended a weak U.N. plan for fighting global warming until 2020, averting a new setback to two decades of U.N. efforts that have failed to halt rising world greenhouse gas emissions. The extension of the Kyoto Protocol keeps it alive as the only legally binding plan for combating global warming, even though it will cover developed nations whose share of world greenhouse gas emissions is less than 15 percent."

d) role of the U.S.

- The U.S. signed but never ratified the original Protocol. The signature alone was merely symbolic, as the Kyoto Protocol was non-binding on the United States unless ratified.
- The America's Climate Security Act of 2007, the "Cap and Trade Bill," was proposed for greater U.S. alignment with the Kyoto goals.

20.4 Notes

- IV. Response to Climate Change
 - A. Responses
 - 1) **adaptation**—prepare for the changes and protect ourselves
 - a) Less Developed Countries Fund, Special Climate Change Fund
 - b) new research by U.N. committees
 - c) general poverty reduction and sustainable development
 - 2) **mitigation**—take action to reduce GHG emissions
 - a) Intergovernmental Panel on Climate Change (IPCC)
 - b) United Nations Framework Convention on Climate Change (FCCC)
 - c) United States Global Change Research Program (USGCRP) -http://www.globalchange.gov/
 - 3) Global Climate Change Initiatives (GCCI)

From <u>http://internal-voices.blogspot.com/2009/12/global-climate-change-voices-from.html</u> : "Global Climate Change Initiatives (GCCI) is an independent not-for-profit, non-governmental organization (NGO) whose mission is to partner with global institutions and individuals to develop new climate change initiatives. These initiatives will raise awareness, enhance behavioral change, empower bottom-up global governance and assess the effectiveness of current and future climate change programs and projects."

- B. Developments What can be done?
 - 1) CO_2 cap: Limit fossil fuel use in industry and transportation
 - 2) *Promote safe, regulated nuclear power use*
 - 3) Combat deforestation; promote reforestation projects
 - 4) Tighten building codes for energy efficiency
 - 5) Improve mass transit system
 - 6) Invest in renewable energy technology
- C. skepticism—why do anything at all?
 - 1) precautionary principle

Precautionary Principle: *Rio Declaration, 1992, Principle 15*

"In order to protect the environment the Precautionary Approach shall be widely applied by States according to their capabilities. Where there are threats of serious or irreversible damage, lack of full scientific certainty shall not be used as a reason for postponing cost-effective measures to prevent environmental degradation."

- Taking precautionary action before scientific certainty of cause and effect
- Setting goals
- Seeking out and evaluating alternatives
- Shifting burdens of proof
- Developing more democratic, thorough decision-making criteria/methods

2) **polluter pays principle** (polluters should pay for the damage they cause)

3) equity principle (the affluent should be concerned about the disadvantaged)

20.5 Notes

V. Depletion of the Ozone Layer

(see Ch. 21 for more info on tropospheric ozone as a pollutant)

- A. Radiation and Importance of the Shield
 - 1) solar radiation contains both UVA (less dangerous) and UVB rays (more dangerous)
 - 2) UVB is damaging ultraviolet radiation (DUV)
 - 3) ~1% of UVB reaches Earth
 - 4) **ozone shield**—stratospheric ozone (O₃)

Good ozone occurs naturally in the Earth's upper atmosphere -- 10 to 30 miles above the Earth's surface -- where it acts as a shield from the sun's harmful ultraviolet rays.

B. Formation and Breakdown of the Shield

1) chemical reactions

FORMATION OF OZONE:	$O_2 + UVB \rightarrow 2O^*$ $O^* + O_2 \rightarrow O_3$	(O* = singlet oxygen)
DESTRUCTION OF OZONE:	$\begin{array}{c} O^* + O_3 \not \rightarrow 2O_2 \\ O_3 + UVB \not \rightarrow O^* + O_2 \end{array}$	

2) halogens in the atmosphere – CFCs

from http://www.ratical.org/ratville/ozoneDepletion.html

"By the time they were banned internationally during the 1980s, CFCs had been used in roughly 90 million car and truck air conditioners, 100 million refrigerators, 30 million freezers, and 45 million air conditioners in homes and other buildings. *Because CFCs remain in the stratosphere for up to 100 years, they will deplete ozone long after industrial production of the chemicals ceases.*"

Chemical reactions involving chlorine $CFCl_3 + UV \rightarrow Cl^* + CFCl_2$ CHLORINE CYCLE: a) $Cl^* + O_3 \rightarrow ClO^* + O_2$ b) $O^* + ClO^* \rightarrow 2Cl^* + O_2$ $Cl^* + CH_4 \rightarrow HCl + CH_3^*$ One Cl atom could destroy 100,000 ozone molecules before being removed in the above rxn. CIO + NO₂ \rightarrow CIONO₂ CIONO₂ + HCl \rightarrow Cl₂ + HNO₃ CIOOCl + energy \rightarrow Cl^{*} + ClO₂ CIO₂ \rightarrow Cl^{*} + O₂

3) reactions involving NO_x

 $NO_{x} REACTIONS$ $NO + O_{3} \rightarrow NO_{2} + O_{2}$ $NO_{2} + O^{*} \rightarrow NO + O_{2}$ $O^{*} + N_{2}O \rightarrow 2NO$ $HO_{2}^{*} + NO \rightarrow OH^{*} + NO_{2}$ $(HO_{2}^{*}, \text{ the hydroperoxy radical, is an odd oxygen species produced in photochemical rxns.)$ $NO_{2} + OH^{*} \rightarrow HNO_{3}$

4) reactions involving bromine

 U
$Br^* + O_3 \rightarrow BrO + O_2$
$BrO + O^* \rightarrow Br + O_2$

- 5) The Ozone "Hole"
 - a) actually a thinning, not a hole
 - b) first confirmed in 1985-1988
 - c) significant O_3 depletion was observed over the South Pole in the austral (S. Hemispheric) spring
 - d) **chlorine reservoirs** cause depletion of O₃ : high concentrations of Cl* and ClO

$HCI + 2O_3 + NO_2 \rightarrow HNO_3 (s) + 2O_2 + CIO$ (deposition)	$O_2 \rightarrow HNO_3 (s) + 2O_2 + ClO$ (deposition)	$HCl + 2O_3 + NO_2 \rightarrow HNO_3 (s) + 2O_2 + ClO$
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- 6) Controversy over ozone depletion
 - a) first wave of ozone depletion
 - *testing nuclear weapons in the atmosphere*
 - SST (supersonic transport) planes

The NASA High-Speed Research (HSR) Program was phased out in fiscal year 1999. Concorde planes are now popular museum attractions.

- b) second wave of ozone depletion
 - use of CFCs as refrigerants and propellants
 - (Rowland-Molina Theory linked CFCs to O₃ depletion)
- c) skeptics say this has always been going on but our equipment has not been effective enough to detect it

C. Coming to Grips with Ozone Depletion

- 1) international agreements
 - a) **Montreal Protocol** (*AKA "The Montreal Protocol on Substances That Deplete the Ozone Layer"*)
- international treaty designed to protect the stratospheric ozone layer
- originally signed in 1987 and begun in 1989
- four amendments: London Amendment (1990), Copenhagen Amendment (1992), the Montreal Amendment (1997) and Beijing Amendment (1999).

From the Protocol:

..."Recognizing that world-wide emissions of certain substances can significantly deplete and otherwise modify the ozone layer in a manner that is likely to result in adverse effects on human health and the environment ... Determined to protect the ozone layer by taking precautionary measures to control equitably total global emissions of substances that deplete it, with the ultimate objective of their elimination on the basis of developments in scientific knowledge ... Acknowledging that special provision is required to meet the needs of developing countries..."

b) The Vienna Convention for the Protection of the Ozone Layer (1985), which outlines responsibilities for protecting human health and the environment against the adverse effects of ozone depletion, established the framework for the Montreal Protocol

2) action in the U.S.

Clean Air Act (CAA) - amended in 1990: CAAA (a few minor changes since then)

- a) regulation servicing refrigeration and AC units
- b) ozone-depleting substance restrictions

- Class I substances:
 - o Group I: CFC-11, CFC-12, CFC-113, CFC-114, CFC-115
 - Group II: halon-1211, halon-1301, halon-2402
 - Group III: CFC-13, CFC-111, CFC-112, CFC-211, CFC-212, CFC-213, CFC-214, CFC-215, CFC-216, CFC-217
 - Group IV: carbon tetrachloride
 - Group V: methyl chloroform
- Class II Substances:

HCFC-21, HCFC-22, HCFC-31, HCFC-121, HCFC-122, HCFC-123, HCFC-124, HCFC-131, HCFC-132, HCFC-133, HCFC-141, HCFC-142, HCFC-221, HCFC-222, HCFC-223, HCFC-224, HCFC-225, HCFC-226, HCFC-231, HCFC-232, HCFC-233, HCFC-234, HCFC-235, HCFC-241, HCFC-242, HCFC-243, HCFC-244, HCFC-251, HCFC-252, HCFC-253, HCFC-261, HCFC-262

"PHASE-OUT OF PRODUCTION AND CONSUMPTION OF CLASS II SUBSTANCES.

(a) Restriction of Use of Class II Substances.- Effective January 1, 2015, it shall be unlawful for any person to introduce into interstate commerce or use any class II substance unless such substance

(1) has been used, recovered, and recycled;

(2) is used and entirely consumed (except for trace quantities) in the production of other chemicals; or

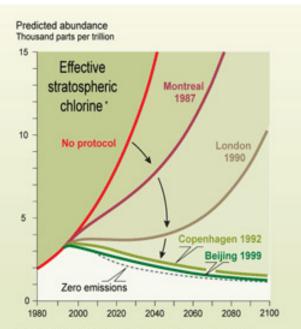
(3) is used as a refrigerant in appliances manufactured prior to January 1, 2020."

3) alternatives: *HFCs—hydrofluorocarbons*

from http://www.cmdl.noaa.gov/noah/flask/hfc.html

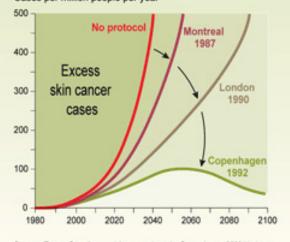
"Hydrofluorocarbons (HFCs) are compounds containing carbon, hydrogen, and fluorine. Certain chemicals within this class of compounds are viewed by industry and the scientific community as acceptable alternatives to chlorofluorocarbons and hydrochlorofluorocarbons on a long-term basis. Because the HFCs contain no chlorine they do not directly affect stratospheric ozone."

THE EFFECTS OF THE MONTREAL PROTOCOL AMENDMENTS AND THEIR PHASE-OUT SCHEDULES



^{*} Chlorine and bromine are the molecules responsible for ozone depletion. "Effective chlorine" is a way to measure the destructive potential of all ODS gases emitted in the stratosphere.

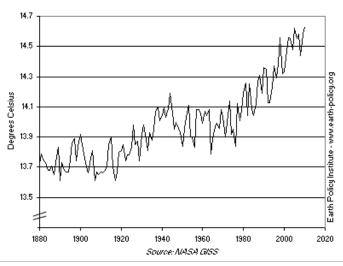
Cases per million people per year



Source: Twenty Questions and Answers about the Ozone Layer: 2006 Update, Lead Author: D.W. Fahey, Panel Review Meeting for the 2006 ozone assessment.







Atmospheric Concentrations of Carbon Dioxide, 1000-2004

