Environmental and Safety Engineering: 24 August, 2005 (B.Sc. Chem. Engg. 3rd Year)

- **Topic: Human Environmental Disturbances: Phenomena , Causes and Remedies**

Agenda:

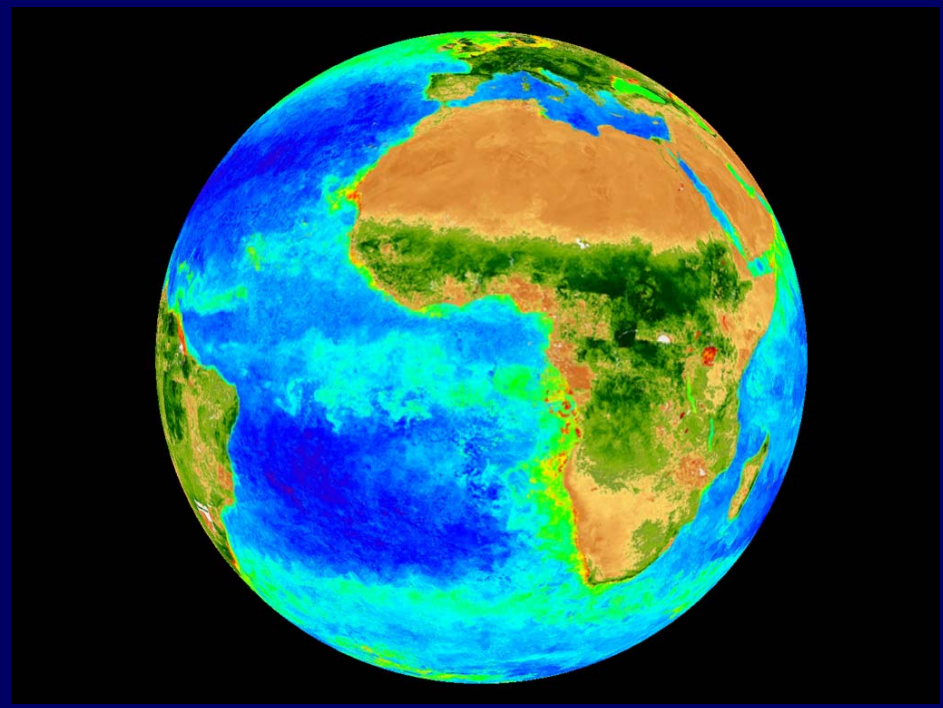
- Recap of Last Session on 17 August
- Completion of last Topic (Environmental Chemistry)
- Awareness Campaign of Environmental Problems
- Overview of Preventive Technologies
- Environmental Global Issues (Global Warming and Ozone Depletion) Causes and Effects
- Environmental Regional Issues (Acid Rain) Causes and Effects

Recap: Summarize your knowledge about (Recap: 17 August 2005)

- **Environmental Chemistry**
- Pollution is any **Undesirable change**

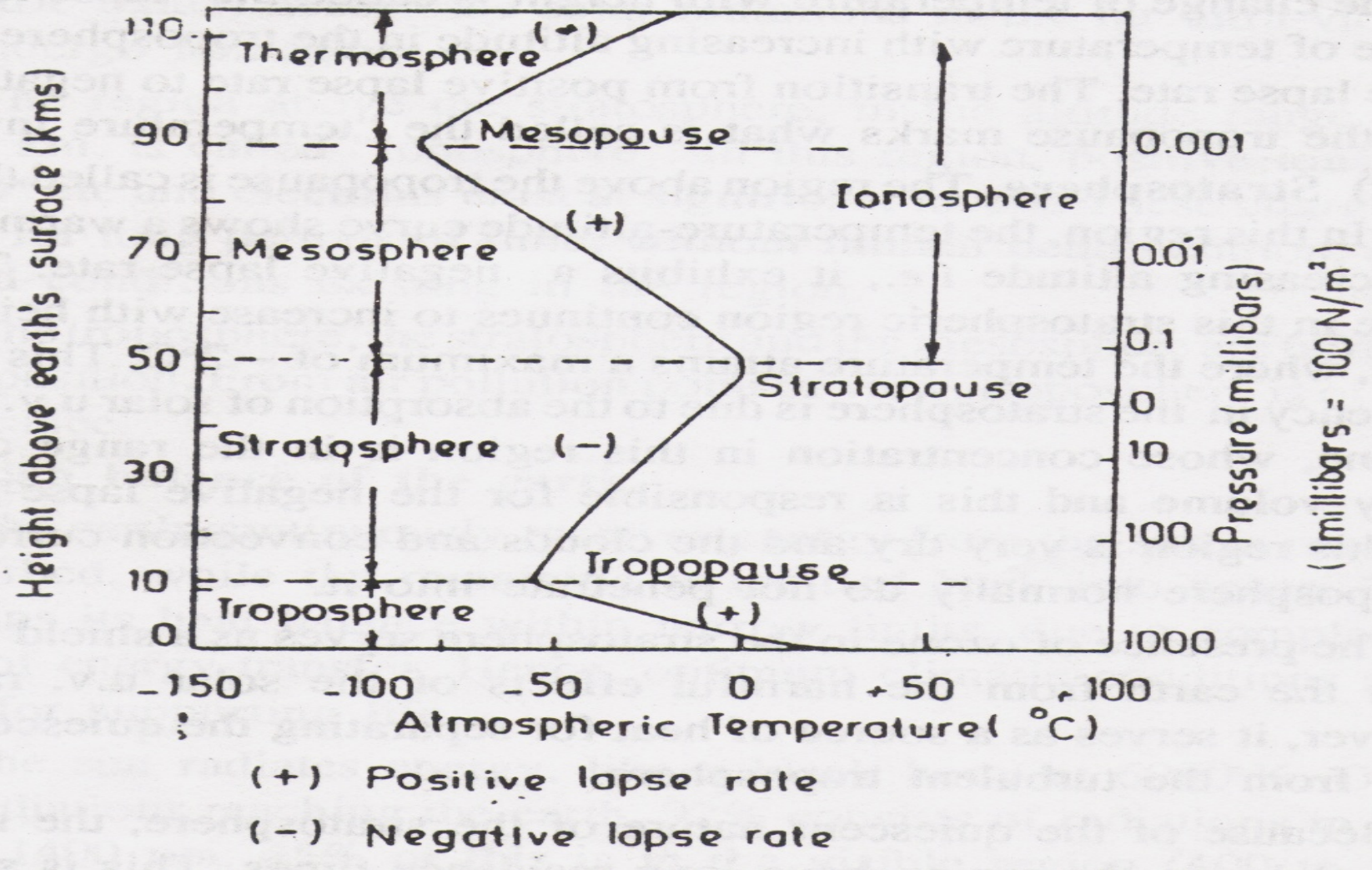
Environmental Segments

- **Hydrosphere**
- **Lithosphere**
- **Biosphere**
- **Atmosphere**



Recap: Atmospheric segments

Temperature & Pressure Distributions with Height



Electro-Magnetic Radiations and Atmospheric Composition (Gases, Ions/ Radicals, Particles)

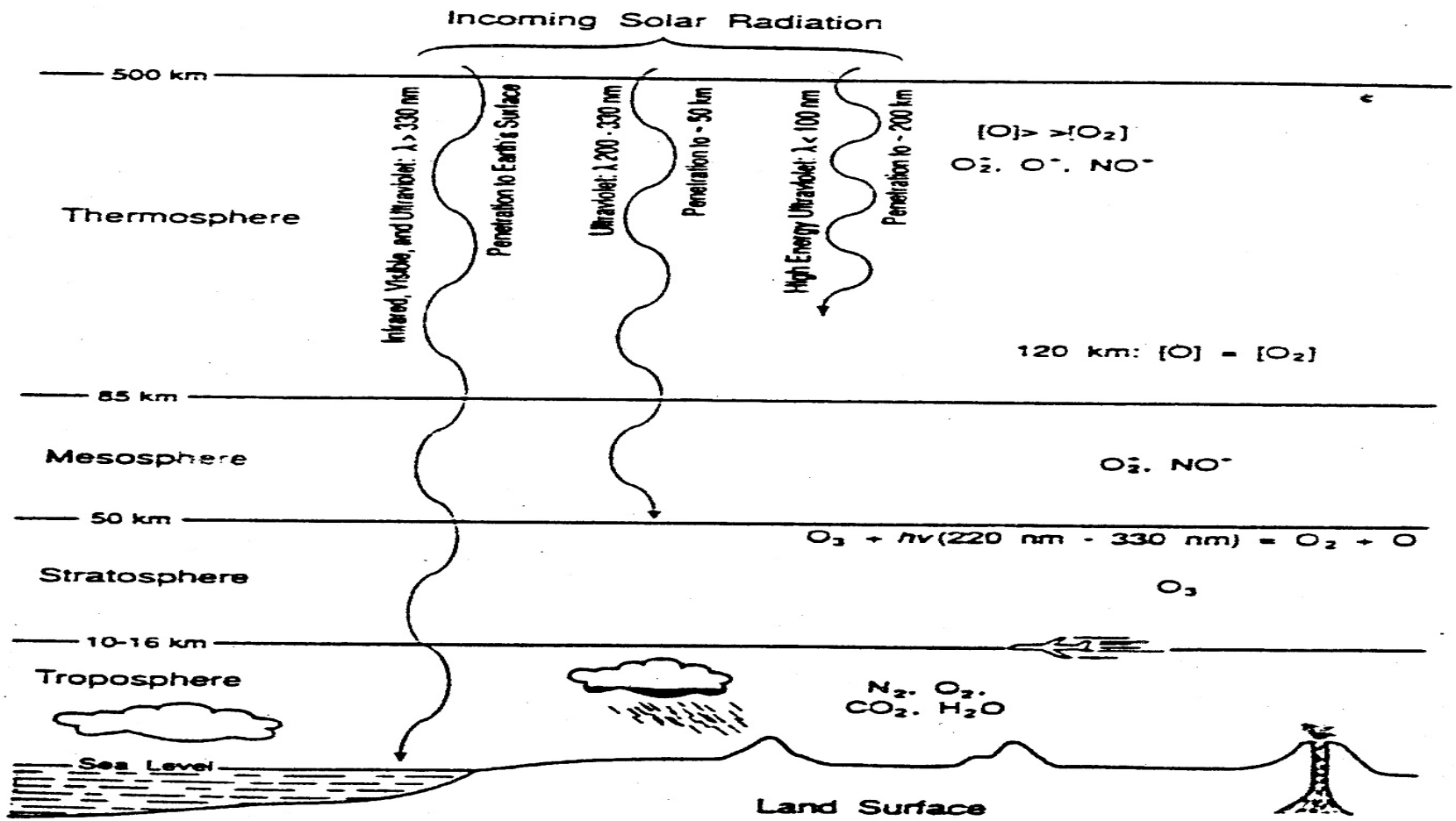


Figure 5.1: The structure of the atmosphere

Chemical Species & Particulates present in Atmosphere.

- Role of Particles (0.1u—100 u)
- Gases and Segments- there Roles
- Radiation balance
- Radiations in Troposphere
- Colloidal Sized (< 0.1 micron) are called Aerosol
- Mist, Smokes, Dust, Ash, Org. Particle from Vegetation, Bacteria, Fog, Pollen Grains

Role of Particles

- Electrification phenomenon
- Nuclei for condensation
- Fog & cloud formation
- Absorb gases.
- Change the absorption spectrum of gases
- Reactions on their surfaces- neutralization, photo chemical oxidation, decomposition of O_3, Reactions of SO_2, O_3, NO_2, etc.

Role of Particles contd.
Radiation Balance of Earth

- Recall e.m. waves and Radiant Heat Transfer.
- Sun is like black body at 6000^{o}K
- 92 % rad. in range 315 to 1400 nm.
- 40 % of above is in VISIBLE REGION
- Earth absorbs rad in VR and emits in INFRA RED REGION

Role of Particles contd.
Radiation Balance of Earth

- Heat input to our planet is 2.68x 10 ^{24} Joul/ year
- Earth is like a black body at approx. 288 K emission of rad. 4 000 to 50 000 nm
- 30% reflected back, 17% absorbed, 53% transmitted to earth crust.

Reactions in the Atmosphere

- Reactions involving oxides of nitrogen/ NOx, N2O/ N2O4

(Ozone depletion)

- $N_2O + UV = N_2 + O$ (most important)
- $N_2O + O = NO + NO$
- $NO + \mathbf{O_3} = NO_2 + O_2$
- $NO_2 + \mathbf{O_3} = NO_2 + O_2$

Reactions in the Atmosphere contd.

Oxides of Sulphur dioxide.

SOx

- $SO2 + hv = SO_2^{(Activated)}$
- $SO_2^{(Activated)} + O_2 = SO_4$
- $SO_4 + O_2 = SO_3 + O_3$ (dangerous at ground level/ in troposphere)

Acid in Atmosphere

- $4NO_2 + O_2 + 2H_2O = 4\ \mathbf{HNO_3}$
- $2NO_2 + \mathbf{O_3} + H2O = 2\ \mathbf{HNO_3} + O_2$
- $SO_3 + H_2O = \mathbf{H_2SO_4}$
- $SO_2 + ½\ O_2 + H_2O = \mathbf{H_2SO_4}$

Oxidation of Organic Compounds

- Photochemical and Chemical Reactions of Hydrocarbons like Aldehydes, Ketones, etc, and Contribute to **Smog** Formation
- R-H + O_2 + hv + M (other species) = various ions, activated atoms/ molecules, radicals involving organic radicals, C, O, etc.

Complex Reactions in Atmosphere

- HNO_2 & HNO_3 + hv = NO_2 + H ^{activated} / NO + HO ^{activated}/ NO_2 + HO ^{activated}
- SO_2 + HO ^{activated} + O_2 = HSO_3 ^{activated} + NO_2 ^{activated}
- All these activated ions/ radicals undergo various complex reaction.
- Difficult to understand the exact pathways and reaction mechanisms.

Environmental Awareness Campaign (early 1970s to date)

- Luxury of Clean Water and Air can't be afforded by Poor Countries.
- Mistakes of Developed Countries to Pollute Environment
- Legislations began in Late 1960s and 1970s
- US EPA 1970, followed by EU countries
- UN Conference on Human Environment 1972 Stockholm14

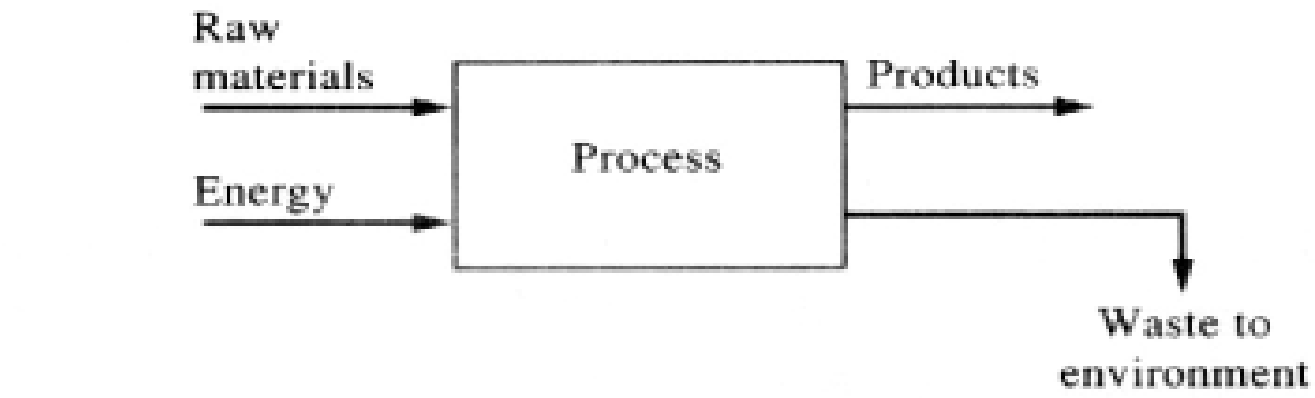
Environmental Awareness Campaign (Contd.)

- **UN efforts and under developing countries environmental protection programs**
- **Several UN conferences on population, food, women's right, desertification, human settlements, science and technology**
- **UN Earth Summit 1992; the largest event- but less effective**
- **UN Conference on Population and Development 1994 but again un productive.**
- **Economical Problems of Under developing Countries.**
- **Pak EPA 1997**
- **Volunteers Group** "International and National Efforts to Protect Environment"

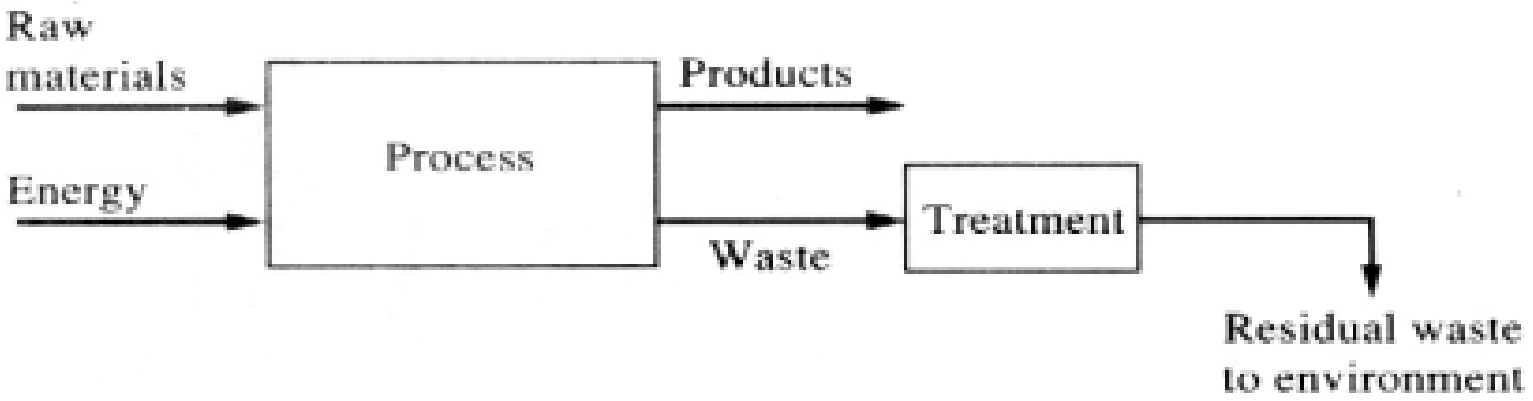
Preventive Technologies and Sustainable Development

- Environmental Protection- Pollution Control Approach
- Reactive Approach - End of Pipe Treatment (Dominated 20 years)
- Cost Minimization and Profit Maximization Philosophies- changed (Recall 5E Model of Business Excellence)
- Still Pollution Control is emphasized in Under developing and Poor Nations

Pollution Control to Pollution Prevention:

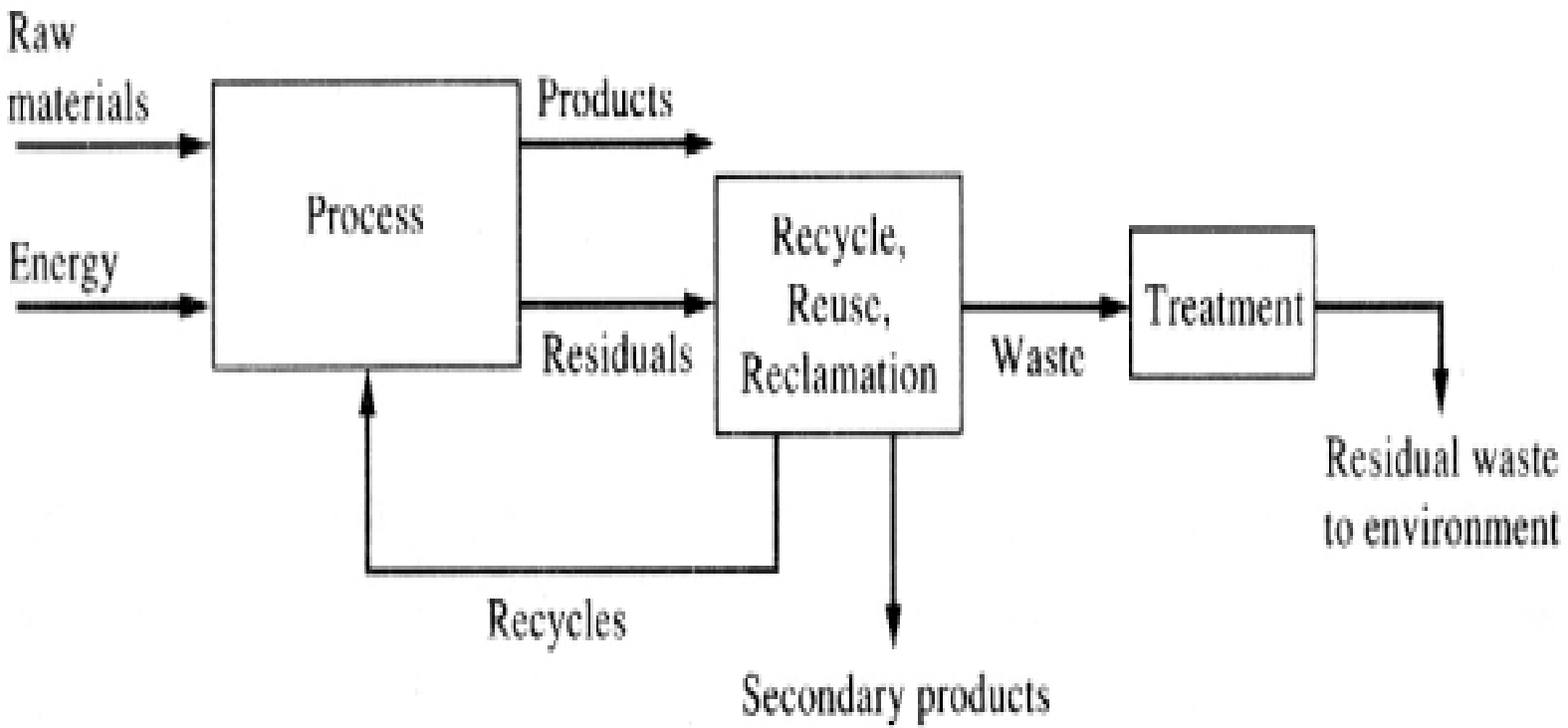


(*a*) **Past industrial practices**



(*b*) **Recent industrial practices**

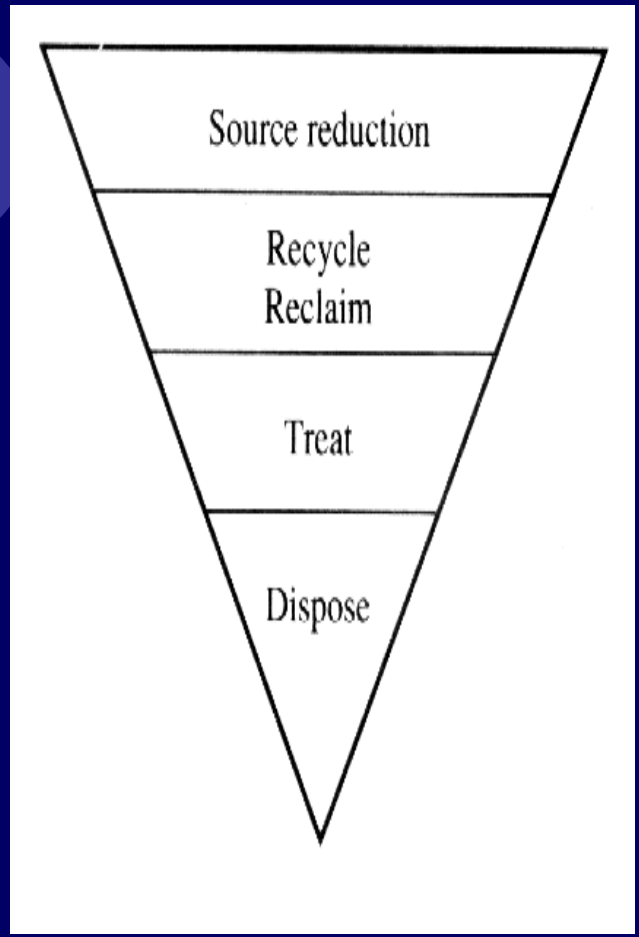
Pollution Control to Pollution Prevention (contd.):



(c) Current pollution prevention practices

Pollution Prevention: Preventive Technologies

- Modern philosophy "Green Organizations"
- **Sustainable Development**
  "philosophy which emphasizes on meeting the needs of present without compromising the ability of future generations to meet their needs"
- Environmental Protection-Preventive Approach

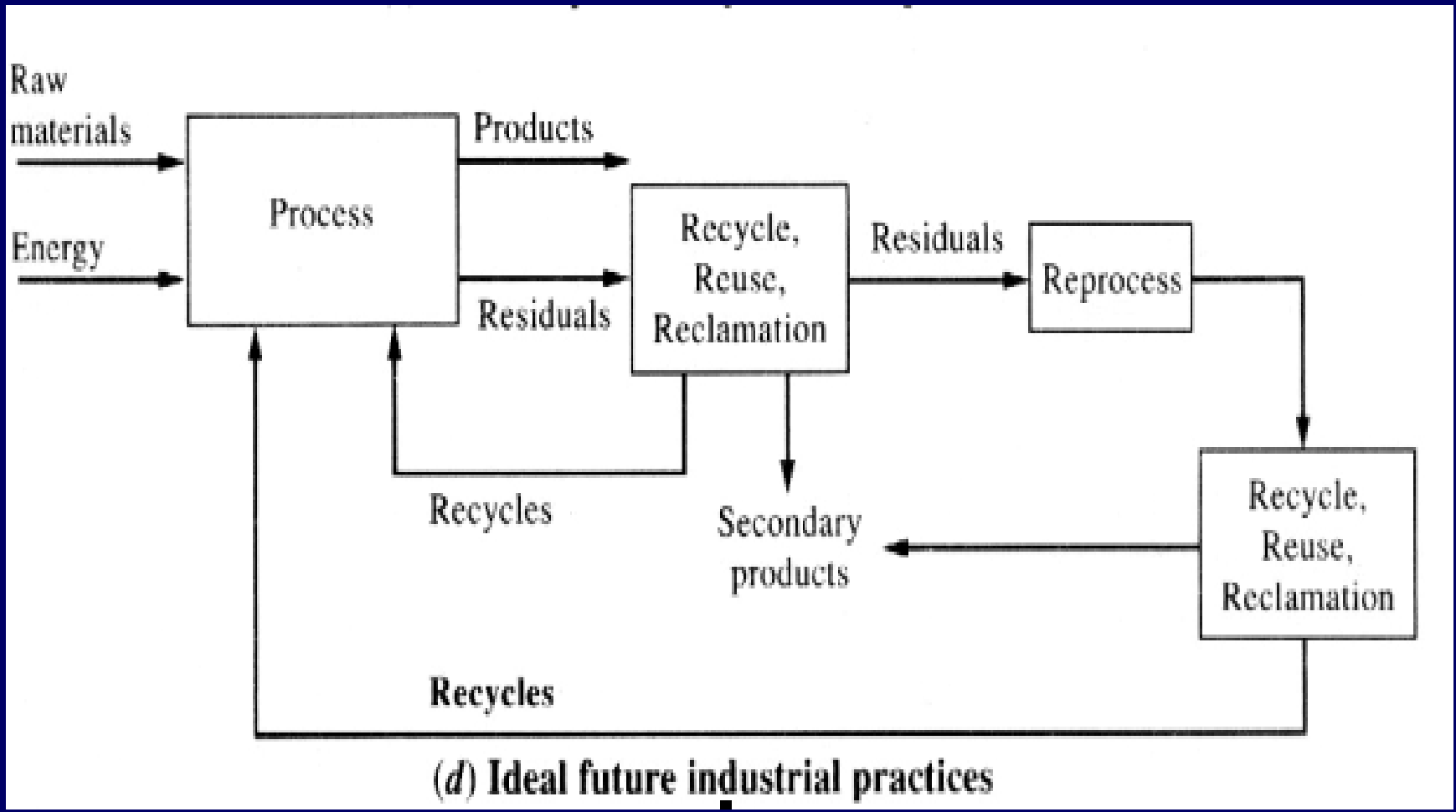


Pollution Prevention Hierarchy

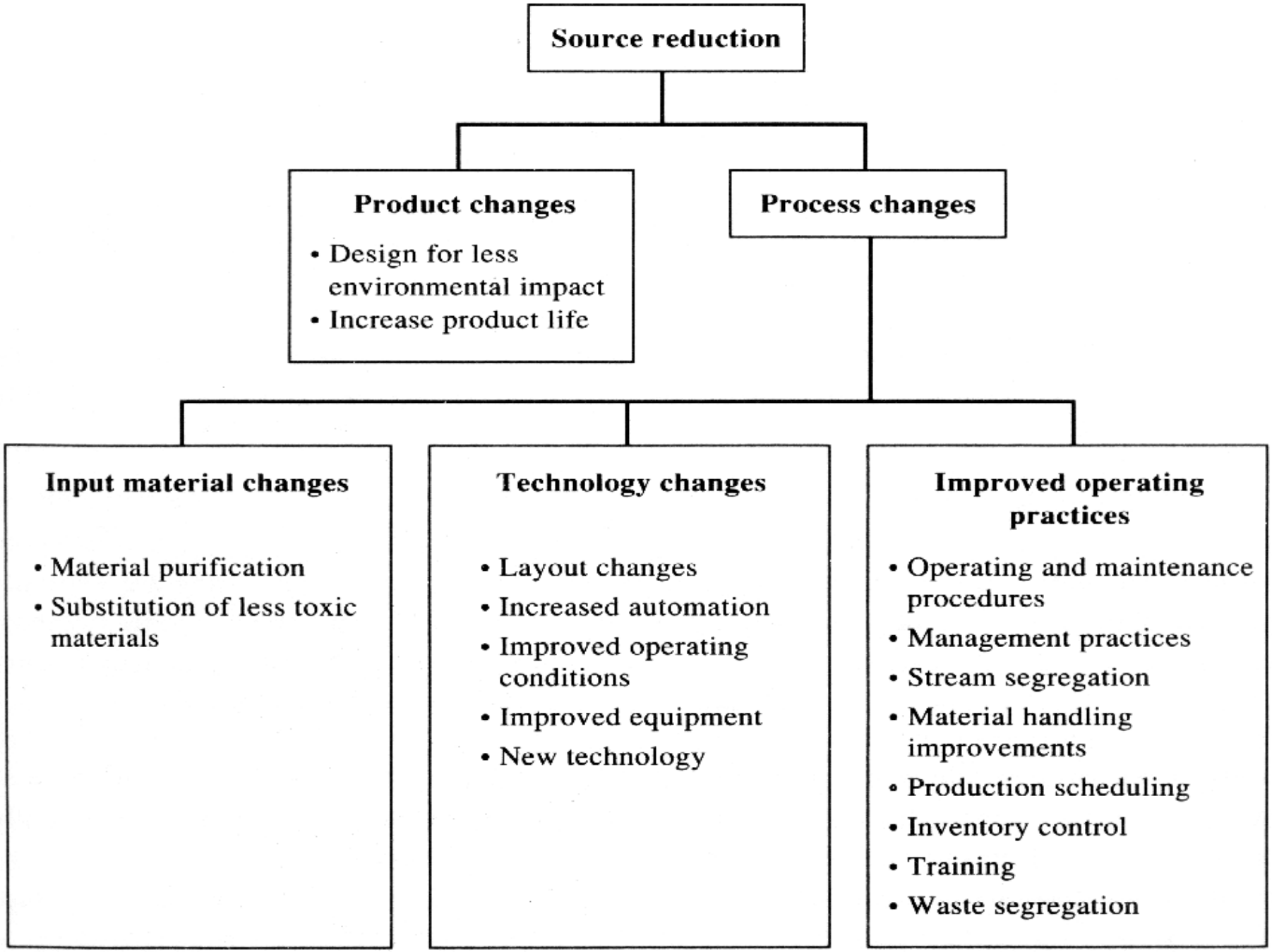
Preventive/ Future/ Emerging/ Cleaner Technologies

- Redesign of Process, Operations and Products under New Philosophy of SD
- New Technological Paradigm- Capital Intensive
- Low Operating cost and Long term economical returns
- Pro-active rather than Re-active Approach
- Within Process/ Operation Treatment rather than End of Pipe
- Parco's Sulfer Recovery Unit and SOx Problems
- "Green Fuel" as a Marketing Tool

Pollution Prevention: Preventive Technologies (Zero Level Pollution)



(*d*) Ideal future industrial practices


Source reduction
Product changes
• Design for less environmental impact
• Increase product life
Process changes
Input material changes
• Material purification
• Substitution of less toxic materials
Technology changes
• Layout changes
• Increased automation
• Improved operating conditions
• Improved equipment
• New technology
Improved operating practices
• Operating and maintenance procedures
• Management practices
• Stream segregation
• Material handling improvements
• Production scheduling
• Inventory control
• Training
• Waste segregation

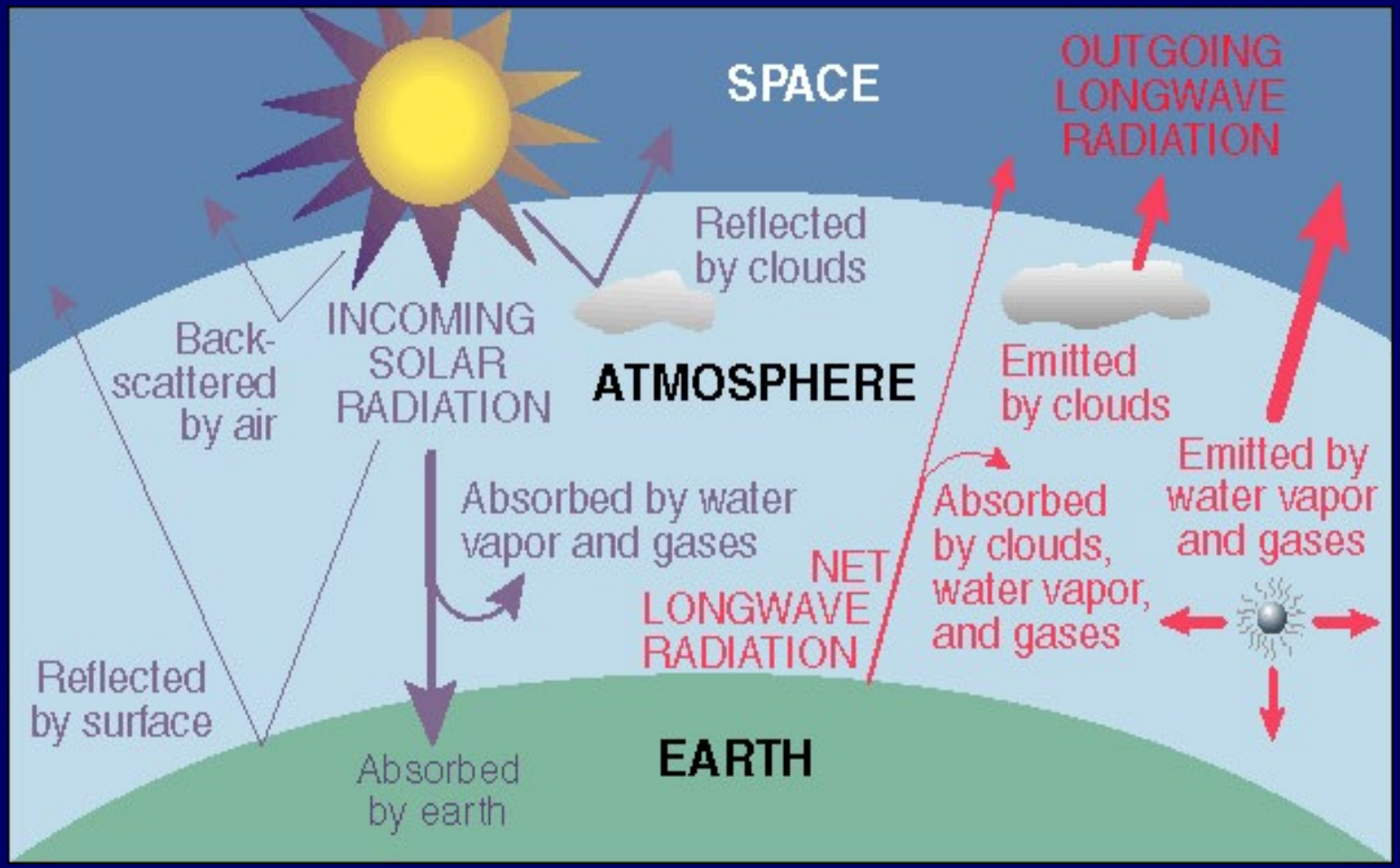
Global and Regional Environmental Issues

- Global Issues (Greenhouse Gasses Build up and Ozone Depletion
  - Impact is global not local
- Regional Issues (Acid Rain, Industrial and Photo chemical Smog)
  - Impact is regional neither global nor local

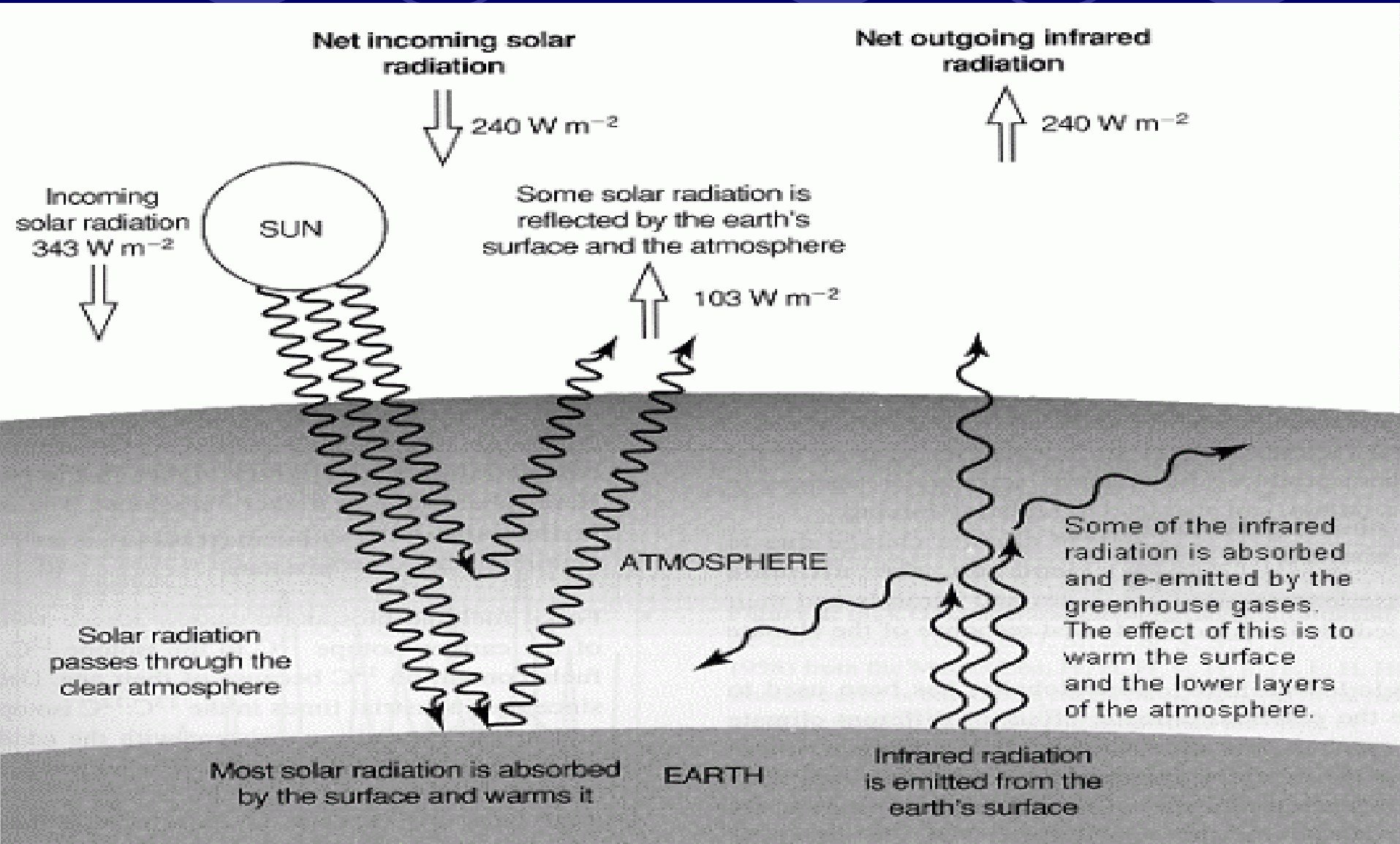
Science of Radiations

- E.m. waves: properties, energy and wave length, Energy, color and effects on human life
- Green House Gases: (4000 to 5000 nm UV, VR, IR)
- Water vapors absorption/Emission Regionn (5000 to 7000 nm and >17000 nm)
- CO_2 (4500 nm and >13500)
- O_3 (9600 nm)
- CH_4 Green House
- CFCs / HCFCs Green House
- What is a Green House gas?

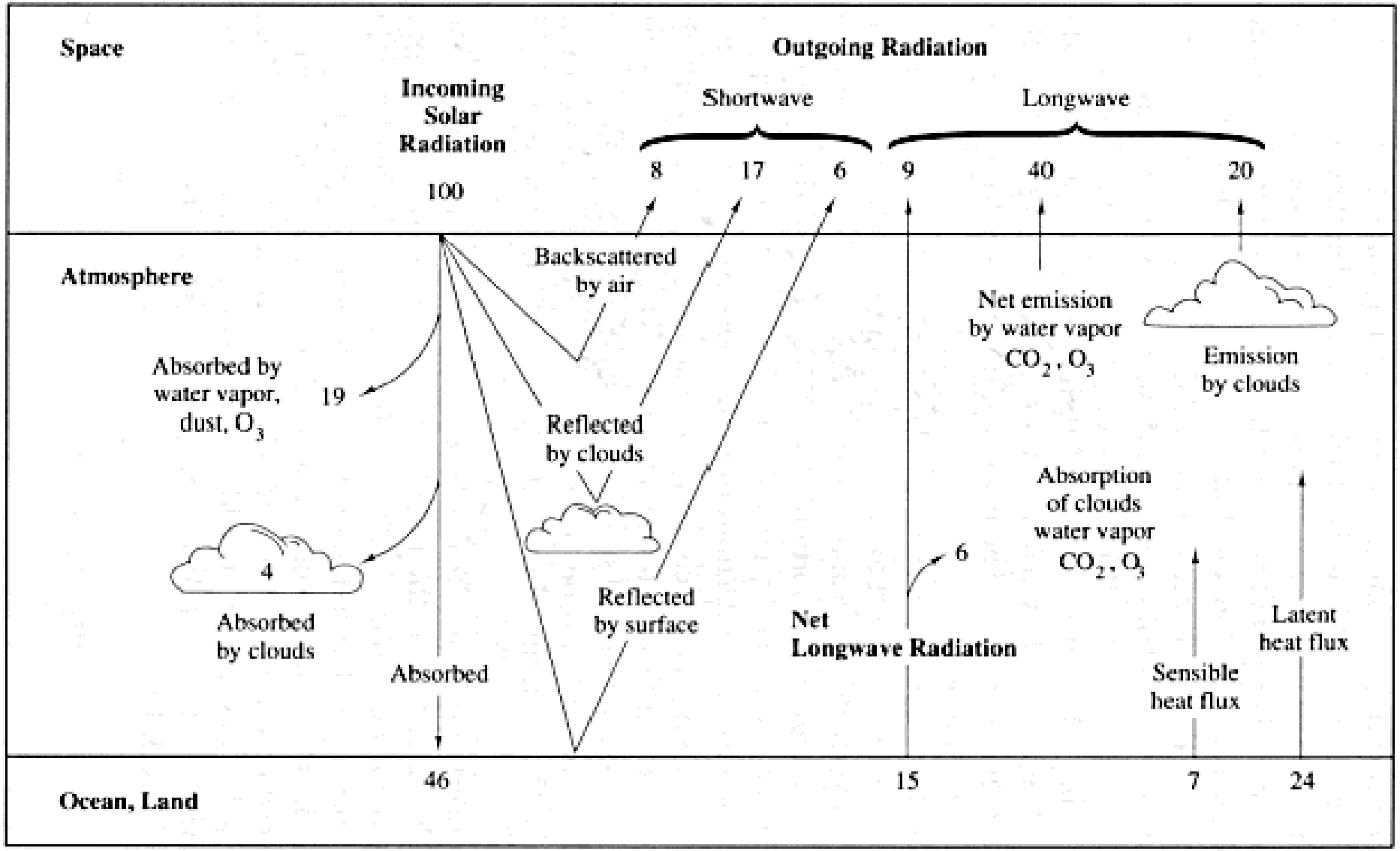
Effects of GH Gases Increase and Temperature Rise on ENVIRONMENT



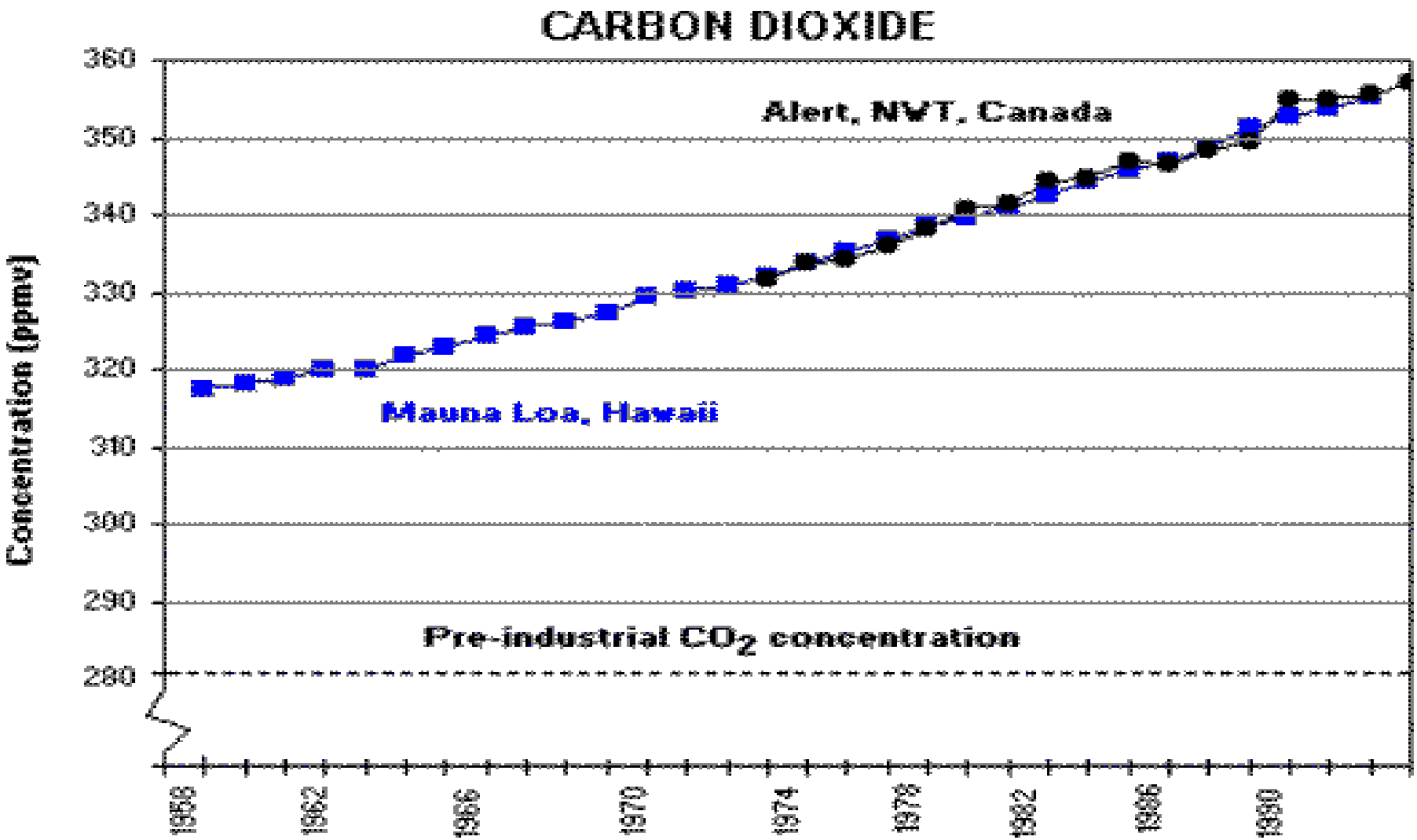
Radiation Balance on Earth:



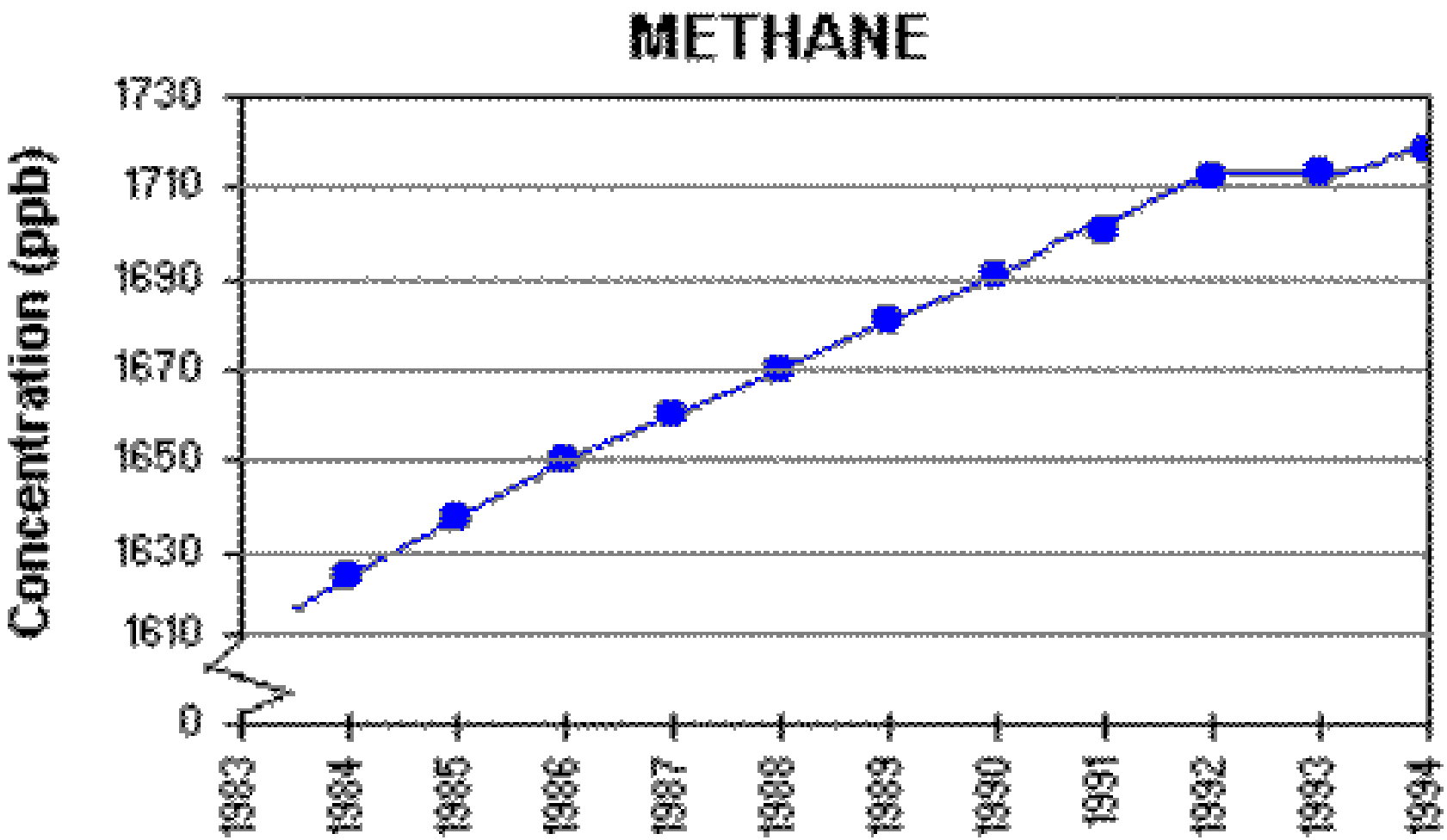
Radiation Balance on Earth Contd.:



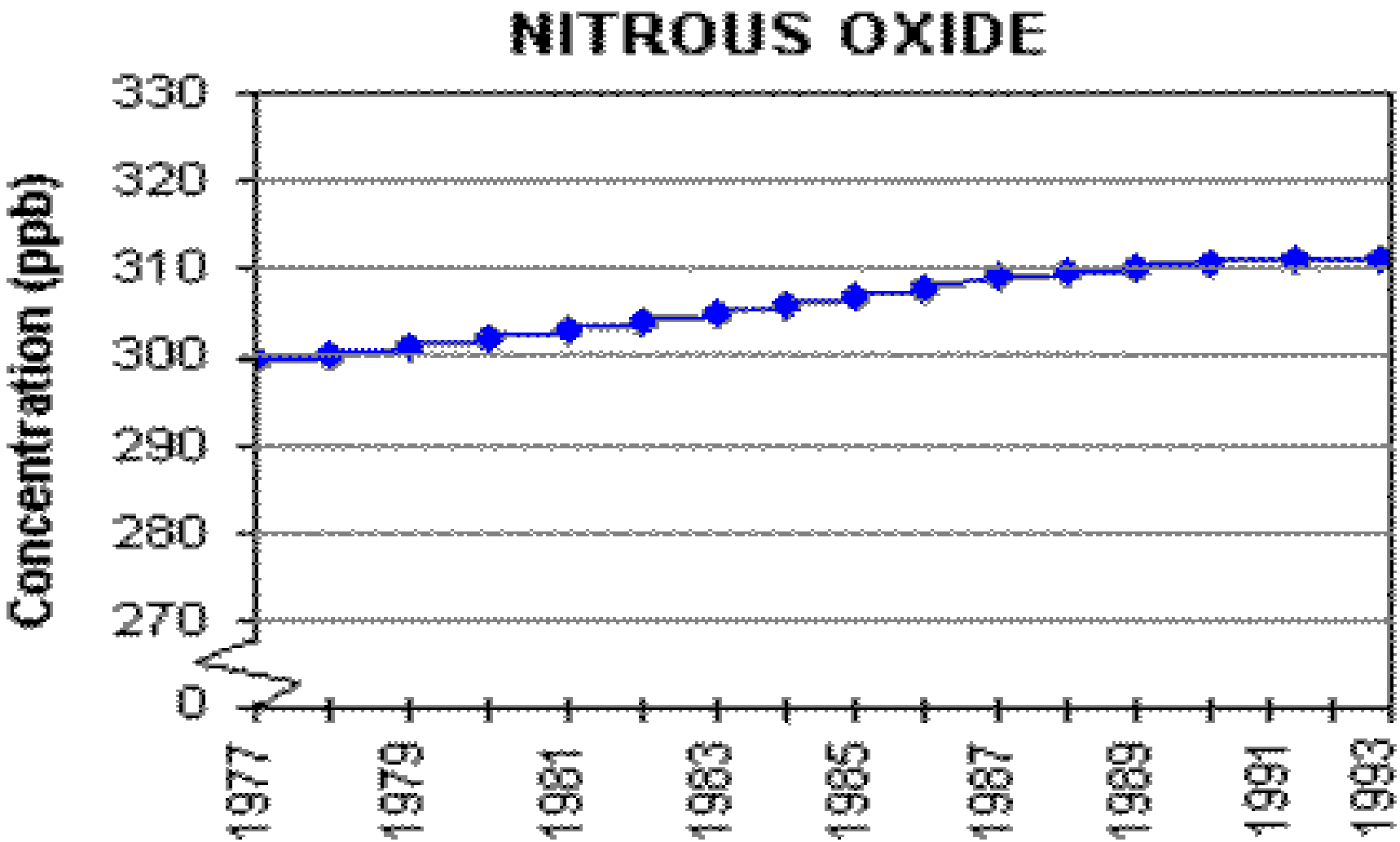
Greenhouse Gases Build UP:



Greenhouse Gases Build UP (Contd.):



Greenhouse Gases Build UP (Contd.):



Summery Greenhouse Effect Global Warming :

The Greenhouse Effect

Physics: Earth absorbs incoming solar radiation and then trys to cool by emitting long wavelength infrared radiation. This radiation is absorbed by Greenhouse Gases and hence can't escape → net effect should be to increase mean annual temperature.

Greenhouse Gases:

- **CO_2 → burning of carbon based fuels**
- **CH_4 → anerobic bacteria in rice fields, cows, sewage**
- **N_20 → fossil fuels and fertilizer**
- **CFCs → refrigeration and spray cans**

Importance:

- **CO_2 → 65% ; 0.4 % (150 years) ; 1**
- **CH_4 → 25% ; 1 % (70 years) ; 25**
- **CFCs → 10% ; 5 % (14 years) ; 10,000 !**

Summery

Greenhouse Effect and Global Warming (Contd.):

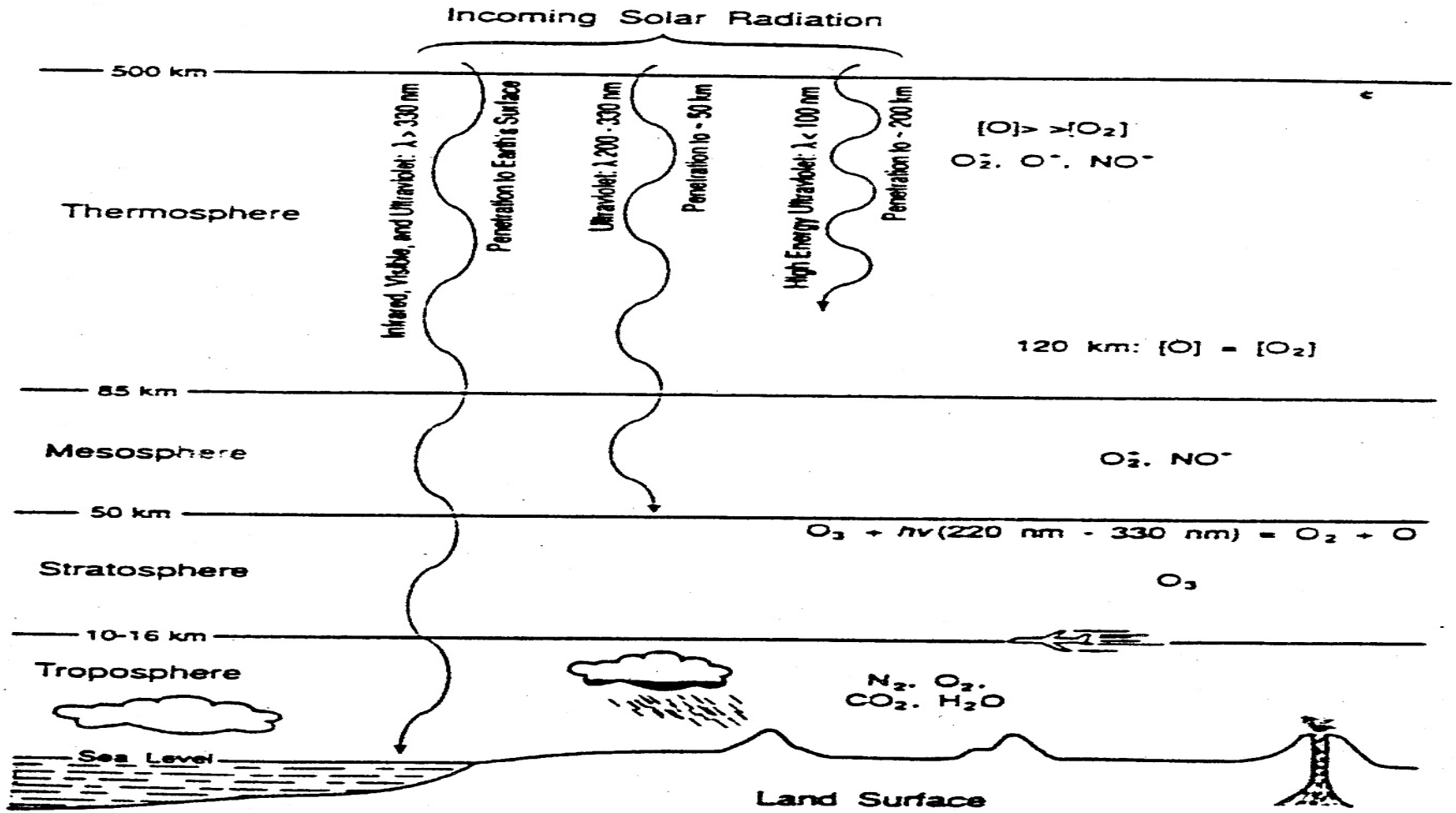


Figure 5.1: The structure of the atmosphere

Ozone O_3
Ozone Depletion: A Global Issue

- Triatomic form of oxygen
- A strong smelling, pale blue
- Photochemical product
- Pollutant which is produced due to presence of UV rad. in lower atmosphere
- Very Reactive, powerful Oxidizing agent, it is Undesirable on Ground

Ozone O_3 Contd.

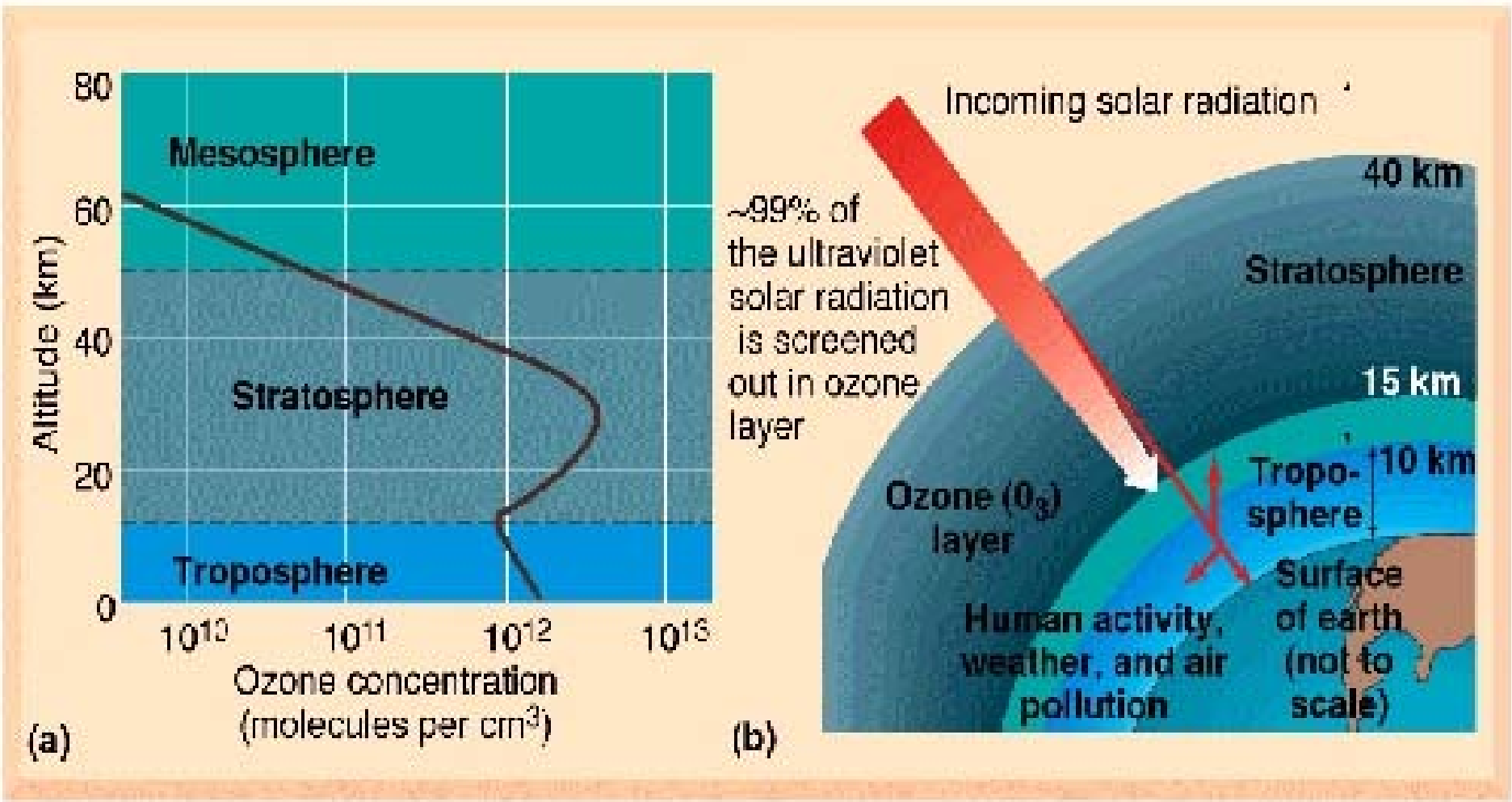
- Corrodes masonry, Darken Paints
- Unhealthy to Breathe
- Damage to DNA, Skin, Sunburn and Cancer, Death of Unicellular Organisms
- A Greenhouse Gas (already discussed)

Ozone O_3 Contd.

- **Ozone in the stratosphere, is also formed by solar ultra-violet light**
- **Created in N- Cycle naturally**
  O_2 + hv (242 nm) **= O + O**

  O + O_2 + M (third body, N_2 or O_2) **= O_3 + M**
- **Very Important for Life in Stratosphere**
- **It absorbs UV Radiation and protects the life (already discussed)**
- **Ozone formation and spread depends upon Atmospheric Temperature/ Season**

Reduction UV Radiation by Ozone:



(Source: Ozone concentrations from R. T. Watson, "Atmospheric Ozone," in J. G. Titus, ed., *Effects of Change in Stratospheric Ozone and Global Climate*, vol. 1, Overview, U.S. Environmental Protection Agency, p. 70.)

Ozone Depletion in Stratosphere
Contd.

- Reactions involving oxides of nitrogen/ NOx, N_2O/ N_2O_4

(Ozone depletion)

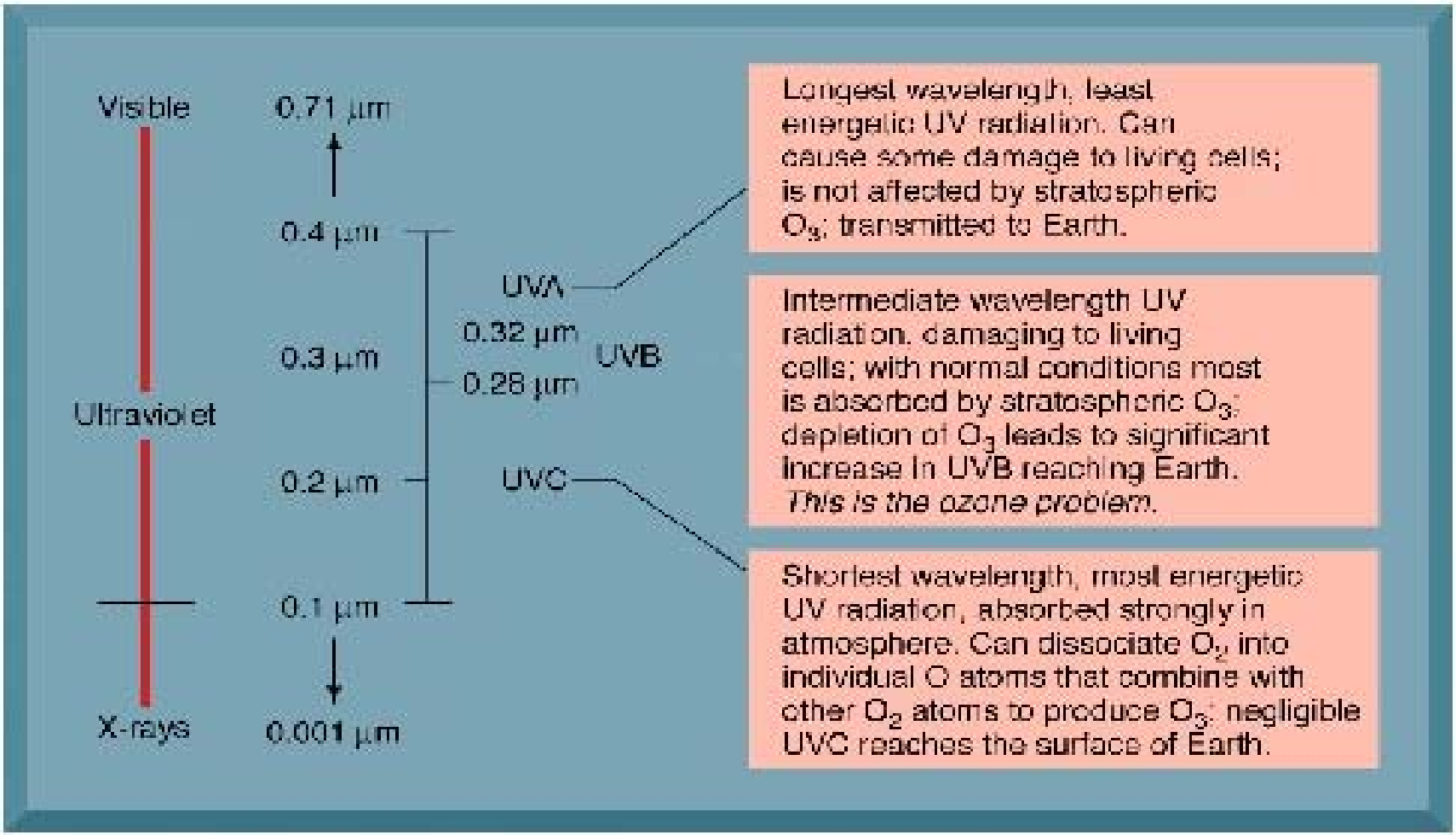
- $N_2O + UV = N_2 + O$ (most important)
- $N_2O + O = NO + NO$
- $NO + \mathbf{O_3} = NO_2 + O_2$
- $NO_2 + \mathbf{O_3} = NO_2 + O_2$

Ozone Depletion in Stratosphere
Contd.

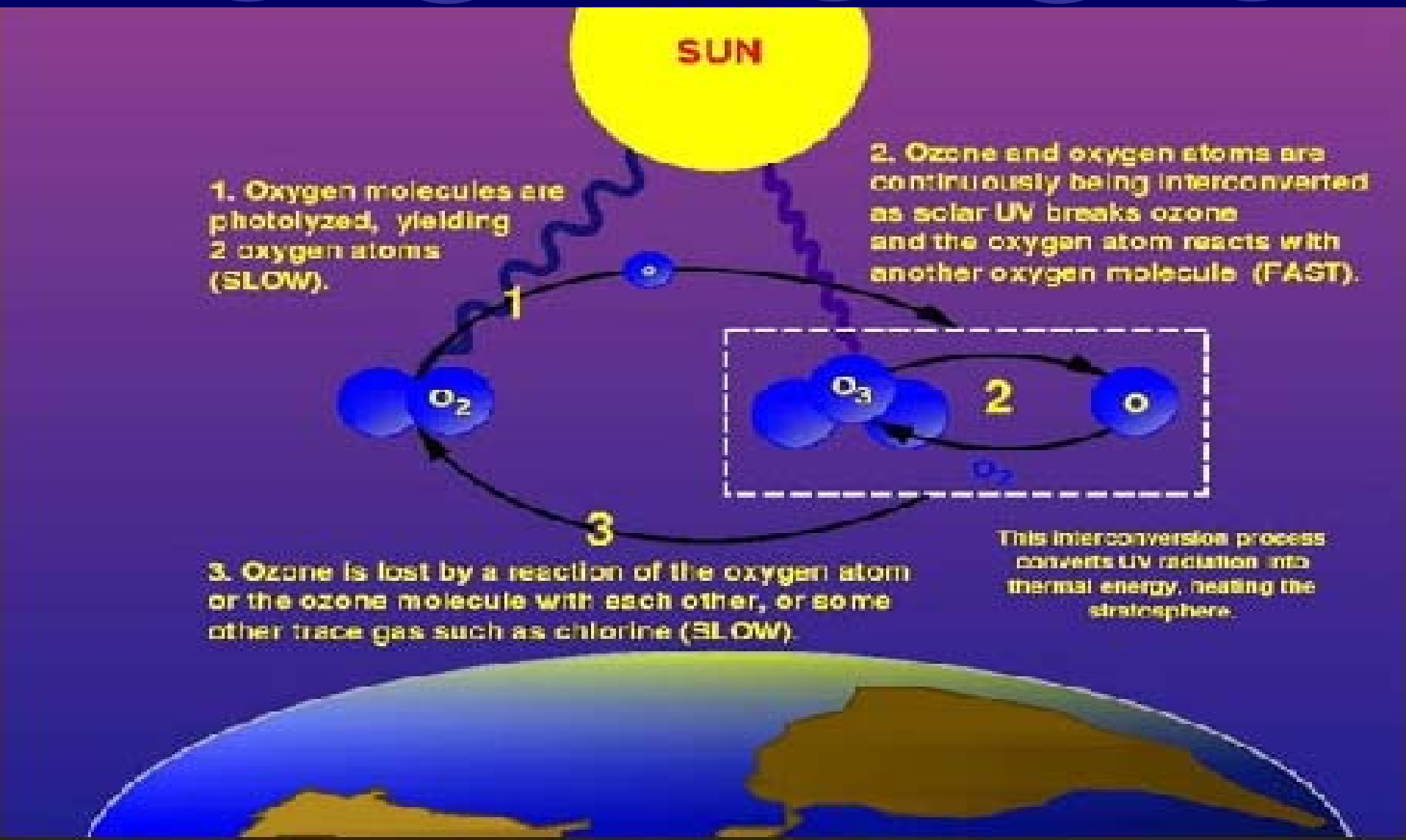
- $4NO_2 + O_2 + 2H_2O = 4\ HNO_3$
- $2NO_2 + \mathbf{O_3} + H2O = 2\ HNO_3 + O_2$
- $SO_3 + H_2O = H_2SO_4$
- $SO_2 + ½\ O_2 + H_2O = H_2SO_4$

UV Radiation

Classification, Accordance and Potential Damages



Life Cycle of an Ozone Molecule



Ozone formation and Depletion

$$h\nu + O_2 \rightarrow O + O$$
$$O + O_2 \xrightarrow{M} O_3$$

Formation

$$h\nu + O_3 \rightarrow O + O_2$$
$$O + O_3 \rightarrow O_2 + O_2$$

Depletion

* Due to the need of a third body (air=M), O_3 is more abundant below altitudes of 70 Km.

Nitric oxide (NO) released by high-flying supersonic aircraft

$$NO + O_3 \rightarrow NO_2 + O_2$$
$$NO_2 + O \rightarrow NO + O_2$$

NO acts as a catalyst

$$O_3 + O \rightarrow 2O_2$$

Stratospheric Ozone Production and Loss Cycle

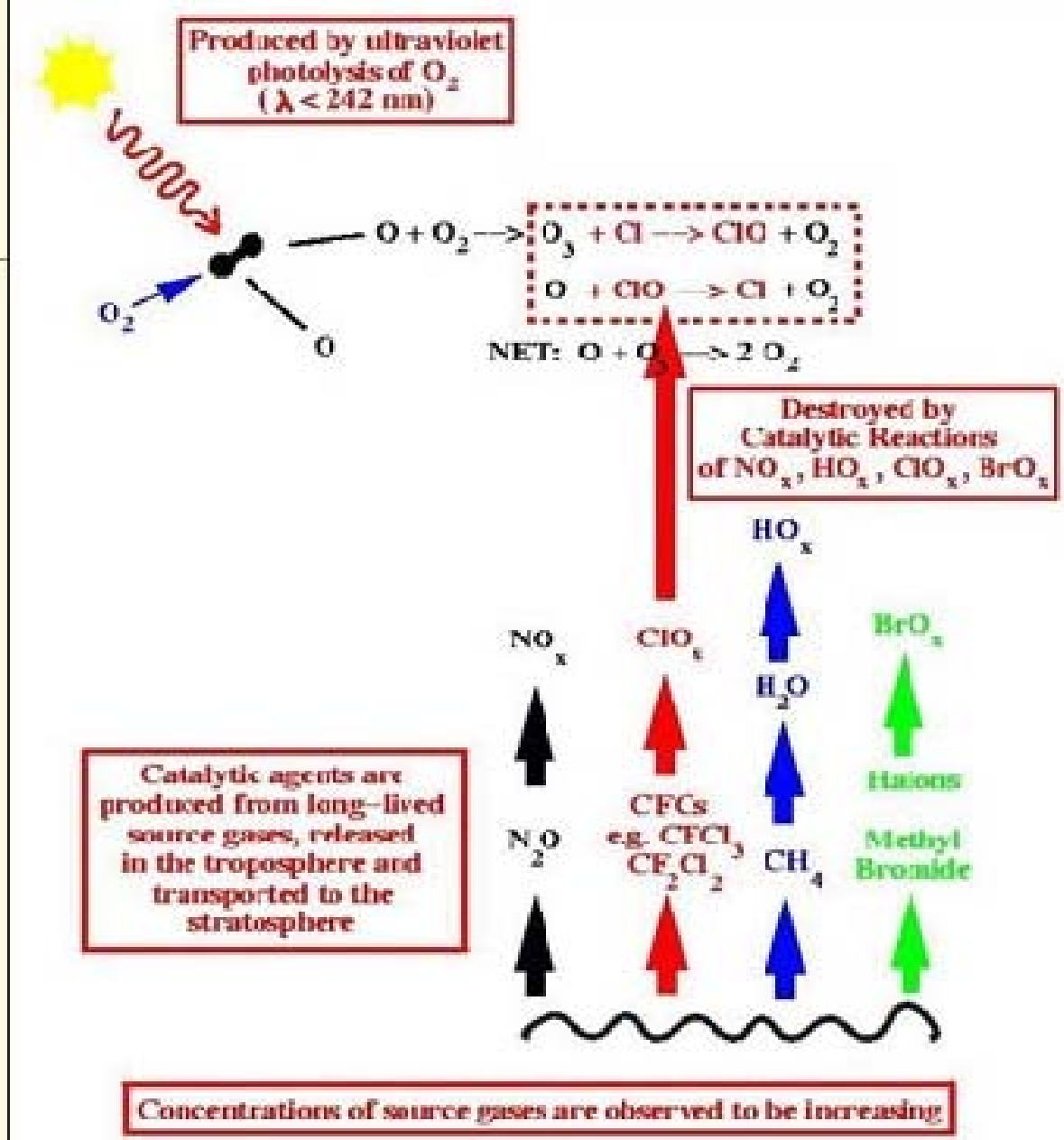


Figure 1. Simplified schematic of flows within the nitrogen biogeochemical cycle. Boxes indicate forms of nitrogen while arrows indicate processes converting nitrogen from one form to another.

Ozone Depletion in Stratosphere
Contd.

Contribution of Oxides of Sulphur (SOx)

- $SO_2 + hv = SO_2^{(Activated)}$
- $SO_2^{(Activated)} + O_2 = SO_4$
- $SO_4 + O_2 = SO_3 + \mathbf{O_3}$

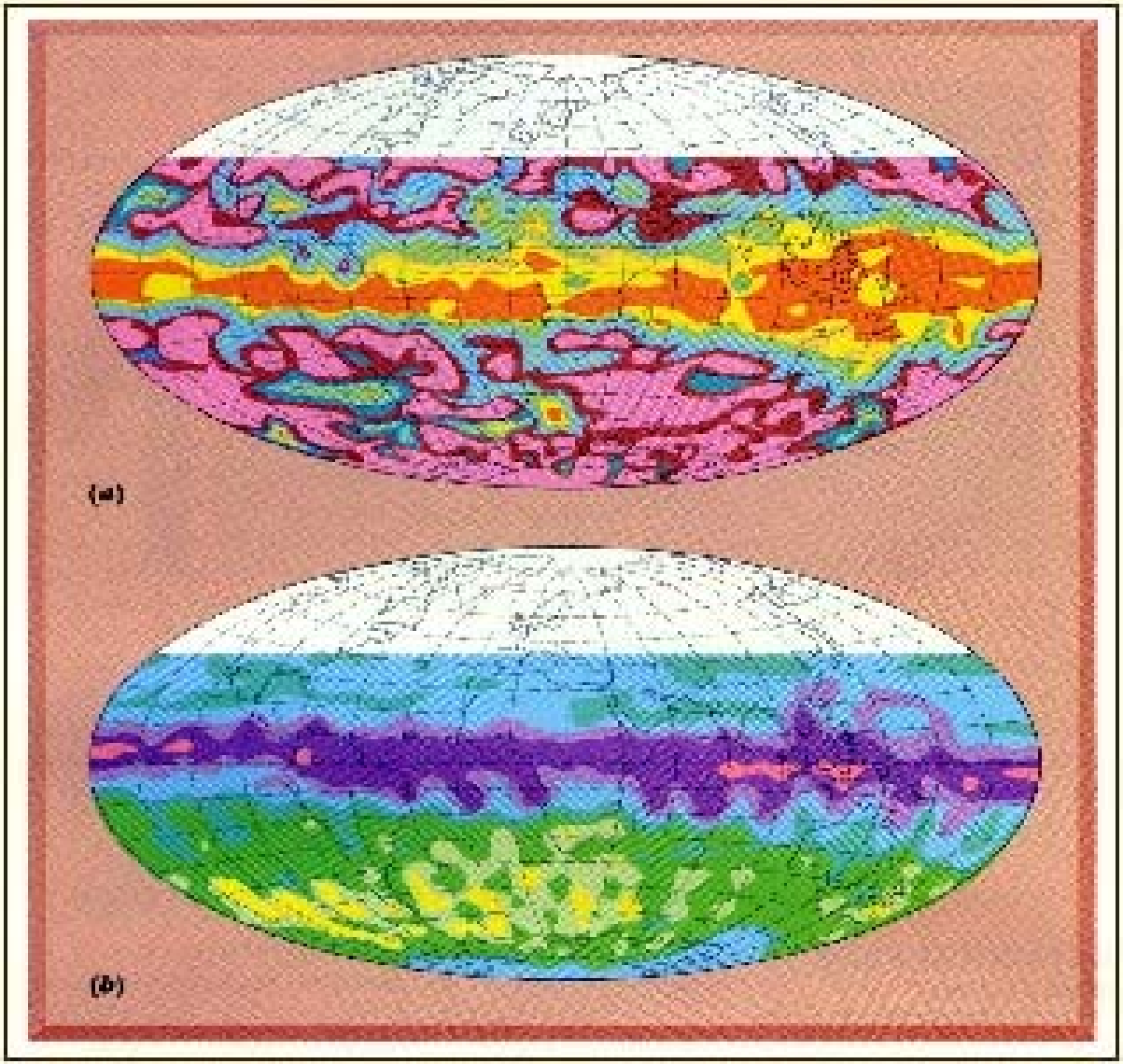
(O_3dangerous at ground level/ in troposphere)

SO_2 and Ozone Depletion

(a)

Sulfur-dioxide rich aerosol cloud

(orange)



(b)

Correspondi
belt of air wit
lower
concentratio
of ozone

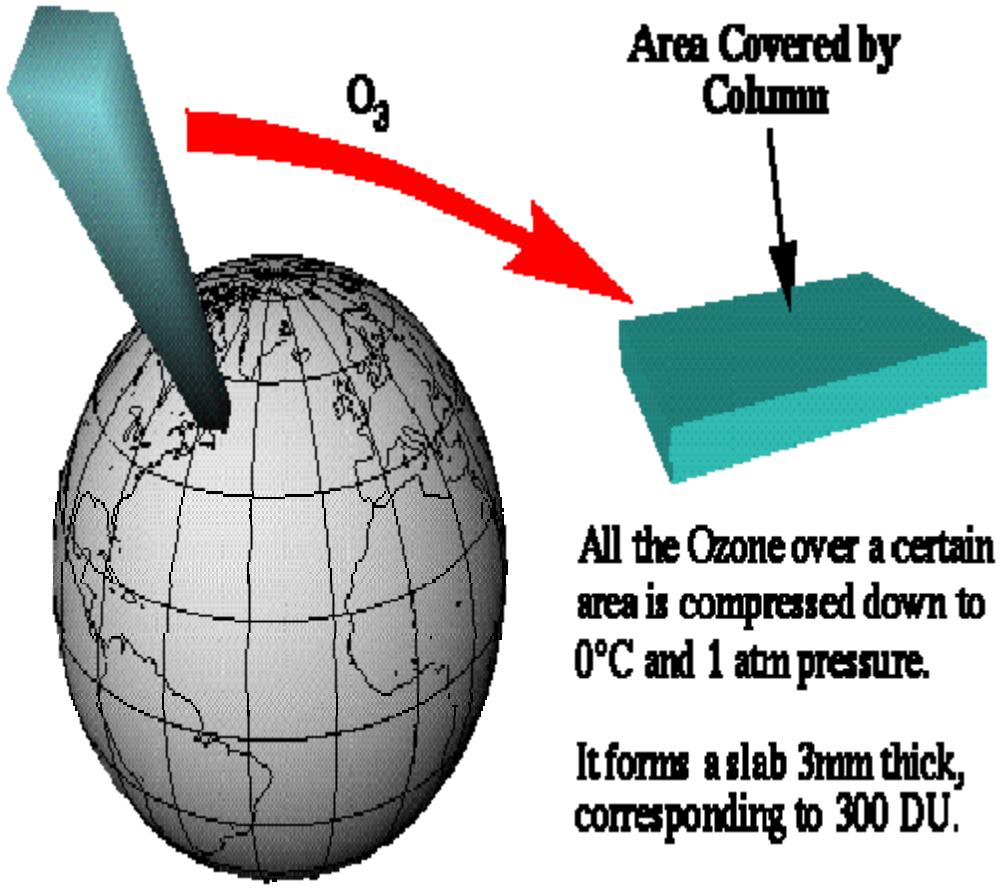
(violet)

Measurement of Ozone in Environment (DB unit or DU)

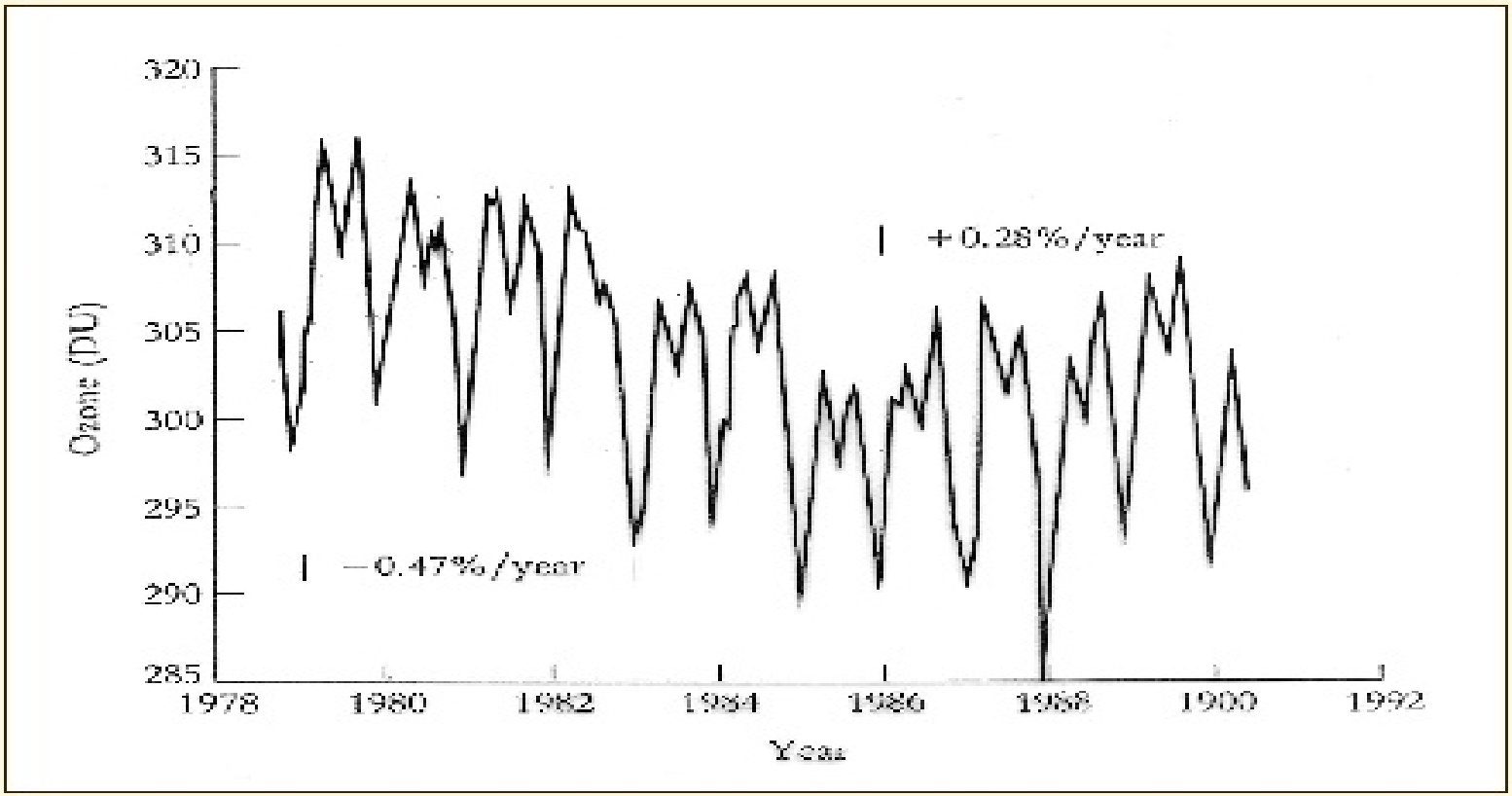
- A column reaching from an area on the Earth's surface to the top of the atmosphere were concentrated in a single layer of pure ozone at a temperature of 0°C and a pressure of 1. The thickness of that layer, measured in hundredths of a millimeter, would be the concentration of ozone expressed in Dobson Units.

Measurement of Ozone in Environment

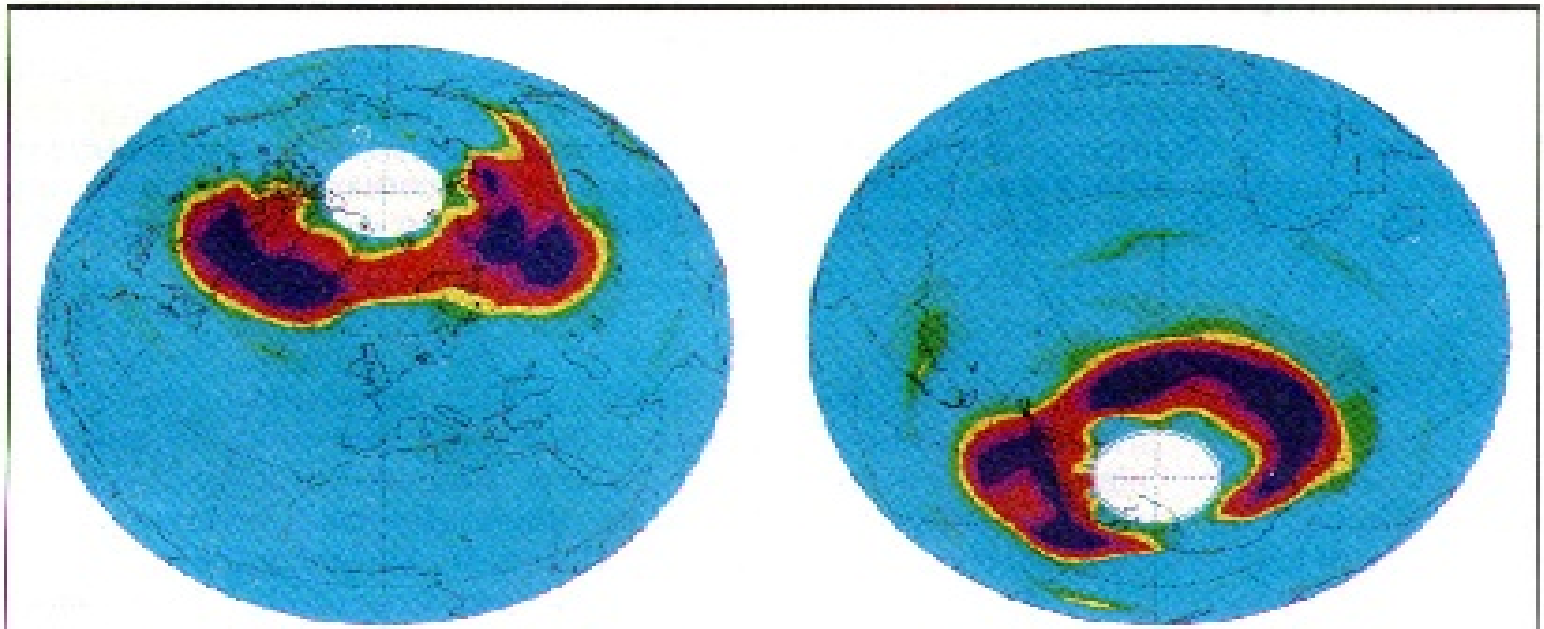
1 DU equt.
$2.69 \times 1016\ O_3$
molecules in
a column with
a cross
section of 1
square
centimeter.



Ozone Change: Over the Last 1 ½ Decade

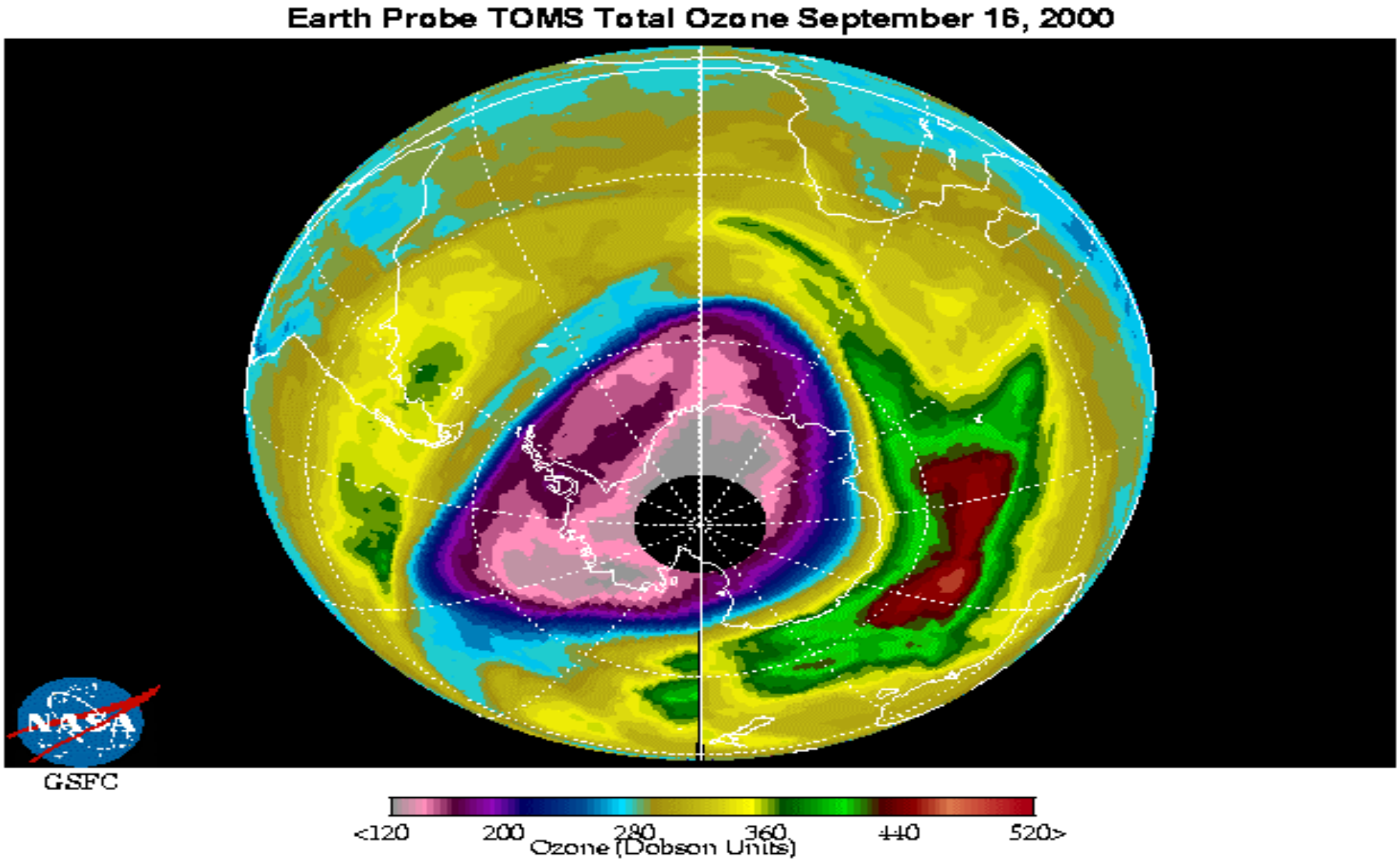


NASA's Releases: Ozone Holes



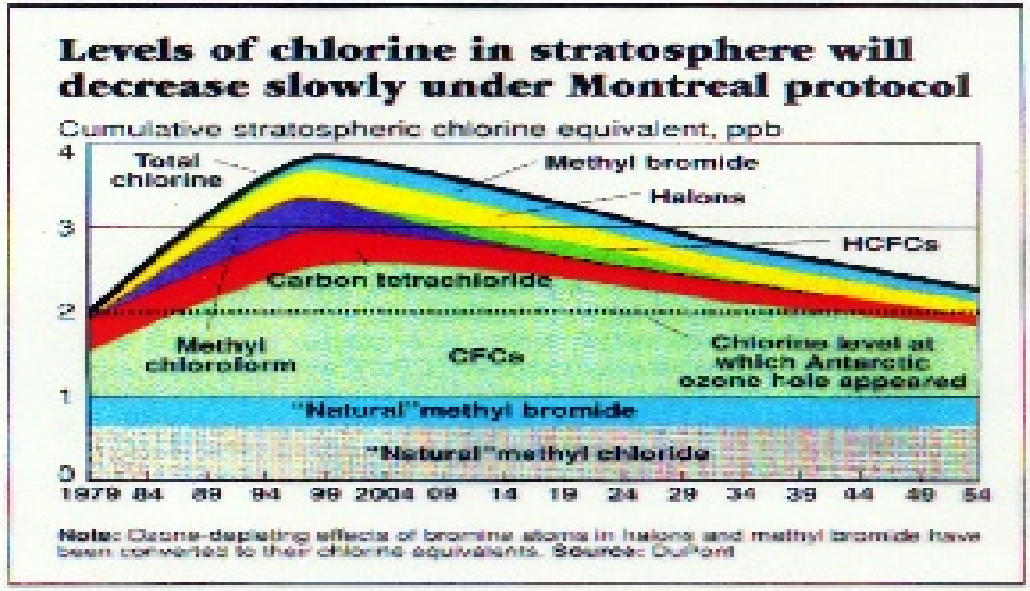
Maps of ozone-destroying chlorine monoxide in the stratosphere reveal similarities between the north (left) and south polar regions in winter. Red and darker colors indicate chlorine monoxide abundances of 1 ppb or more as observed by the microwave limb sounder on NASA's Upper Atmosphere Research Satellite. White circles at pole are where no measurements are made

NASA's Releases:
Regional Ozone Concentrations



What is needed (Collective Efforts)

CFC Reduction



Montreal Protocol (1987)

57 countries
50% decrease in CFC by 2000
Halt increase in bromated halocarbons

London Ozone Agreement

93 nations
Phase-out CFCs by 2000
Limit production of chloroform and carbon tetrachloride
Amendments to help developing countries find alternatives

Bush administration

Phase-out CFCs by 1995

Montreal Protocol

Effective 01/01/1989

$C_2Cl_3F_3$, CCl_2F_2, $CHClF_2$, and $C_2Cl_4F_2$; reduction (50%) of the 1986 levels during the next 10 years

Use of specified brominated halons ($CBrClF_2$ and $CBrF_3$) is prescribed not to exceed 1986 levels

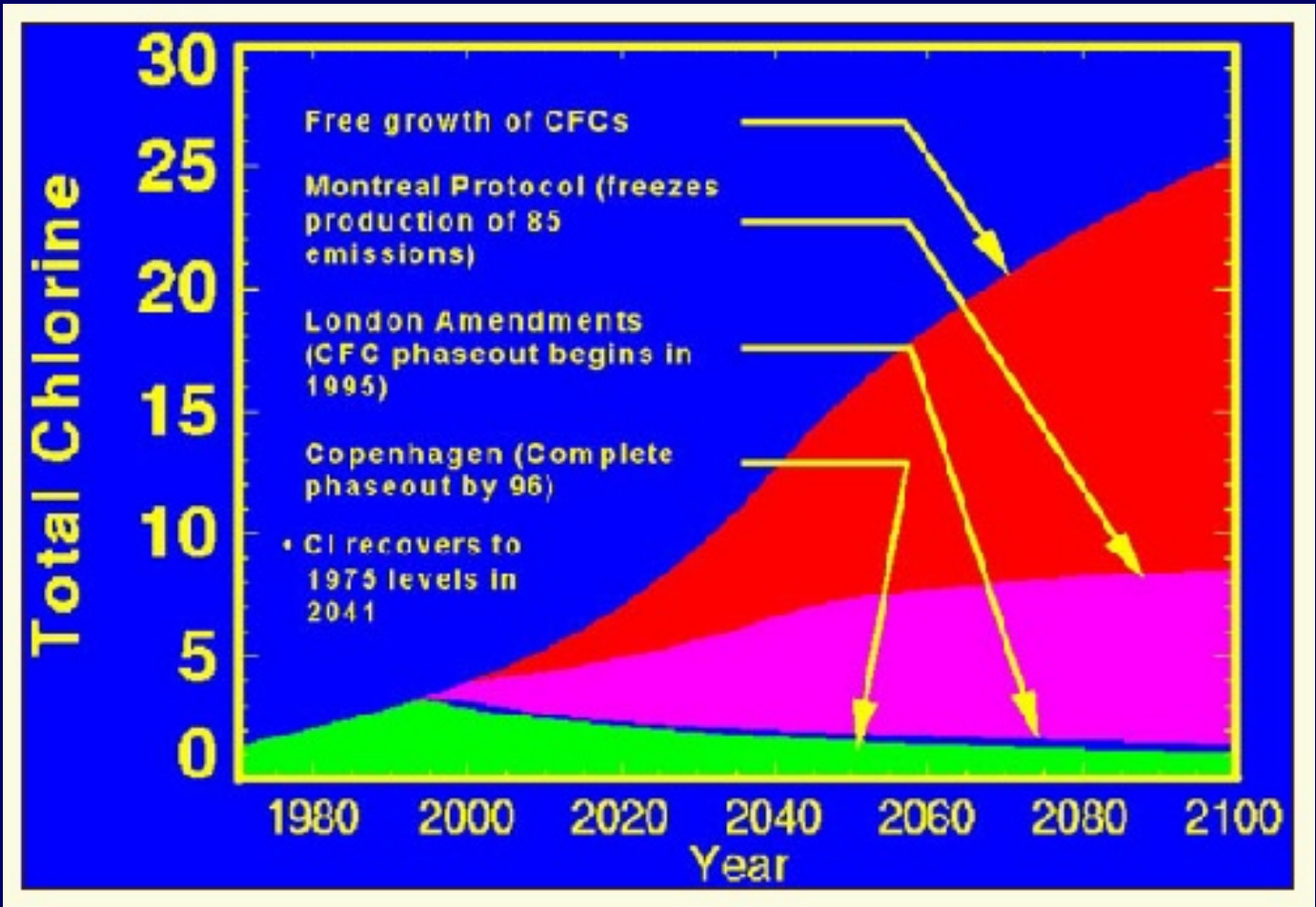
Developing countries are permitted a ten year grace period

Soviet Union is allowed to increase production and consumption by two-thirds before it also committed to cut back

Control Measures: Greenhouse Effect Global Warming and Ozone Depletion

- The Climate Change Convention 1992 (present in reading Assignment)
- Collective Efforts.
- Source Reduction by producers
- Redesigning of Processes, Operations and Products
- Technological Improvements
- Enforcements by law
- Social Awareness and pressure on producers

What is needed



EPA plans to phase out HCFCs in stages

Date[a]	Compounds affected	Restriction
1994	All HCFCs	Ban on use in aerosols (except medical devices) and plastic foams (except foam insulation)
2003	HCFC-141b (CH_3CCl_2F, ODP^b = 0.12)	Ban on production and imports
2010	HCFC-22 ($CHClF_2$, ODP = 0.05) HCFC-142b (CH_3CClF_2, ODP = 0.06)	Production and imports frozen at 1989 baseline levels. Ban on use of virgin chemical, unless used as feedstock or for servicing refrigeration or air-conditioning equipment manufactured before Jan. 1, 2010
2015	All other HCFCs	Production and imports frozen at 1989 baseline levels. Ban on use of virgin chemical, unless used as feedstock or for servicing refrigeration or air-conditioning equipment manufactured before Jan. 1, 2020
2020	HCFC-22, HCFC-142b	Ban on production and imports
2030	All other HCFCs	Ban on production and imports

Note: HCFCs = Hydrochlorofluorocarbons. **a** Effective date is Jan. 1 of the given year. **b** ODP = Estimated ozone depletion potential, which depends on chlorine content and atmospheric lifetime. Potentials are relative to CFC-11, which is assigned a value of 1.0. **Source:** *Federal Register*, March 18, 1993, page 15014 and Sept. 27, 1993, page 50,464

Acid Rain- a regional issue: Overview

- **Why Regional? (North America and northern Europe are mostly Affected)**
- **Precipitation made acidic by the presence of acids stronger than CO2(aq).**
- **Natural rainfall which contains nitric and sulfuric acids due to oxides of nitrogen and sulfur dioxide discharged into the air by industries, power plants, and automobiles.**

Acid Rain- a regional issue: Overview Contd.

- **"Acid rain" can be wet as well as dry**
- **Wet: acidic rain, fog, and snow.**
- **Dry: acidic gases and particles.**
- **About half of the acidity in the atmosphere falls back to earth through dry deposition.**
- **runoff water adds those acids to the acid rain, making the combination more acidic than the falling rain alone**

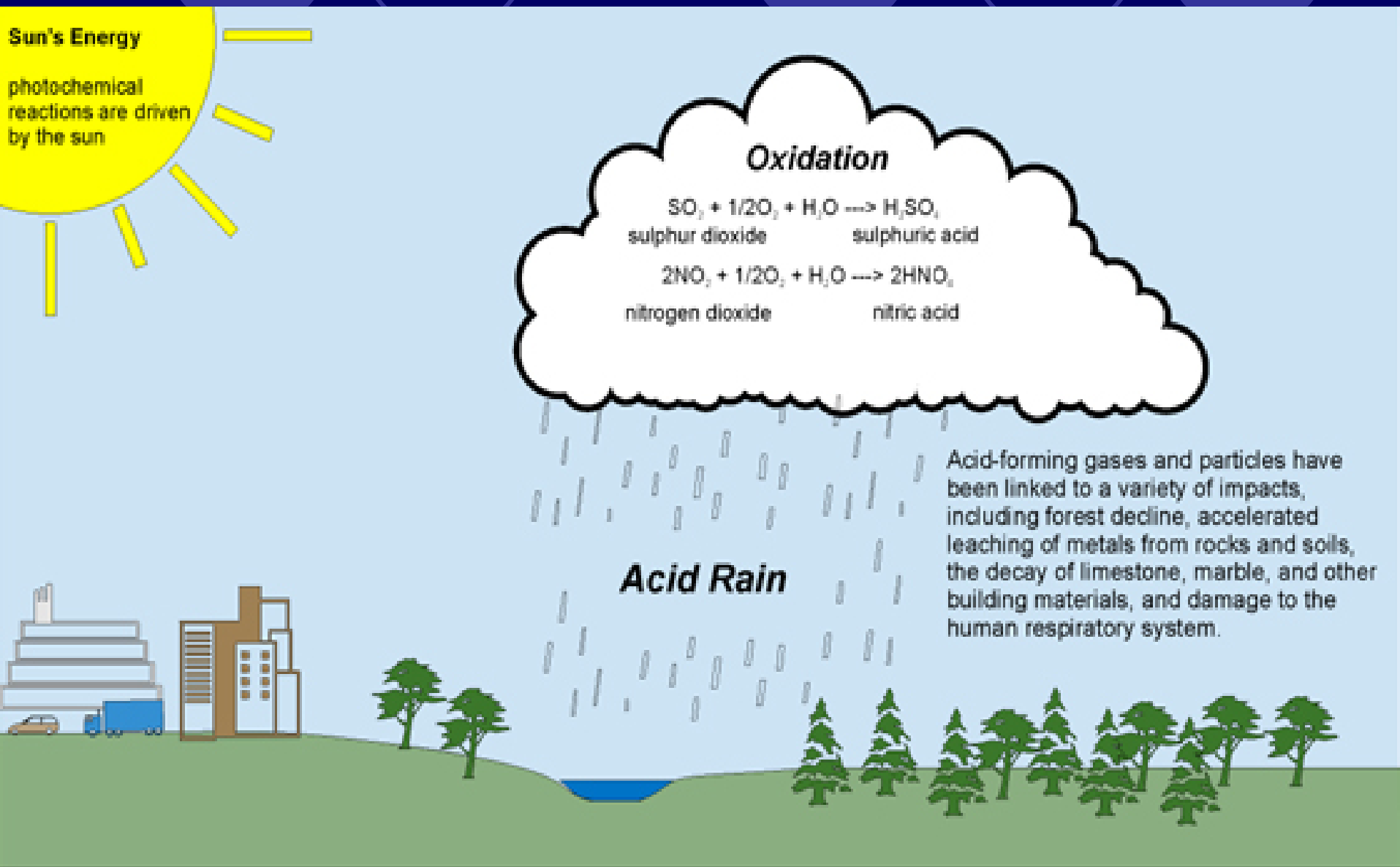
Acid Rain contd.:

- **Attributed to additional SOx, NOx, and industrial pollutants in atmosphere.**
- **Clean Rain pH 5.6 due to CO_2 / week carbonic acid.**
- **Acid Rain pH close to 4.0 and in rare cases 3.0**

How Acid is Developed in atmosphere?

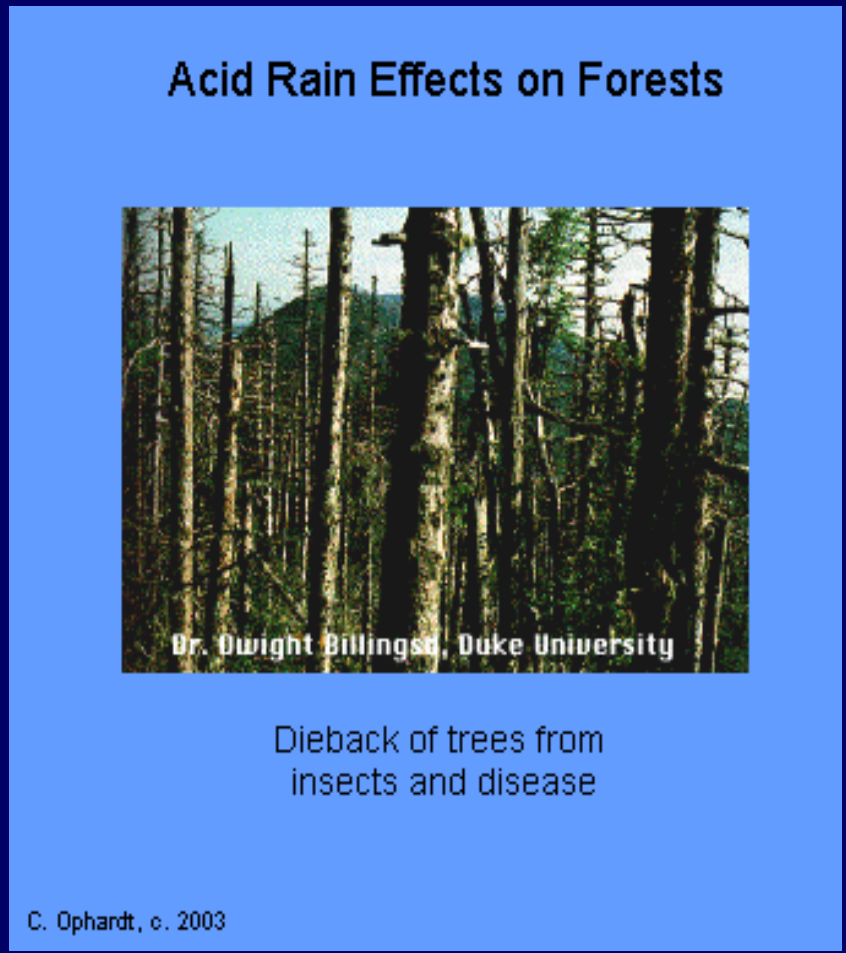
- $4NO_2 + O_2 + 2H_2O = \mathbf{4\ HNO_3}$
- $2NO_2 + O_3 + H2O = \mathbf{2\ HNO_3} + O_2$
- $SO_3 + H_2O = \mathbf{H_2SO_4}$
- $SO_2 + ½\ O_2 + H_2O = \mathbf{H_2SO_4}$

Acid Rain- Recap



Effects of Acid rain : Plants

- **In 1983, a survey in West Germany showed that 34 % of the country's total forest is damaged pollution.**



Acid rain Effects: Corps and Plants

- **Direct Foliar Damage, readily effected.**
- **Presented in reading material**
- **Pollens and fertilization tubes are very sensitive to low pH (Apple and Grapes)**
- **Limited Fertilizing Effects**

Acid rain Effects: Forests

Victims of acid rain - dead and dying Red Spruce in Maine. Photo by Paul Donahue

Acid rain Effects: Forests

- **Forests in America, Canada and Scandinavia, are of Economical Importance**
- **Forest and wood associated Industry and Employment**
- **Seeding even effected at 4.6 pH**
- **Resistant to disease may increase**
- **Al toxicity increases as leaching of Ca and Mg**
- **Various studies presented in reading material**

Acid Rain Effects: Material

- **Sandstone figure over the portal of a castle in Westphalia, Germany, photographed in 1908 (left) and again in 1968 (right).**

Acid Rain Effects: Material

- **Erosion and damage to color, strength Increases in Steels, cement, masonry, limestone, sand stone and marble. Billions of $ Cost**
- **Combined Effect of Various Environmental Pollutions**
- **Italy experienced accelerated losses in disfigurations and dissolution of Monuments and Sculptures of historical and architectural importance**

Effects of Acid Rain: Ground and drinking water

- **Surface Water proculates down through soil and bedrock to form ground water**
- **Contamination of groundwater by metals (Al, Pb, Cu, Zn) due to leaching in acidic conditions**
- **Lakes are also effected**
- **Untreated/ less treated water supplies in underdeveloping nations**
- **Corrosion on water pipes**

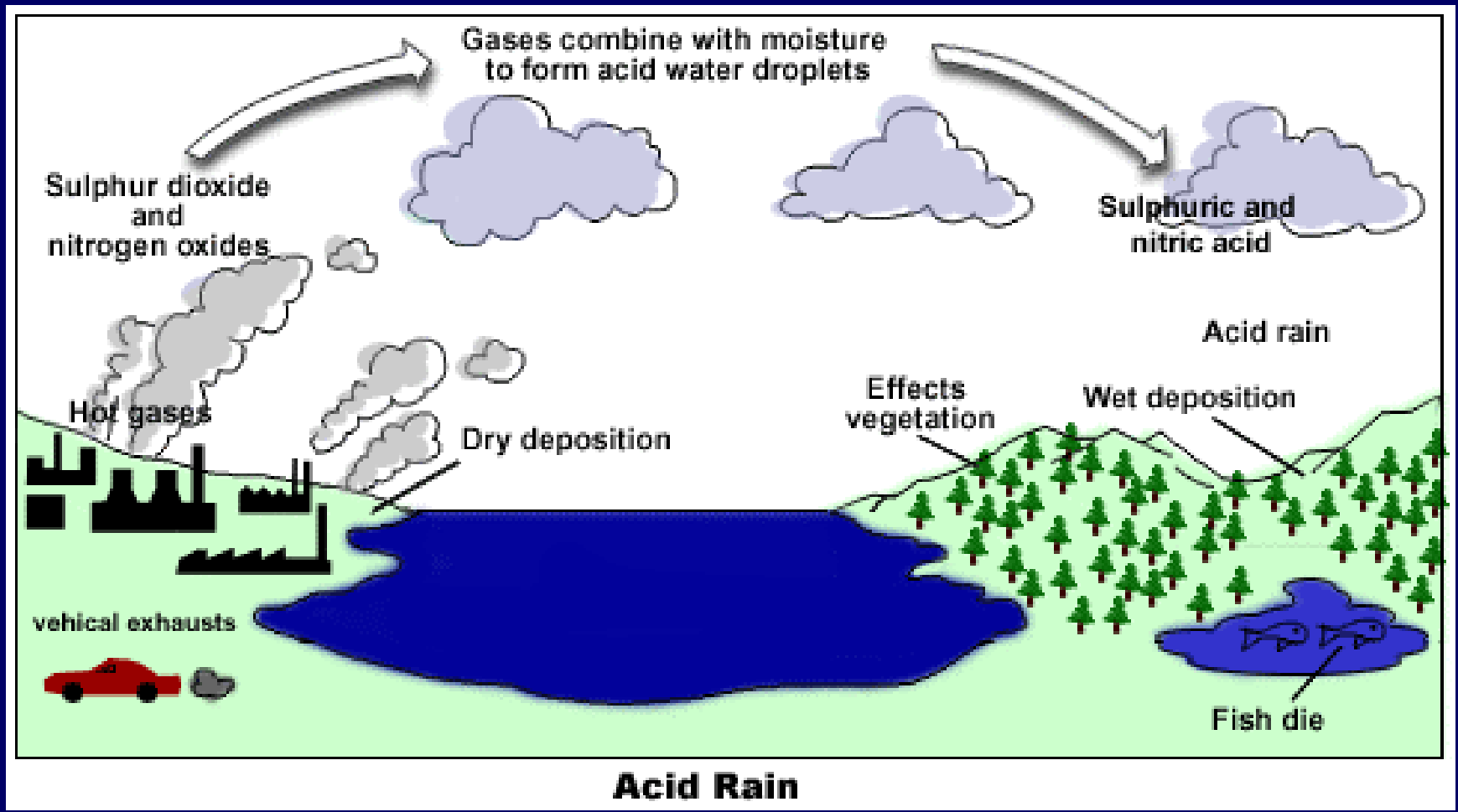
Acid Rain Effects: Material

Destruction of the Taj Mahal's White Marble Surface due to Air Pollution

Effects on Acid rains: Aquatic Biota

- **Aquatics life: Fish Population Decline**
- **pH increase in water increases Al, killing fish and other biota**
- **Toxicity of fish occurs at low pH**
- **Skin Burning and Respiratory Problems in Animals and Human**
- **Algae and Aquatic plants are threatened by low pH**

Summery: Acid Rain



Useful Web Links:

- EPA Global Warming site: http://www.epa.gov/globalwarming/
- United Nations Environment Programme: http://www.unep.ch/
- Global Warming Central: http://www.law.pace.edu/env/energy/globalwarming.html
- Global Warming Update: http://www.ncdc.noaa.gov/ol/climate/globalwarming.html
- Global Warming: Focus on the Future: http://www.envirolink.org/orgs/edf/
- Global Warming: Understanding the Forecast: http://www.edf.org/pubs/Brochures/GlobalWarming/
- The U.S. Global Change Research Information Exchange Office: http://gcrio.ciesin.org/
- Public Perceptions of Global Warming: http://www.gcrio.org/ASPEN/science/eoc94/EOC2/EOC2-2.html
- World Climate Report: http://www.greeningearthsociety.org/climate/
- World Wildlife Fund Climate Change Campaign: http://www.panda.org/climate/
- IEA Greenhouse Gas R&D Programme: http://www.ieagreen.org.uk/
- Global Warming Games: http://www.envirolink.org/orgs/edf/games/index.html
- Global Warming and Climate Change: http://www.gcrio.org/gwcc/toc.html
- Global Warming: Myth vs. fact: http://www.edf.org/pubs/FactSheets/e_GWFact2.html
- 20 Simple Steps to Reduce Global Warming: http://www.edf.org/Want2Help/b_gw20steps.html
- Evidence For and Against Global Warming: http://krusty.eecs.umich.edu/people/jreed/GWLetter/node7.html
- Global Warming, *Lessons from the Past*?: http://energy.usgs.gov/factsheets/cret.coals/cret.coals.html
- Global Warming Workshop: http://www.middlebury.edu/~rosenber/DR-personal-homepage/globalwarming/globwar.html
- Chemistry 110 CHEMISTRY AND ISSUES IN THE ENVIRONMENT (Elmhurst College): http://elmhcx9.elmhurst.edu/~chm/onlcourse/chm110/issues/issue197.html

Reading Material:

- **F. Kenneth Hare and T. C. Hutchinson, "Human Environmental Disturbances" appeared in Environmental Science and Engineering, 2nd Ed. PrenHall, 1996 Pp. 111-140**
- **J. G. henry and G. W. Heike "Environmental Science and Engineering" , 2nd Ed. PrenHall, 1996 Pp. 3- 11**
- **P. L. Bishop, "Pollution Prevention: Fundaments and Practice", McGrawHill, Pp 1-6**
- **Class Notes**

Acknowledgments

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- **IQTM**-PU for providing logistic support
- P.E. **Coutrakis** of Harvard University's Science Network. http://lab.dce.harvard.edu/~environment/lecture20010321-Stratospheric-Ozone-pek(v4)97/sld029.htm for figures.

Smog

- Industrial Smog:
- huge gray smoke from stacks of factories.
- burning of coal for heat and energy
- the main pollutant of industrial smog is sulfur dioxide-a compound largely responsible for acid precipitation.

Smog contd.

- Photochemical Smog
- motor vehicles, use of fossil fuels for heating, industry, and transportation
- slashing-and-burning of trees
- volatile organic compounds (VOCs) and nitrogen oxides
- Interacting with sunlight
- pollutants-namely peroxyacetyl nitrates (PAN) and ground-level (tropospheric) ozone

Industrial Smog:

- Polluted air associated with industrial activities is often called Industrial Smog.
- Produced by the burning of coal of high level sulfur.
- **In London on Thursday 4th December, 1952 at valley of Thames River**
- Saturday was a day of darkness.
- 20 miles around London no light came out through the weak-end.
- On Monday 8th December – 100 people died of heart attack.
- Before cleaned on Tuesday 9th December 4000 deaths were attributed to the smog.
- The total death count was 8000.

The Chemistry of Industrial Smog:

- Coal:
  - 3% Sulfur
  - 97% Carbon
  - Varying amount of mineral matter
  - $C + O_2 \rightarrow CO_2$
  - $2C + O_2 \rightarrow 2CO$
  - Unburned carbon ends-up as soot.

- Sulfur Oxides:
- $S + O_2 \rightarrow SO_2$
- S readily absorbed in respiratory system
- $2SO_2 + O_2 \rightarrow 2SO_3$
- $SO_3 + H_2O \rightarrow H_2SO_4$
- Particulate Matter:
- Solid & liquids particles of greater than molecular size e.g. soot and mineral matter in coal.
- A six city of Harvard Researchers in the 1990s 60,000 premature deaths per year in USA because of there tiny particles.

Health & Environmental Effects of Industrial Smog:

- Damage the Lungs.
- Dangerous for Plants.
- Leaves become Bleached.
- Yield and Quality of Farm Corps severely damaged.
- Cause Acid Rain.

How to Handle Industrial Smog:

- Electrostatic precipitation.
- Bag Filtration.
- Cyclone Separator.
- Wet Scrubber.

Photochemical Smog:

- Occurs in dry sunny weather.
- Main Causes:
  - Unburned hydrocarbons.
  - Nitrogen oxides from automobiles.