Air pollution II

Air pollution II

- Air pollution problems
 - Indoor air pollution
 - Acid rain
 - Ozone depletion
 - Global warming

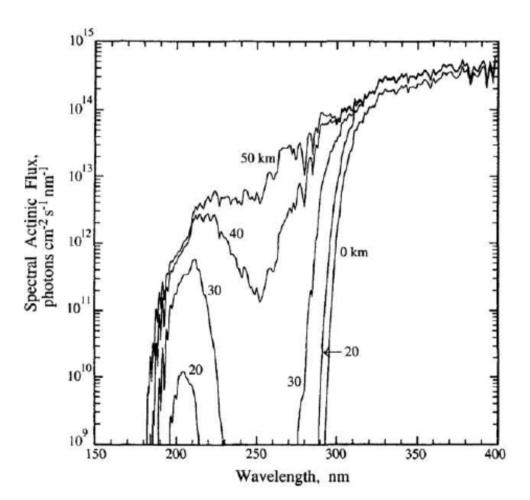
Indoor air pollution

- Difficult to regulate!
- CO and NO_x from gas ranges, ovens, heaters, and cigarette smoke
- Cigarette smoke also contains toxic compounds including carcinogens
- Bioaerosols: bacteria, viruses, fungi, mites, and pollen
- Radon: emitted from the ground (high in basements)
- Volatile organic compounds
 - ex) formaldehyde: emitted from building materials ("sick building syndrome")
- Heavy metals: emitted from paints

Acid rain

- SO₂ and NO_x in the air undergo series of reactions to form sulfuric acid (H₂SO₄) and nitric acid (HNO₃)
- pH in natural rain has a pH near 5.6 (why?)
- Rain pH in polluted areas can go below 5, sometimes even close to 2
- Adverse effects
 - Acidification of rivers, lakes, and soil: damage aquatic/terrestrial ecosystem including fish deaths
 - Nutrient leaching from soil (ex: Mg)
 - Mobilize aluminum from soil: enhanced uptake of Al by plants, increase Al concentration in waters (toxic effect)

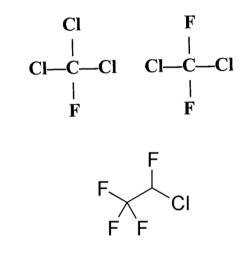
- Ozone protects life if it is in the stratosphere
- Ozone layer (20-40 km or up above the ground): absorbs UV light



Photoreactions of ozone to absorb UV light

 $O_2 + UV \rightarrow 2O$ $O + O_2 + M \rightarrow O_3 + M$ (*M*: a third molecule) $O_3 + UV \rightarrow O_2 + O$

- CFCs (chlorofluorocarbons)
 - Good for refrigerants, propellants, and solvents
 - Stable in the troposphere → can reach the stratosphere without break-down
 - Causes ozone depletion



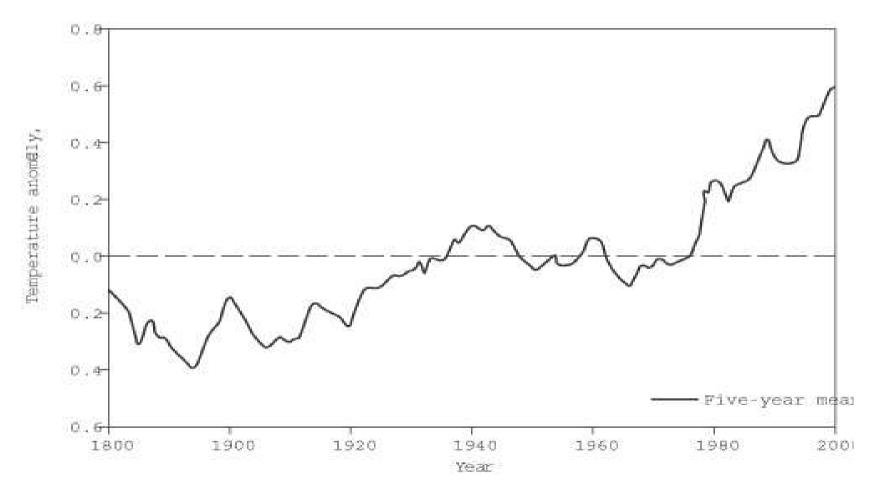
• Ozone destruction mechanism by CFCs

$$\begin{array}{ccc} CCl_{3}F + UV & \rightarrow CCl_{2}F + Cl \\ \\ Cl + O_{3} & \rightarrow ClO + O_{2} \\ \\ ClO + O & \rightarrow Cl + O_{2} \end{array} \right] \begin{array}{c} O_{3} + O & \rightarrow 2O_{2} \end{array}$$

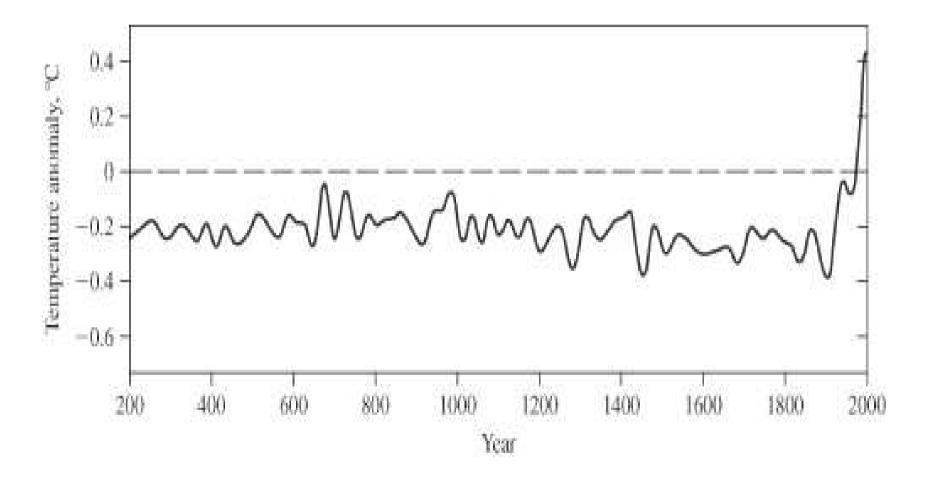
- Cl atom acts as a catalyst
- One CFC molecule can destroy uncountable number of ozone molecules

- Efforts to stop ozone depletion
 - Montreal Protocol on Substances That Deplete the Ozone Layer
 - An international treaty agreed on September 16, 1987
 - Became effective in January 1989
 - Eight revisions: 1990, 1991, 1992, 1993, 1995, 1997, 1999, and 2007
 - Goal: complete phase-out of CFCs

- Substitutes: HFCs and HCFCs
 - Hydrochlorofluorocarbons (HCFCs)
 - More reactive than CFCs in the troposphere
 - ightarrow only small amount reaches the stratosphere
 - Still has some ozone depletion potential
 - \rightarrow used just as a transitional substitute of CFCs, amendments of Montreal Protocol also targets on the phase-out of HCFCs
 - Hydrofluorocarbons (HFCs)
 - No chlorine atoms \rightarrow no ozone depletion potential
 - Problem: HFCs and HCFCs are greenhouse gases
 - HFCs are not considered as a permanent substitute of CFCs as well!

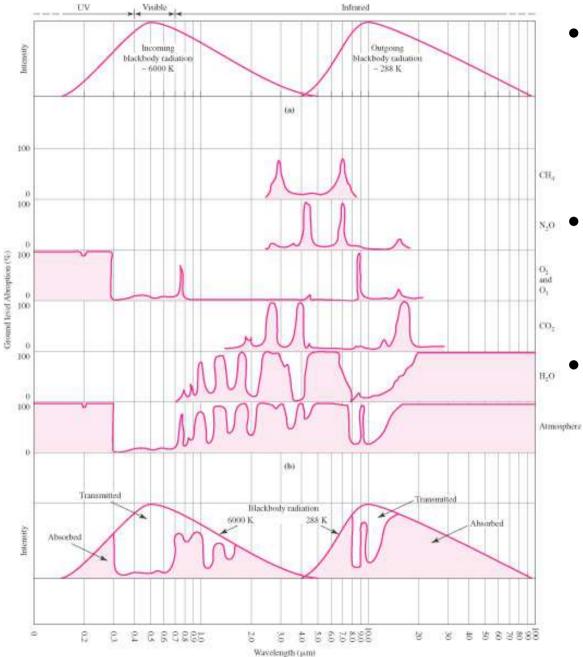


The temperature of the globe is really increasing!

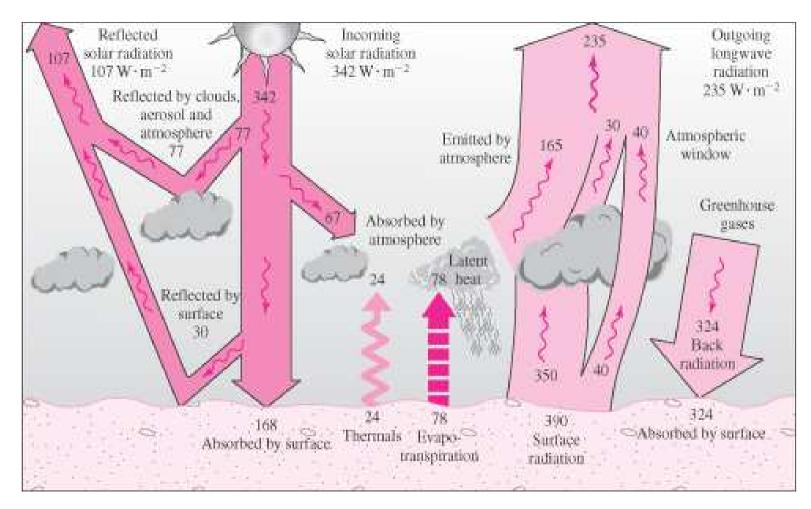


The "hockey stick" graph

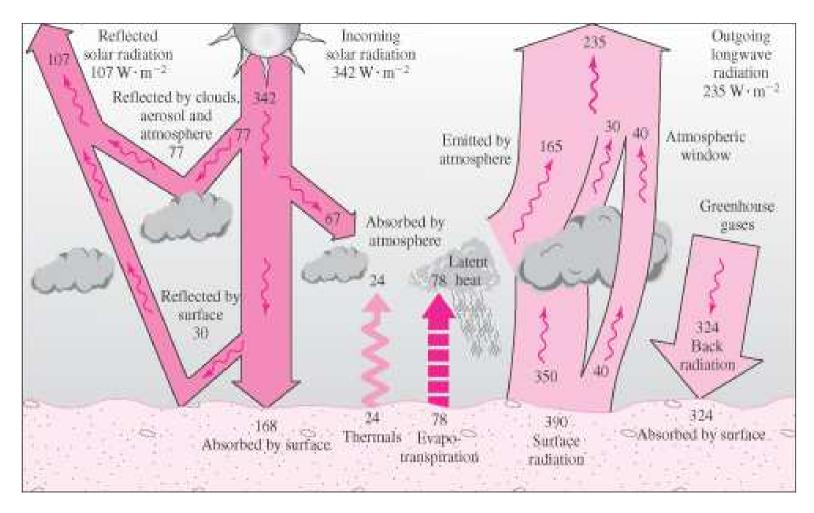
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- The earth receives short-wave radiation from the Sun
- The Earth's surface emits long-wave radiation
- Some molecules
 absorb the long wave radiation →
 prevent energy to
 be released out of
 the Earth



- The greenhouse gases (GHGs) work like the glass on a greenhouse or a blanket
- Maintain the Earth's temperature good for life (without GHGs, the Earth's temperature will be around -17°C)



- 30% increase in the atmospheric CO₂ concentration since 1750
- The increased levels of greenhouse gases changes the radiation balance: greater back radiation → higher surface temperature

Greenhouse gases (GHGs)

- CO₂ is major, but others can also be significant
- Overall greenhouse effect depends on concentration, global warming potential, and lifetime

Chemicals	Lifetime (year)	Global warming potential (kg CO ₂ /kg chemical)
Carbon dioxide (CO ₂)	30-200	1
Methane (CH ₄)	12	62
Nitrous oxide (N ₂ O)	114	275
CFC-12 (CF_2CI_2)	100	10200
HCFC-22 (CHF ₂ Cl)	12	4800
Tetrafluoromethane (CF ₄)	50000	3900
Sulfur hexafluoride (SF ₆)	3200	15100

- Efforts to reduce GHG emissions: Kyoto Protocol
 - Adopted on December 11, 1997
 - Became effective in 2005
 - Targets to reduce GHG emissions in developed countries by an average of 5.2% compared to 1990 levels during the first commitment period (2008-2012)
 - U.S. did not ratify the protocol
 - Korea: classified as a "developing country", no binding targets

- Kyoto Protocol
 - Doha amendment (2012)
 - Reduce GHG emissions by 25-40% compared to 1990 levels during the second commitment period (2013-2020)
 - Major CO₂-producing countries (U.S., China, and India) are not included
 - U.S. (2nd), Japan, Russia, Canada did not participate
 - China (1^{st}) and India (3^{rd}) are classified as developing countries
 - Korea: still classified as a developing country, but "voluntarily" promised to reduce the GHG emissions

• Paris agreement (Dec 2015)



- For post-2020 reduction of GHG emissions (effect of Kyoto Protocol ends in 2020)
- A bottom-up approach (cf. Kyoto Protocol: top-down)
 - Each country submit "Nationally Determined Contributions (NDC)" for GHG reduction
 - The NDC should be "ambitious", "represent a progression over time", and set "with the view to achieving the purpose of this Agreement"
 - Korea: set NDC as "37% reduction compared to 2030 BAU* value"

*BAU: Business As Usual

Air pollution I

Air pollution I

- Units for air pollutants
- Classification of air pollution problems
- Types of air pollutants



Units of measurement

- volume/volume units (for gas phase pollutants)
 - ppm = parts per million
 - ppb = parts per billion
 - ppt = parts per trillion
- mass/volume (for gas & particle phase pollutants)
 - usually $\mu g/m^3$

Unit conversion

Consider a pollutant "i" Ideal gas law: PV = nRT $\frac{n_{air}}{V_{air}} = \frac{P_{air}}{RT} = \frac{mole_{air}}{m^3_{air}}$ R = ideal gas constant = 8.21 x 10⁻⁵ m³-atm/K-mole $ppm_i = \frac{moles \ of \ pollutant \ i}{moles \ of \ air} \times 10^6 = \frac{\mu mole_i}{mole_{air}}$ So, $\frac{\mu g_i}{m_{ain}^3} = ppm_i \times MW_i \times \frac{P_{air}}{RT}$



Q: Convert 10 ppb of SO₂ to μ g/m³ at 20°C, 1 atm.

- Classification of air pollution problems
 - Microscale: less than the size of a house or slightly bigger
 - Mesoscale: a few hectares to the size of a city or slightly bigger
 - Macroscale: size of a county to a country and to the globe

- Microscale air pollution problems
 - Indoor air pollution: pollutants from burners, ovens, heaters, cigarette smoke, and underground
 - Cigarette smoke on streets



http://www.compacappliance.net



http://www.odamindia.org



http://www.edaily.co.kr

- Mesoscale air pollution problems
 - Vehicle exhaust
 - Smoke from power plants, factories, etc.
 - Smog

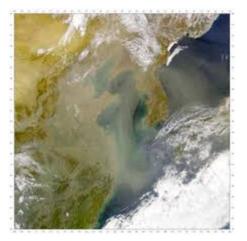


http://web.ornl.gov



http://www.bbc.com

- Macroscale air pollution problems
 - Acid rain
 - Yellow dust
 - Ozone depletion
 - Global warming



http://en.wikipedia.com



http://breitbart.com

• Carbon monoxide (CO)

- Generated by incomplete combustion of carbon
- Natural sources: oxidation of methane (CH₄) in the atmosphere
- Anthropogenic sources: motor vehicles, fossil fuel burning, solid waste disposal, burning of plant materials
- Reacts with hemoglobin in the blood to form carboxyhemoglobin (CoHb)
- Carbon monoxide poisoning: lots of deaths in 1950s-1980s in Korea caused by indoor briquette burning

• Lead (Pb)

- A cumulative poison
- Usually occurs in the atmosphere as a particulate
- Natural sources: volcanic activity and airborne soil
- Anthropogenic sources: smelters and refining processes, and incineration of lead-containing wastes
- In the past, lead used to be added to gasoline → significant air pollution problems → lead addition currently prohibited



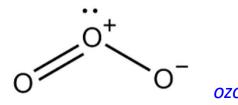
• Nitrogen oxides

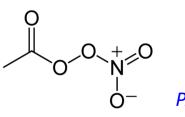
- NO, NO₂, N₂O, NO₃, N₂O₃, N₂O₄, N₂O₅
- NO2 itself has adverse effects on respiratory tract
- NO and NO₂ are involved in the formation of photochemical smog and acid rain
- $NO_x = NO + NO_2$
- Anthropogenic sources: combustion processes in motor vehicles, power plants, and the industry
- N₂ is an inert gas, but reacts with oxygen at high temperature (>1600 K):

 $N_2 + O_2 \rightarrow 2NO$

Photochemical oxidants

- Chemicals produced by reaction in the atmosphere in the presence of sunlight
- Classified as secondary pollutants
- O₃ (major), peroxyacetyl nitrate (PAN), acrolein, peroxybenzoyl nitrates (PBzN), aldehydes, nitrogen oxides
- Toxic effects because of their oxidizing ability: cause eye, nose, and throat irritation, and affect lung function
- Major pollutants in photochemical smog





Primary vs. secondary pollutants

• Primary pollutants

 Pollutants that are emitted directly from sources

Secondary pollutants

 Pollutants that are formed in the atmosphere by chemical reactions between primary pollutants and chemical species normally found in the atmosphere

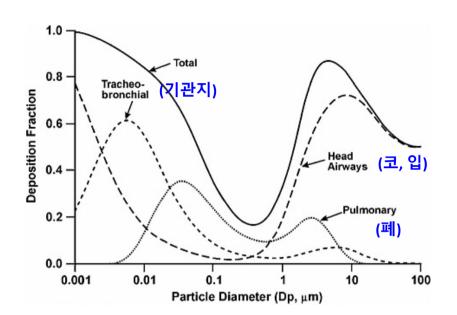
eq. 1 NO₂ + hv
$$\rightarrow$$
 NO + O
eq. 2 O + O₂ + M \rightarrow O₃ + M
eq. 3 NO + O₃ \rightarrow NO₂ + O₂ Ozone
eq. 4 O* + H₂O \rightarrow 2 OH*
eq. 5 $\begin{bmatrix} RH + OH^{\bullet} \rightarrow H_{2}O + R^{\bullet} \\ R^{\bullet} + O_{2} \rightarrow RO_{2}^{\bullet} \text{ very fast} \end{bmatrix}$
eq. 6 $\begin{bmatrix} RO_{2}^{\bullet} + NO \rightarrow NO_{2} + RO^{\bullet} \\ RO^{\bullet} + O_{2} \rightarrow R'CHO + HO^{\bullet}_{2} \text{ very fast} \end{bmatrix}$
eq. 7 $\begin{bmatrix} R'CHO + OH^{\bullet} \rightarrow R'CO^{\bullet} + H_{2}O \\ R'CO^{\bullet} + O_{2} \rightarrow R'C(O)O_{2}^{\bullet} \text{ very fast} \end{bmatrix}$
eq. 8 $R'C(O)O_{2}^{\bullet} + NO_{2} \rightarrow R'C(O)_{2}NO_{2} \rightarrow PAN$

- Sulfur oxides
 - SO₂, SO₃, SO₄²⁻
 - Called SO_x
 - Sources
 - Direct emission of SO_x from power plants, industry, volcanoes, and the oceans (as a primary pollutant)
 - Oxidation of H₂S produced by natural biological processes or the industry (as a secondary pollutant)
 - Involved in "London smog" and acid rain

• Particulates

- Particles suspended in the air
- Natural sources: sea salt, soil dust, volcanic particles, smoke from forest fires
- Anthropogenic sources: fossil fuel burning, industrial processes
- Damage respiratory organs

- Particulates
 - Large particles are trapped at the upper respiratory system, but small particles go deeper
 → small particles are more significant!
 - Korean government regulate "PM₁₀" and "PM_{2.5}"



Deposition of inhaled particles in the human Raabe (1994) Internal Radiation Dosimetry

- PM_{10} : particulate matter less than 10 μ m size
- $PM_{2.5}$: particulate matter less than 2.5 μ m size

• Other hazardous air pollutants

- Toxic organic compounds, heavy metals, arsenic, etc.
- Korean government regulates 35 hazardous air pollutants
- Some examples: cadmium, mercury, asbestos, dioxin, benzene