


Air Pollutants

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Classification of air pollutants

- According to formation process:
  - ✓ Primary pollutants: those emitted directly from the sources
  - ✓ Secondary pollutants: those formed in the atmosphere by chemical reactions among primary pollutants

HNO_3, H_2SO_4

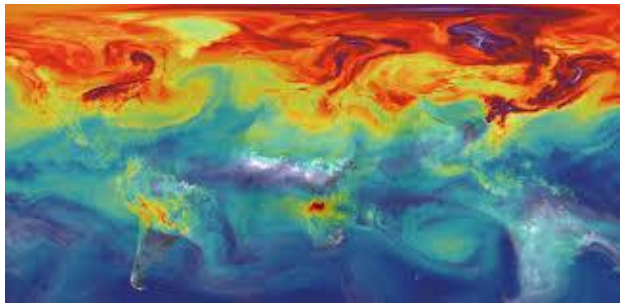
Organic aerosols

O_3, PAN

Classification of air pollutants

- According to source:
  - ✓ Biogenic: those emitted from natural sources
  - ✓ Anthropogenic: those formed by human activities

- According to the space scales of their effects:
  - ✓ Local (or indoor)
  - ✓ Regional
  - ✓ Global



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Classification of air pollutants

- According to physical state:
  - ✓ Gaseous
  - ✓ Liquid (aqueous)
  - ✓ Solid (particles or aerosols)
  - ✓ Forms of energy

- According to chemical composition:
  - ✓ Sulfur-containing compounds
  - ✓ Nitrogen-containing compounds
  - ✓ Carbon-containing compounds
  - ✓ Halogen-containing compounds
  - ✓ Toxic substances
  - ✓ Radiative compounds

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What are emissions?

The amount of pollutant(s) a source puts in the air during a fixed time

Emissions classification

- Stationary: sources with a fixed location
  - ✓ Point: usually a large source, often a stack
  - ✓ Area: sources that are considered as a group
- Mobile: sources that move
  - ✓ On-road: highway vehicles
  - ✓ Non-road: non-highway vehicles

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Criteria Pollutants

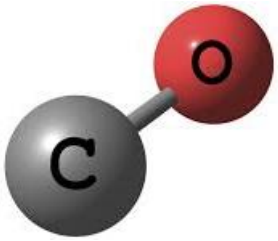
A group of air pollutants that have been regulated and are used as indicators of air quality. The regulations or standards are based on criteria that relate to health and/or environmental effects

- Carbon Monoxide (CO)
- Nitrogen Dioxide (NO_2)
- Sulfur Dioxide (SO_2)
- Ozone (O_3)
- Lead (Pb)
- Particulate Matter

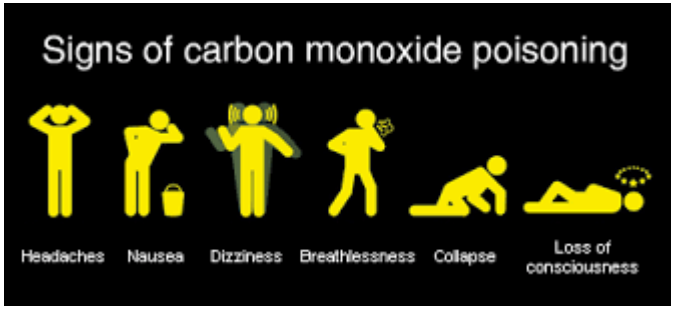
Hazardous air pollutants (air toxics)

Those known to cause cancer and other serious health impacts

Carbon monoxide (CO)



- Colourless, odourless, tasteless and poisonous gas
- Haemoglobin has 200 times more affinity for CO than Oxygen
- Atmospheric concentration: 0.6-0.12 ppm
- Highly toxic at concentrations > 1,000 ppm (death)
- Residence time: 60-200 days
- Natural sources:
  - ✓ Decay of organic matter
  - ✓ Oxidation of methane and non-methane hydrocarbons
- Anthropogenic sources:
  - ✓ Incomplete combustion of fuel
  - ✓ Biomass burning
  - ✓ Industrial activities
- Sinks: reaction with hydroxyl (·OH) radicals



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Carbon dioxide (CO_2)

- The major greenhouse gas involved in global warming
- Atmospheric concentration: 400 ppm
- Residence time: 2-10 years
- Natural sources:
  - ✓ Respiration
  - ✓ Weathering of silicates and carbonates
  - ✓ Oceans (contain 50 times more CO_2 than the atmosphere)

$$CO_2 + H_2O \leftrightarrow HCO_3^- + H^+$$

- Anthropogenic sources: fossil fuels
  - ✓ Cement plants: $CaCO_3 \leftrightarrow CaO + CO_2$
  - ✓ Deforestation
- Sinks: photosynthesis, oceans, soils

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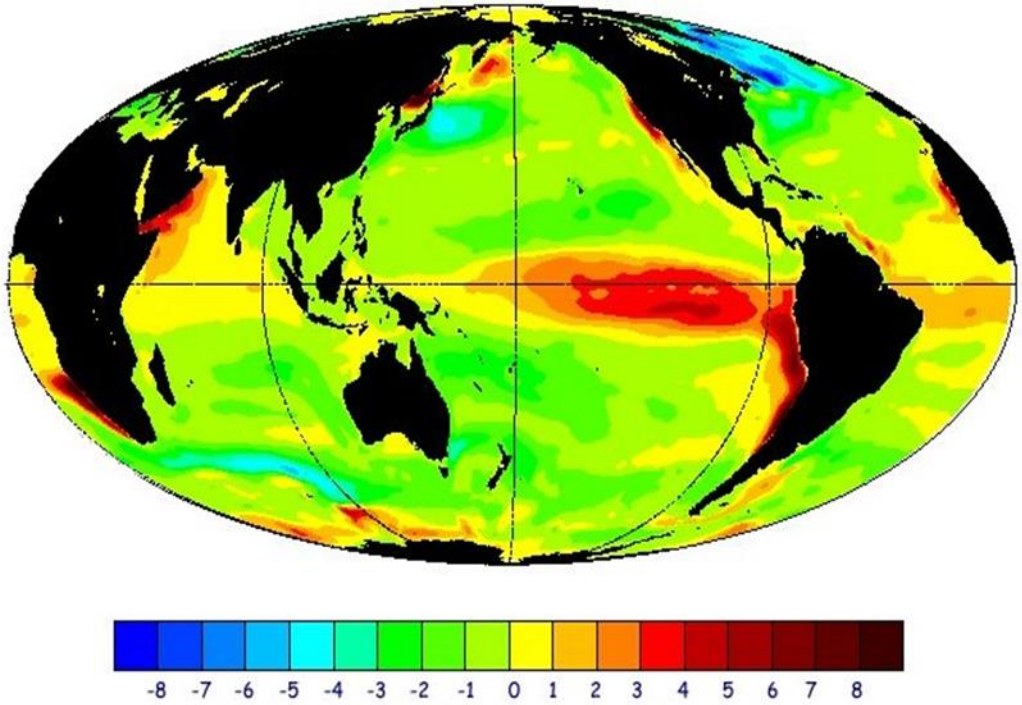
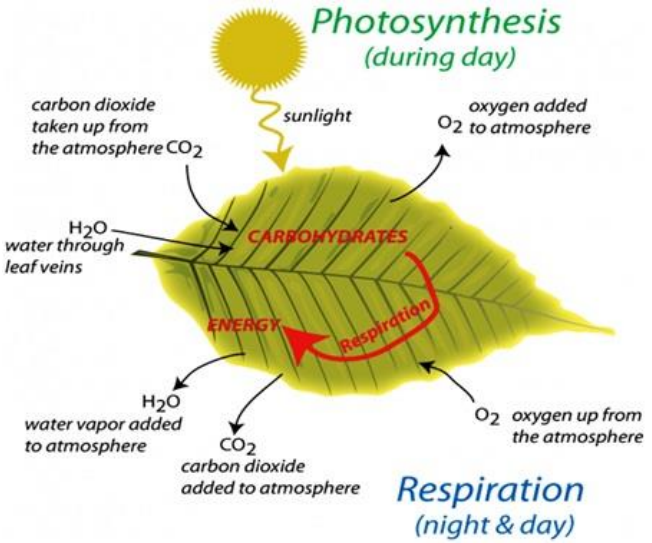
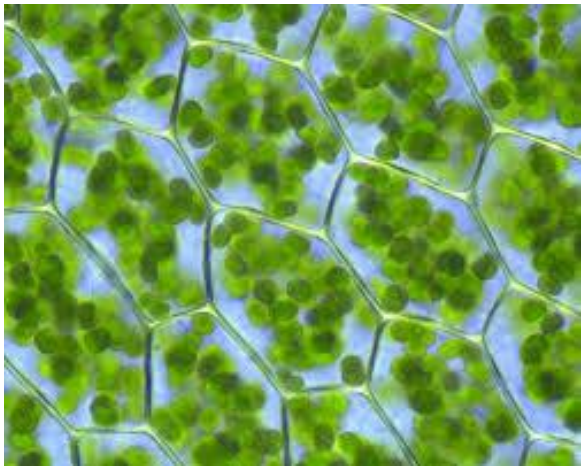
Sources and sinks of CO_2

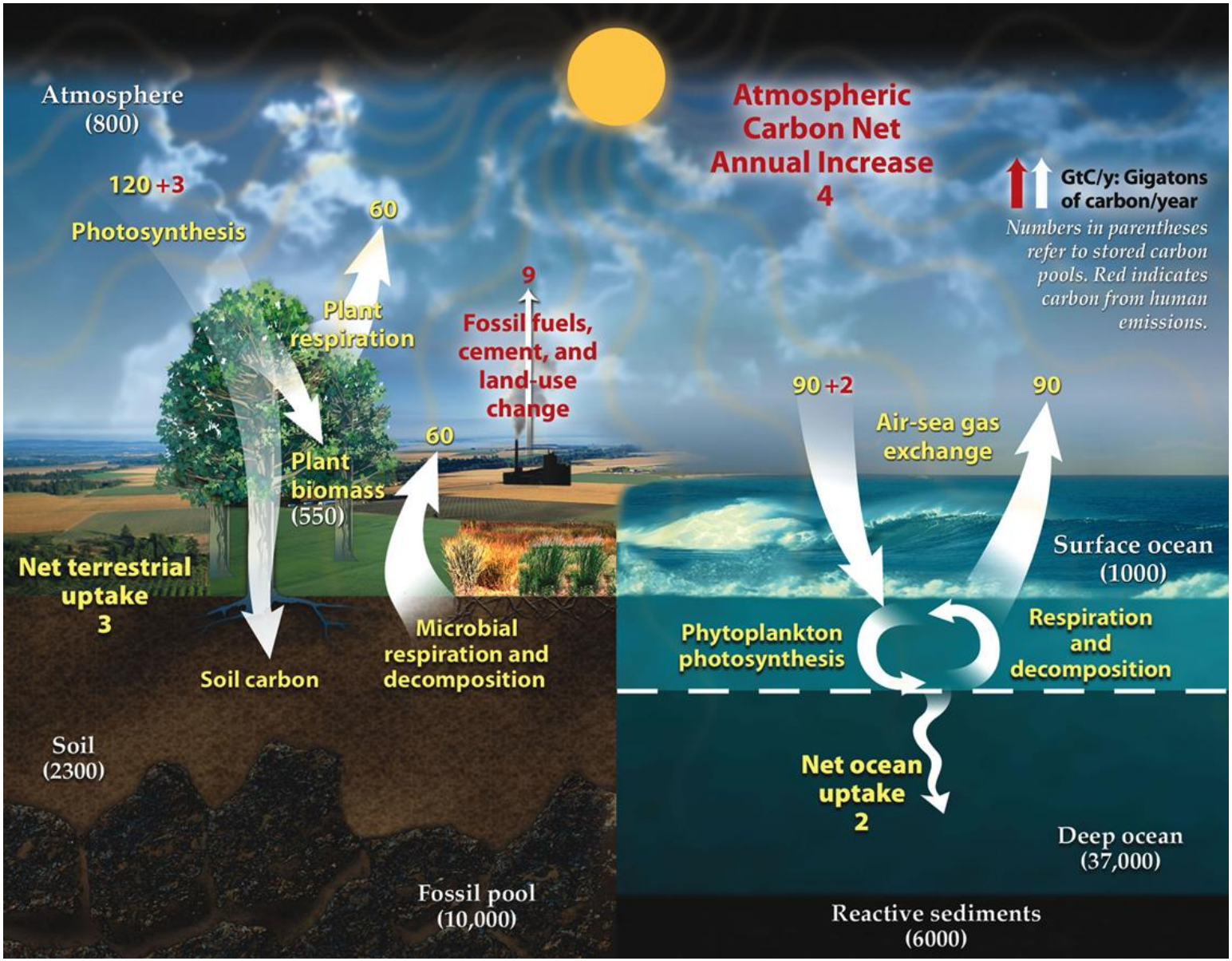


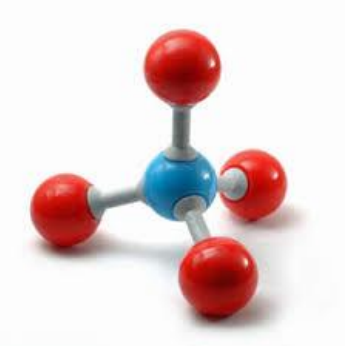
Global air-sea flux of CO_2 ($mol/m^{-2}/year$)





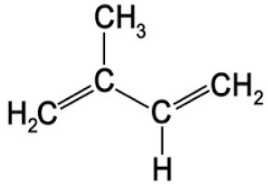
Air Pollutants





Methane (CH_4)

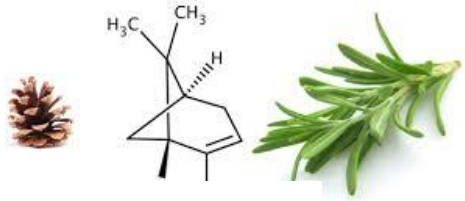
- Great involvement in global warming
- Atmospheric concentration: 1.7 ppm
- Residence time: 2-10 years
- Natural sources:
  - ✓ Degradation of organic matter (wetlands)
  - ✓ Anaerobic fermentation: $CO_2 + 3\ H_2 \leftrightarrow CH_4 + 2\ H_2O$
  - ✓ Intestine of ruminants
- Anthropogenic sources :
  - ✓ Biomass burning and combustion of fossil fuels
  - ✓ Livestock production
  - ✓ Paddy rice fields
- Sinks: reaction with hydroxyl (·OH) radicals, stratosphere, soils

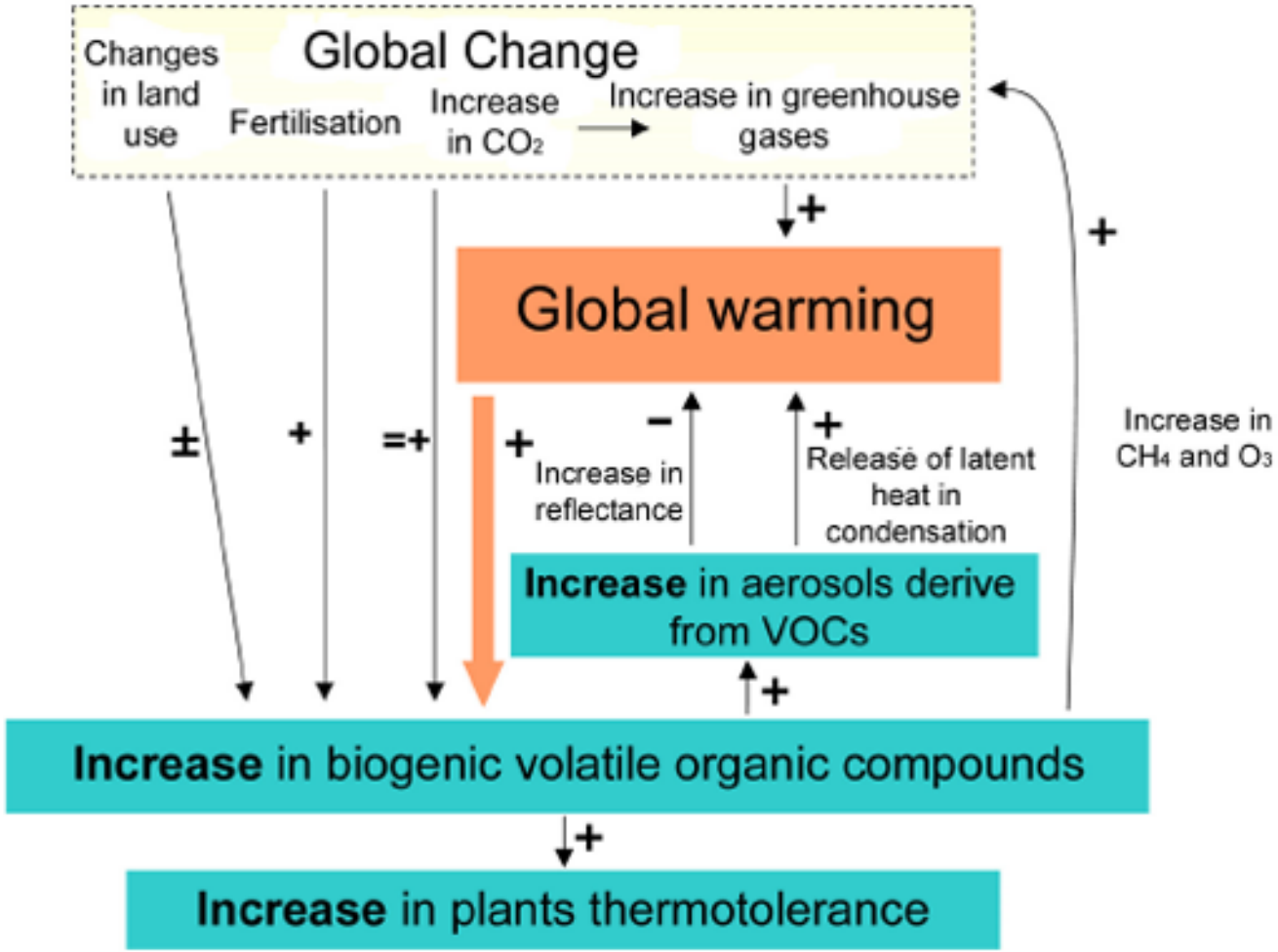


Volatile Organic Compounds (VOC)

- Organic chemicals that have a high vapour pressure at room temperature
- Some of them are carcinogens (benzene, PAH)
- Tropospheric ozone precursors
- Residence time: variable
- Natural sources:
  - ✓ Forests (isoprene, monoterpenes)
  - ✓ Pheromones, essences...
- Anthropogenic sources:
  - ✓ Biomass burning and combustion of fossil fuels
  - ✓ Fugitive losses (leaks from gas and gasoline tanks)
  - ✓ Paints and coatings
  - ✓ Building materials and furnishing…
- Sinks: photo-chemical reactions

Volatile Organic Compounds (VOC)





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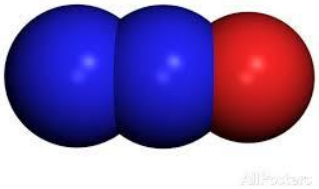
Nitrous oxide (N_2O)



- Global warming potential 300 times higher than CO_2
- Residence time: 110-170 years
- Natural sources:
  - ✓ Biomass burning (fires)
  - ✓ Microbial action in forest soils and oceans

  $C_6H_{12}O_6 + 6\ NO_3^- \leftrightarrow 6\ CO_2 + 3\ H_2O + 6\ OH^- + 3\ N_2O$
- Anthropogenic sources:
  - ✓ Intensive agriculture and livestock
  - ✓ Combustion of fossil fuels and industrial processes
  - ✓ Deforestation
  - ✓ Use of nitrogen fertilizers
- Sinks: photo-chemical reactions, stratosphere, soils

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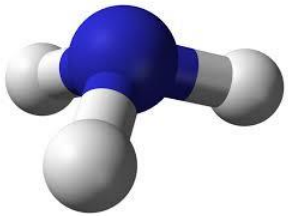
Ammonia (NH_3)

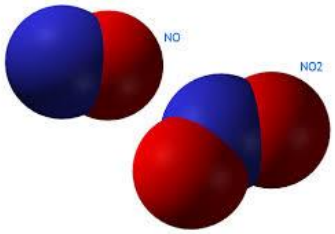


- It is the most abundant alkaline gas in the atmosphere
- It is toxic at high levels
- NH_3 plays a significant role in the formation of particulate matter
- Natural sources:
  - ✓ Animal urine
  - ✓ Bacterial degradation of nitrogen compounds

$$NH_2CONH_2 \text{ (urea)} + H_2O \leftrightarrow 2\ NH_3 + CO_2$$

$$CH_2NH_2COOH \text{ (amino acids)} + 3/2\ O_2 \leftrightarrow 2\ CO_2 + H_2O + NH_3$$

- Anthropogenic sources:
  - ✓ Fertilizers (based on NH_3)
  - ✓ Agriculture
  - ✓ Vehicular emissions
- Sinks: deposition (wet and dry)



Nitrogen oxides: NO_x (NO_2 + NO)

- They play an important role in atmospheric chemistry
- NO_2 is the predominant species in the atmosphere
- NOx are involved in important environmental problems:
  - ✓ Formation of ground-level O_3
  - ✓ Production of acid rain
  - ✓ Eutrophication
  - ✓ Adverse effects on human health
- Natural sources:
  - ✓ NH_3 oxidation
  - ✓ Reaction with oxygen (3,500 ºK): $N_2 + O_2 \leftrightarrow 2\ NO$
  - ✓ Lighting and biological processes
- Anthropogenic sources:
  - ✓ Combustion of fossil fuels
- Sinks: atmospheric reactions, stratosphere

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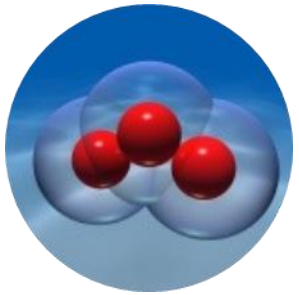
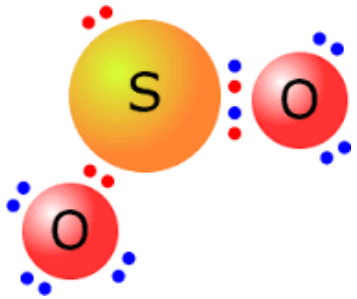
Tropospheric (ground-level) ozone (O_3)

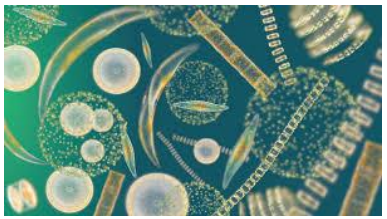


- Ozone is an allotropic form of oxygen
- Blue gas with pungent odour
- It is the main ingredient of the photochemical smog
- Primary sources:
  - ✓ Electrical discharges (storms, photocopiers)
  - ✓ Stratospheric intrusions
- Secondary sources:
  - ✓ VOC, NO_x and solar radiation
- High oxidizing capacity:
  - ✓ Vegetation: cell damage, reduction of crop yield
  - ✓ Health: respiratory diseases
- Sinks: atmospheric reactions, receptors

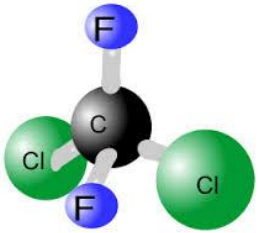
Sulfur-containing compounds



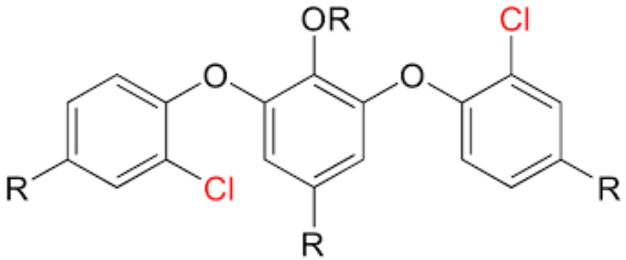
- Reactivity inversely related to its oxidation state
- SOx contribute to the formation of acid rain
- Natural sources:
  - ✓ Oceans (the most abundant is dimethyl sulphide)
    - Marine phytoplankton (*Phaeocystis pouchetii*)
      $(CH_3)_2S^+CH_2CH_2COO^- \leftrightarrow S(CH_3)_2 + CH_2CHCOOH$
    - COS (unreactive in the troposphere)
  - ✓ Volcanoes: SO_2, SH_2, CS_2, OCS
- Anthropogenic sources:
  - ✓ Fuel combustion
  - ✓ Industry
- Sinks: deposition (wet and dry), atmospheric reactions

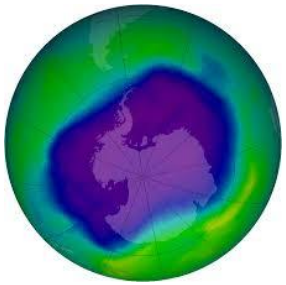


Chlorofluorocarbons (CFC)



- A CFC is an organic compound that contains only C, F and Cl (Freon)
- They are involved in the depletion of stratospheric ozone (1975)
- High residence times
- CFC-11 and CFC-12 were banned by Montreal (1987) protocol
- Natural sources:
  - ✓ Biomass burning, oceans, volcanoes: CH_3Br, CH_3Cl…
- Anthropogenic sources:
  - ✓ Refrigerants: CFC-12, HCFC-22
  - ✓ Aerosol propellants : CFC-11, HCFC-22
  - ✓ Solvents, cleaning: CFC-113, CH3CCl3….
  - ✓ Waste incineration
- Sinks: photo-dissociation in the stratosphere





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Nomenclature of Chlorofluorocarbons

CFCs are alkanes with H atoms replaced by Cl and F: **Alkanes: C_nH_{2n+2}**

CFC = XYZ (nº + 90)	X = number of carbon atoms Y = number of hydrogen atoms Z = number of fluorine atoms

The number of chlorine atoms is found by Cl = 2(C+1) - H - F

Example: Calculate the chemical formula of CFC-11

11 + 90 = 101 (C = 1, H = 0, F = 1) → $CFCl_3$

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Particulate Matter (PM)

- PM is made up of very heterogeneous compounds in terms of chemical composition, solid or liquid state and size
- Size: equivalent diameter
  - ✓ Ultrafine particles (Aitken): < 0.1 μm
  - ✓ Fine particles: 0.1-2.5 μm
  - ✓ Coarse particles: 2.5-10 μm
- Physical processes:
  - ✓ Growing: coagulation, condensation
  - ✓ Deposition: dry and wet
- Chemical relevance:
  - ✓ Catalyse many reactions: $2\ CO + O_2 \leftrightarrow 2\ CO_2$
  - ✓ Large effective surface

Particulate Matter (PM)

- Primary particles: directly released into the atmosphere
  - ✓ Pollen, spores, microorganisms, insects
  - ✓ Biogenic emissions and forest fires
  - ✓ Fugitive emissions from arid or desert areas
  - ✓ Marine aerosols
  - ✓ Combustion processes
  - ✓ Losses in industrial processes (cement, mining ...)
  - ✓ Farming
- Secondary particles: formed from other gaseous pollutants
  - ✓ Nitrate aerosols (oxidation of NO_x)
  - ✓ Sulphate aerosols derived from SO_2
  - ✓ Biological products: terpenes (α-pinene), aerosols of aldehydes or organic acids

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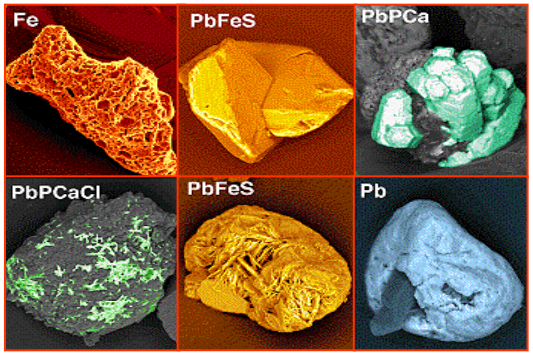
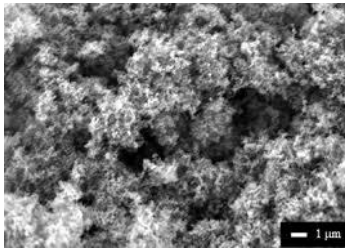
Particulate Matter (PM)



- Metals
  - ✓ Ca and Al (erosion); Na (marine aerosols)
  - ✓ Pb, V, Cr, Ni (gasoline, paints)
  - ✓ Fe (metallurgy); Pb, Sb, As (coal)
  - ✓ Cd, Mn, Pb, Sb, Ni, Cr (incinerators)
- Inorganics
  - ✓ Sulphates and nitrates (secondary)
  - ✓ Chlorides (marine aerosols)
  - ✓ Ammonium aerosols
- Organics
  - ✓ Terpenes (vegetation)
  - ✓ Aliphatic and aromatic hydrocarbons (solvents)
  - ✓ Dioxins and benzofurans (incineration); PAH (combustion)



Emission and immission

- Emission
  - ✓ Release of pollutants into the atmosphere from stationary or mobile sources (chimneys, vehicles…)
- Immission
  - ✓ The concentration in air of a pollutant to which a living being is normally exposed (Ground-level concentration)
  - ✓ Transfer of air pollutants from the free atmosphere to a receptor

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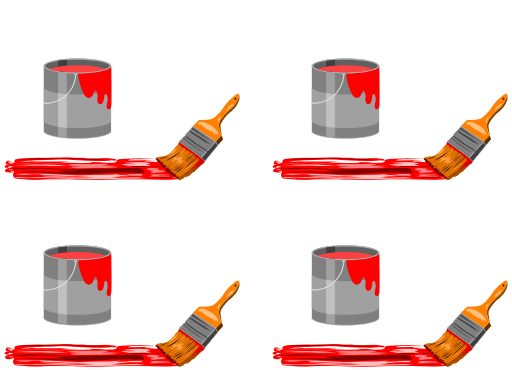
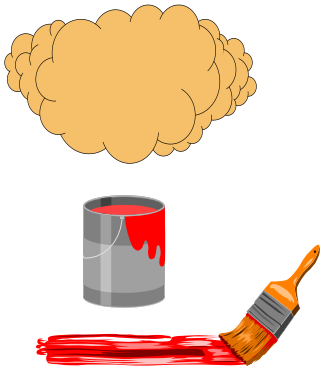
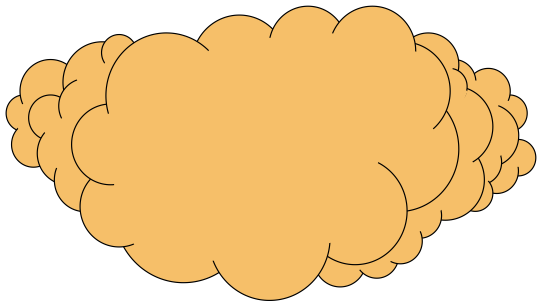
Emission factor

- Representative value that attempts to relate the quantity of a pollutant released into the atmosphere to an activity associated with the release of that pollutant
- They are used to estimate emissions when specific data are not available

Process Rate (Activity) x Emission Factor = Emissions







Number of Units x Emissions per Unit = Total Emissions

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Units for expressing pollutant concentrations

- Concentration units
  - ✓ volume/volume: %, ppm, ppb, ppt
  - ✓ mass/volume: $\mu g/m^3$
  - ✓ Dobson units (stratospheric ozone)

- Decimal multiples

Prefix	Symbol	Factor
kilo	k	10^3
mega	M	10^6
giga	G	10^9
tera	T	10^{12}

Prefix	Symbol	Factor
peta	P	10^{15}
exa	E	10^{18}
zetta	Z	10^{21}
yotta	Y	10^{24}

Units for expressing pollutant concentrations

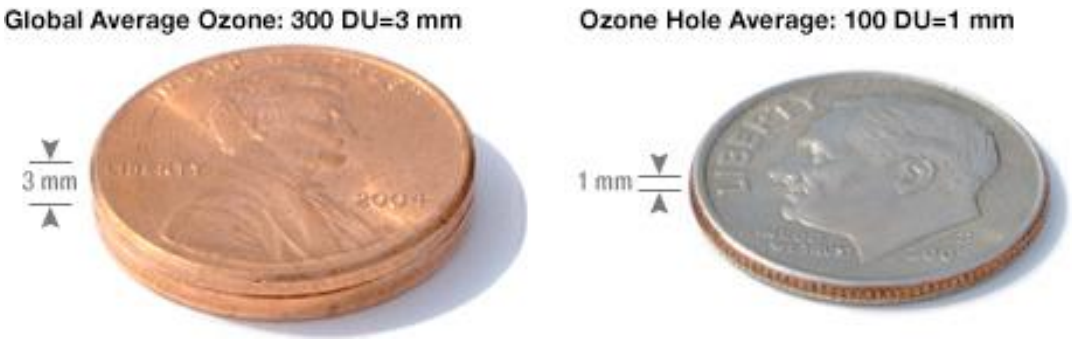
- volume/volume
  - ✓ High levels of pollutants: percent by volume (%)
  - ✓ Small levels of pollutants (mixing ratios):
    - ppm o ppmv → parts per million
    - ppb o ppbv → parts per billion
    - ppt o pptv → parts per trillion

$$\left.\begin{matrix}\text{ppm}\\ \text{ppb}\\ \text{ppt}\end{matrix}\right\} = \frac{\text{Volume pollutant}}{\text{Total air Volume}} \times \left\{\begin{matrix}10^{6}\\ 10^{9}\\ 10^{12}\end{matrix}\right.$$

Units for expressing pollutant concentrations

- Mass Volume Units
  - ✓ They are used both for solid (particles) and gaseous components
  - ✓ The most common units are: $\mu g/m^3$

- Dobson Units (DU)
  - ✓ A unit of measurement for ozone column in the atmosphere
  - ✓ 1 DU = the amount of atmospheric ozone that would form a uniform layer 0.01 millimeter thick at standard temperature (0°C) and pressure



Units for expressing pollutant concentrations

- Ideal gas Law
  - ✓ In most atmospheric calculations it can be assumed that the ideal gas law is met:

$$\mathbf{P\,V = n\,R\,T}$$

P = absolute pressure (atm)
V = volume (m^3)
n = mass (mol)
R = ideal gas constant= 0,082 L atm K^{-1} mol^{-1}
T = absolute temperature (K)

  - ✓ Recall that one mol of any gas has Avogadro's number of molecules in it (6.023 x 1023 molecules/mol) and has a mass equal to its molecular weight:

Units for expressing pollutant concentrations

- Volume of an ideal gas
  - ✓ Find the volume that 1 mol of an ideal gas would occupy at 1 atm of pressure and 0ºC temperature:

$$V = \frac{nRT}{P} = \frac{1\ mol\ x\ 0.082\ L\ atm\ K^{-1} mol^{-1} x\ 273\ K}{1\ atm} = 22.4\ L$$

  - ✓ Repeat the calculation for 1 atm and 25ºC:

$$V = \frac{nRT}{P} = \frac{1\ mol\ x\ 0.082\ L\ atm\ K^{-1} mol^{-1} x\ 298\ K}{1\ atm} = 24.4\ L$$

Remember that ºK = ºC + 273

Units for expressing pollutant concentrations

- Converting air pollutant concentrations (P = 1 atm)
  - ✓ mg m^{-3} to ppmv or μg m^{-3} to ppbv:

$$ppm = \frac{mg}{m^3} x \frac{(0.082 \bullet T)}{M} = \frac{mg}{m^3} x \frac{V}{M}$$

  - ✓ ppmv to mg m^{-3} or ppbv to μg m^{-3}:

$$\frac{mg}{m^3} = ppm\ x \frac{M}{(0.082 \bullet T)} = ppm\ x \frac{M}{V}$$

Where M = molecular weight and V = molar volume

Units for expressing pollutant concentrations

- Convert 123.45 μg m^{-3} of benzene (M = 78 g) to ppmv at 25ºC and 1 atmosphere pressure.

$$ppm = \frac{mg}{m^3} x \frac{(0.082 \bullet T)}{M} = 0.12345 \; x \; \frac{(0.082 \bullet 298)}{78} = 0.039$$

- The federal Air Quality Standard for carbon monoxide (M = 28) based on a 8-hour measurement is 9.0 ppm. Express this standard as percent by volume as well as in mg m^{-3} at 1 atm and 25ºC.

$$\% \text{ CO} = \frac{9}{10^6} \; x \; 100 = 9 \; 10^{-4}$$

$$\frac{mg}{m^3} = ppm \; x \; \frac{M}{(0.082 \bullet T)} = 9 \; x \; \frac{28M}{(0.082 \bullet 298)} = 10.3$$