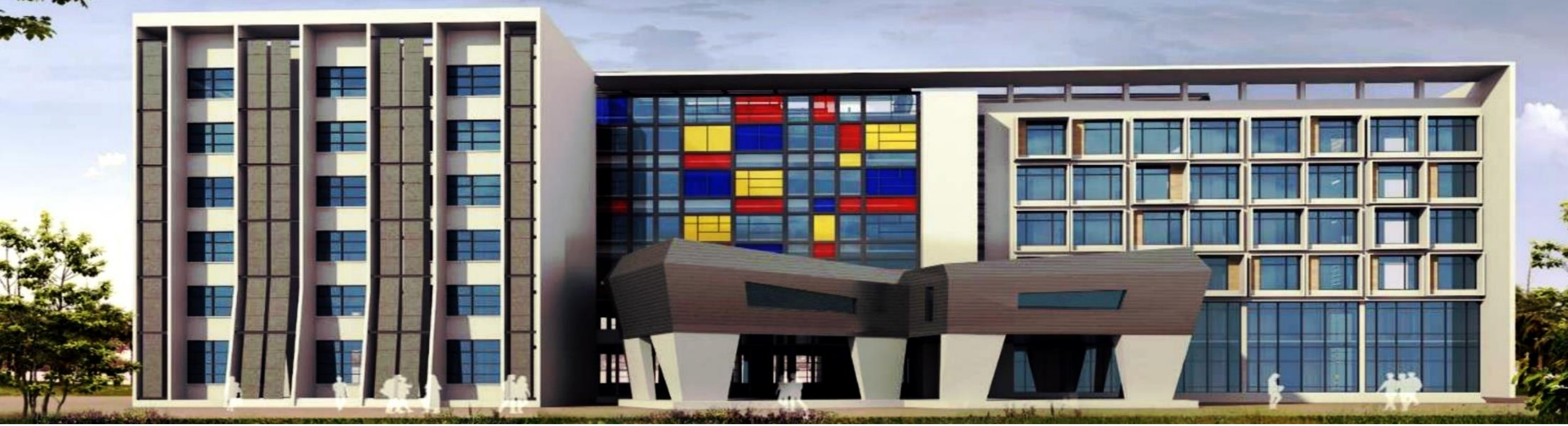

CY1018

भारतीय प्रौद्योगिकी संस्थान हैदराबाद
Indian Institute of Technology Hyderabad

Department of Chemistry

Course Content

Know our environment (chemistry of lithosphere, energy balance, sustainability and recycle), Know about global warming (infrared absorption, molecular vibration, atmospheric window, residence time of greenhouse gases, evidences and effects of global warming)

Deeper analysis of atmospheric pollution (Chemistry of CO, NOx, VOCs, SO_2, Industrial smog, photochemical smog), Ozone depletion (production, catalytic destruction)

Organic Chemicals in the Environment, Insecticides, Pesticides, Herbicides and Insect Control, Soaps, Synthetic Surfactants, Polymers, and Haloorganics. Fate of organic/inorganic chemicals in natural and engineered systems (fate of polymers after use, detergents, synthetic surfactants insecticides, pesticides etc. after use)

Aspects of transformations in atmosphere (microbial degradation of organics-environmental degradation of polymers, atmospheric lifetime, toxicity). Green Chemistry and Industrial Ecology. **Future challenges (CO_2 sequestering, Nuclear energy)**. A project on environment related topic.

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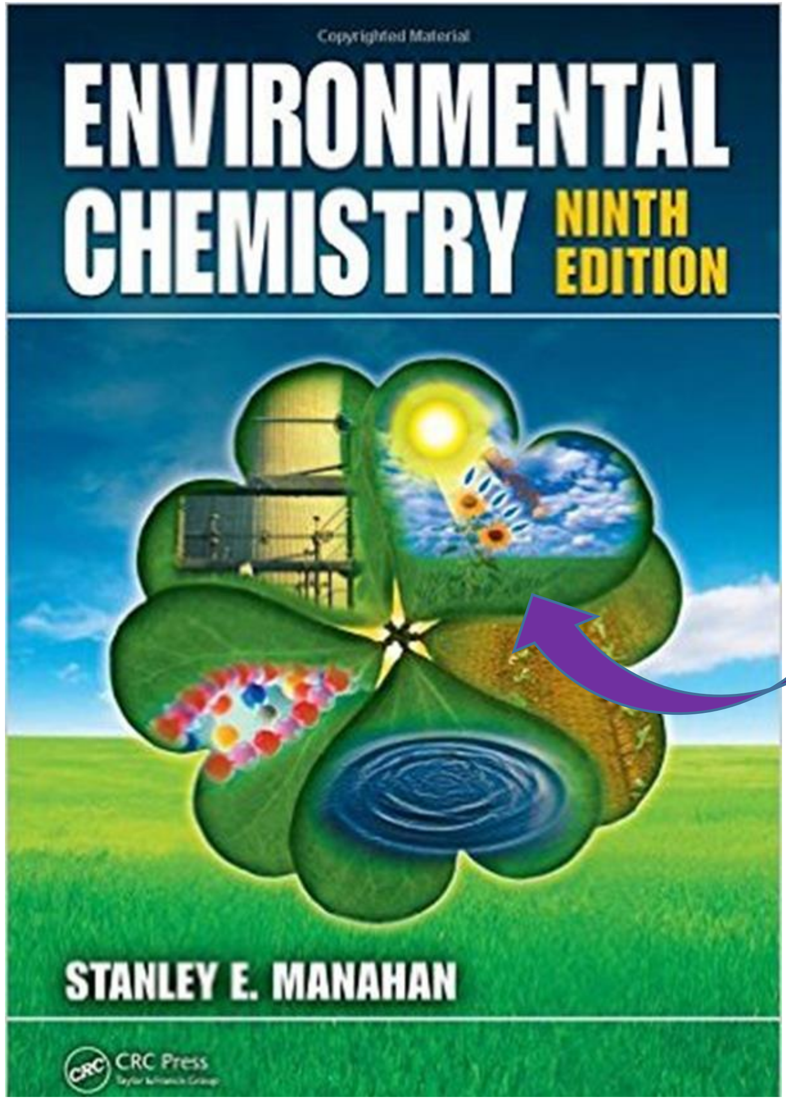
Reference books

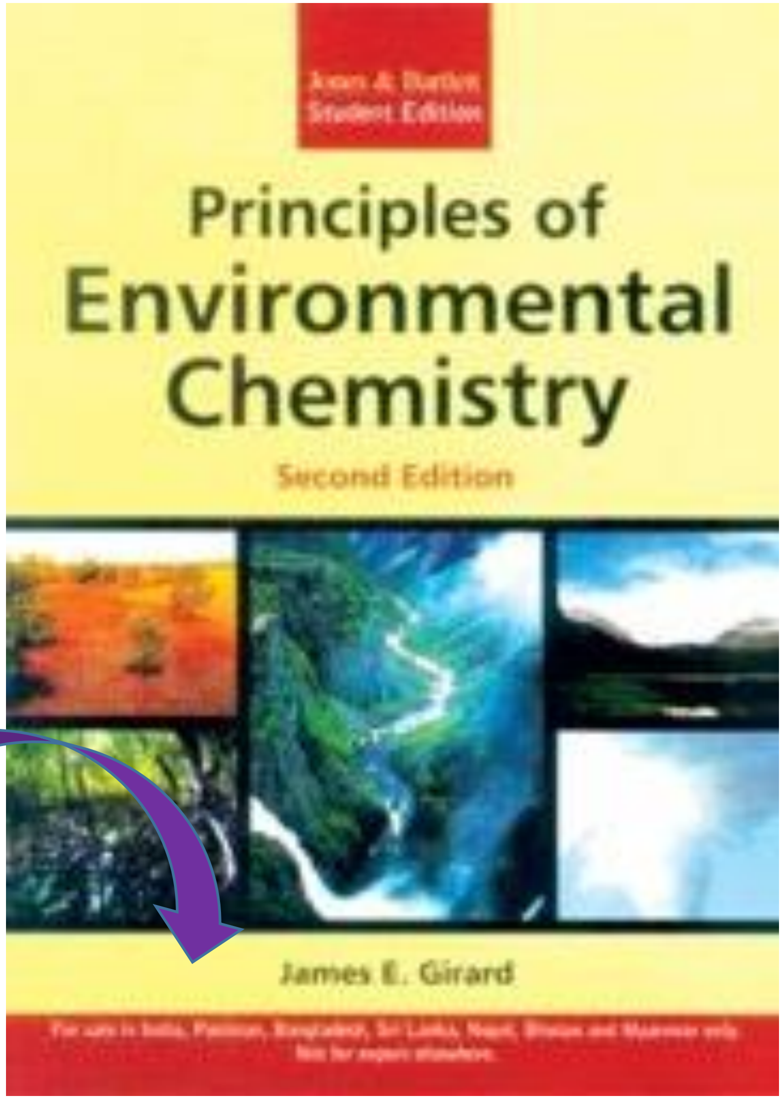


ENVIRONMENTAL CHEMISTRY

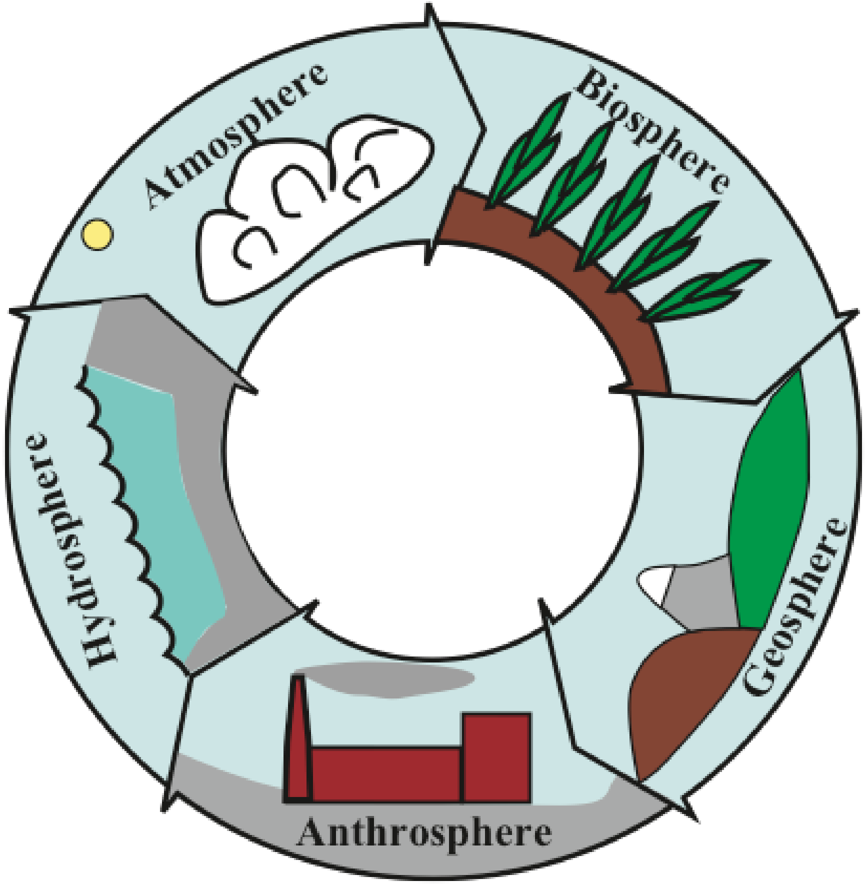
NINTH EDITION

STANLEY E. MANAHAN

Principles of Environmental Chemistry
By James E. Girard

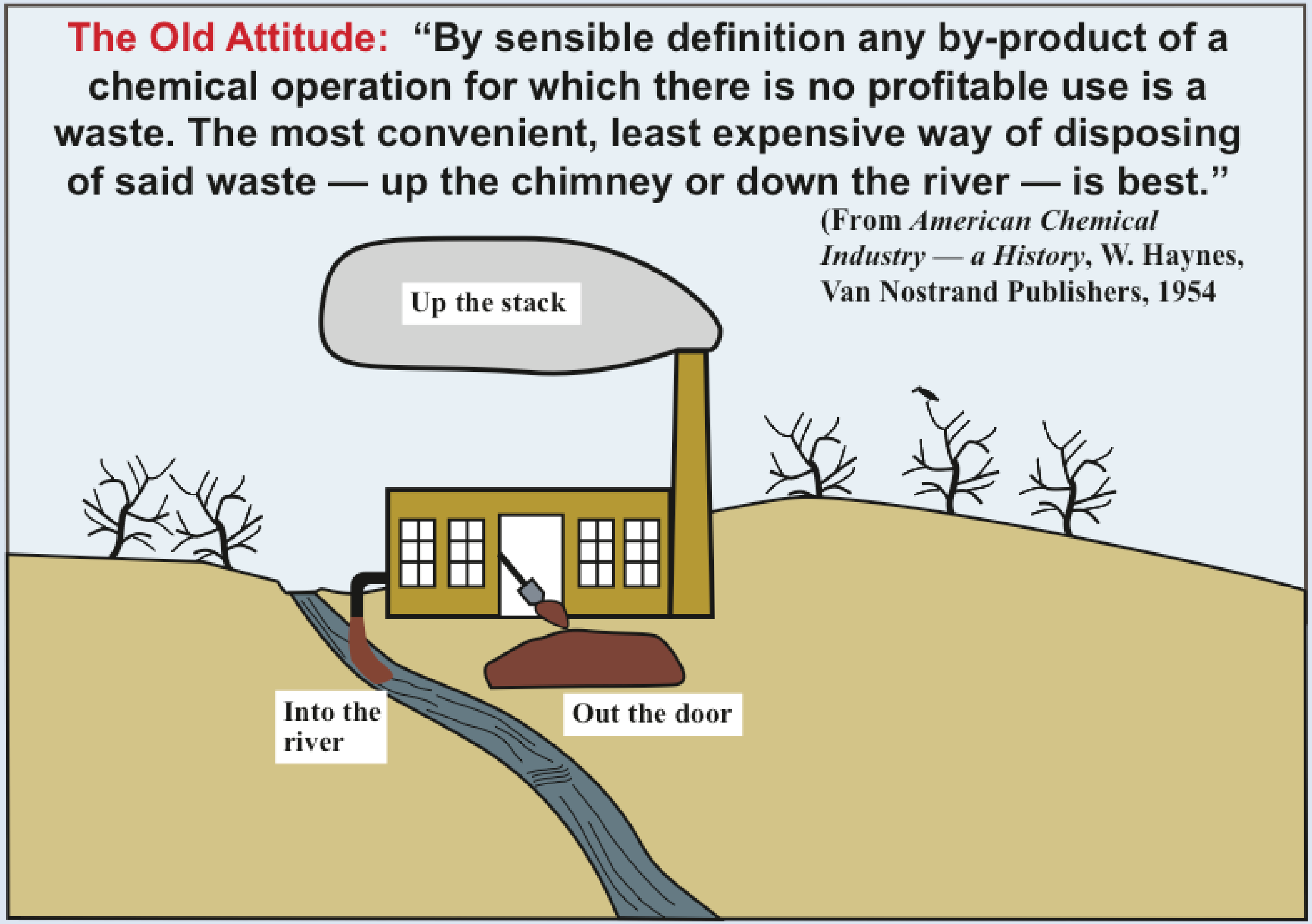


The Five Spheres of the Environment

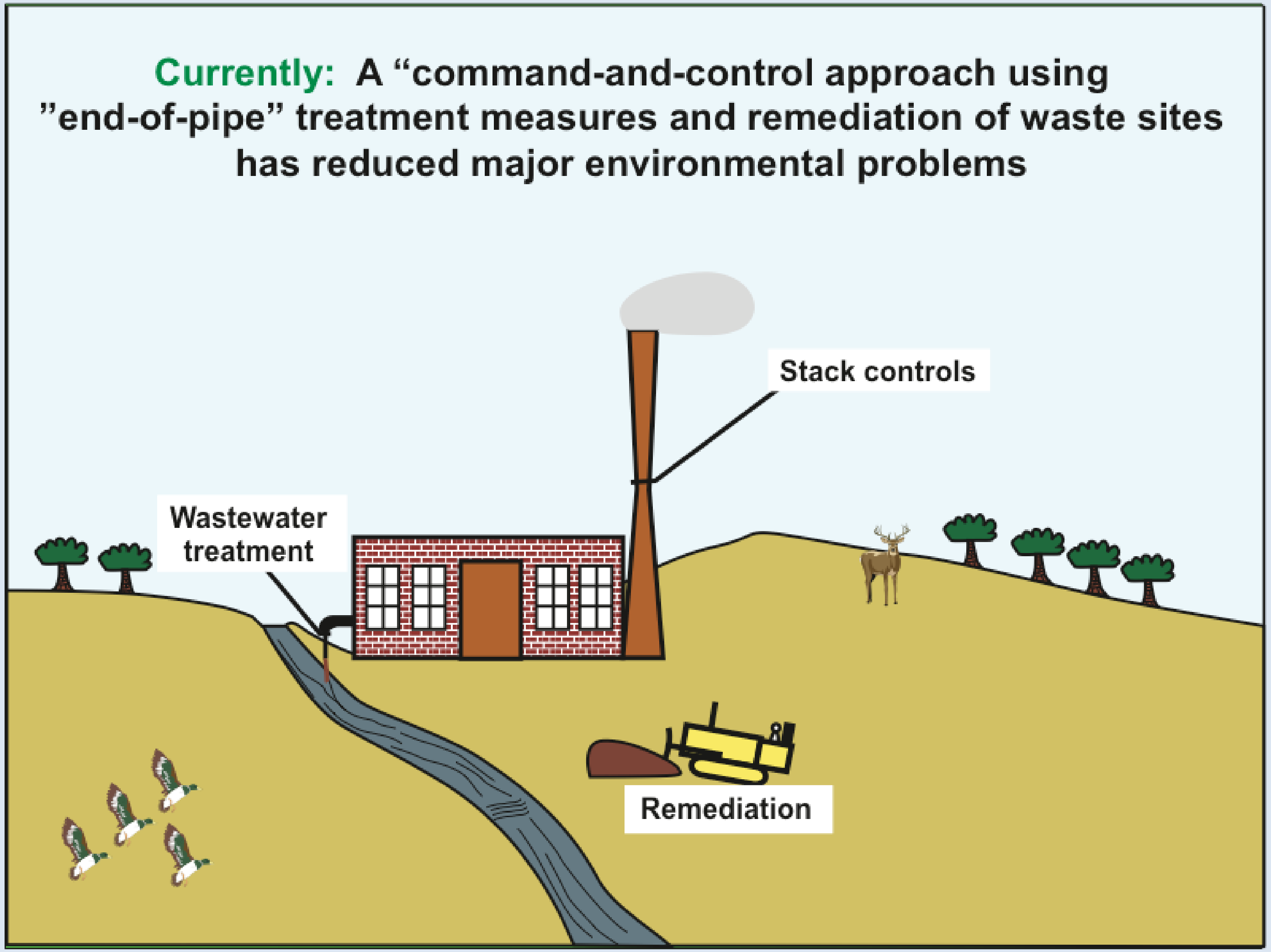


Matter and Energy are Exchanged Largely through Biogeochemical Cycles

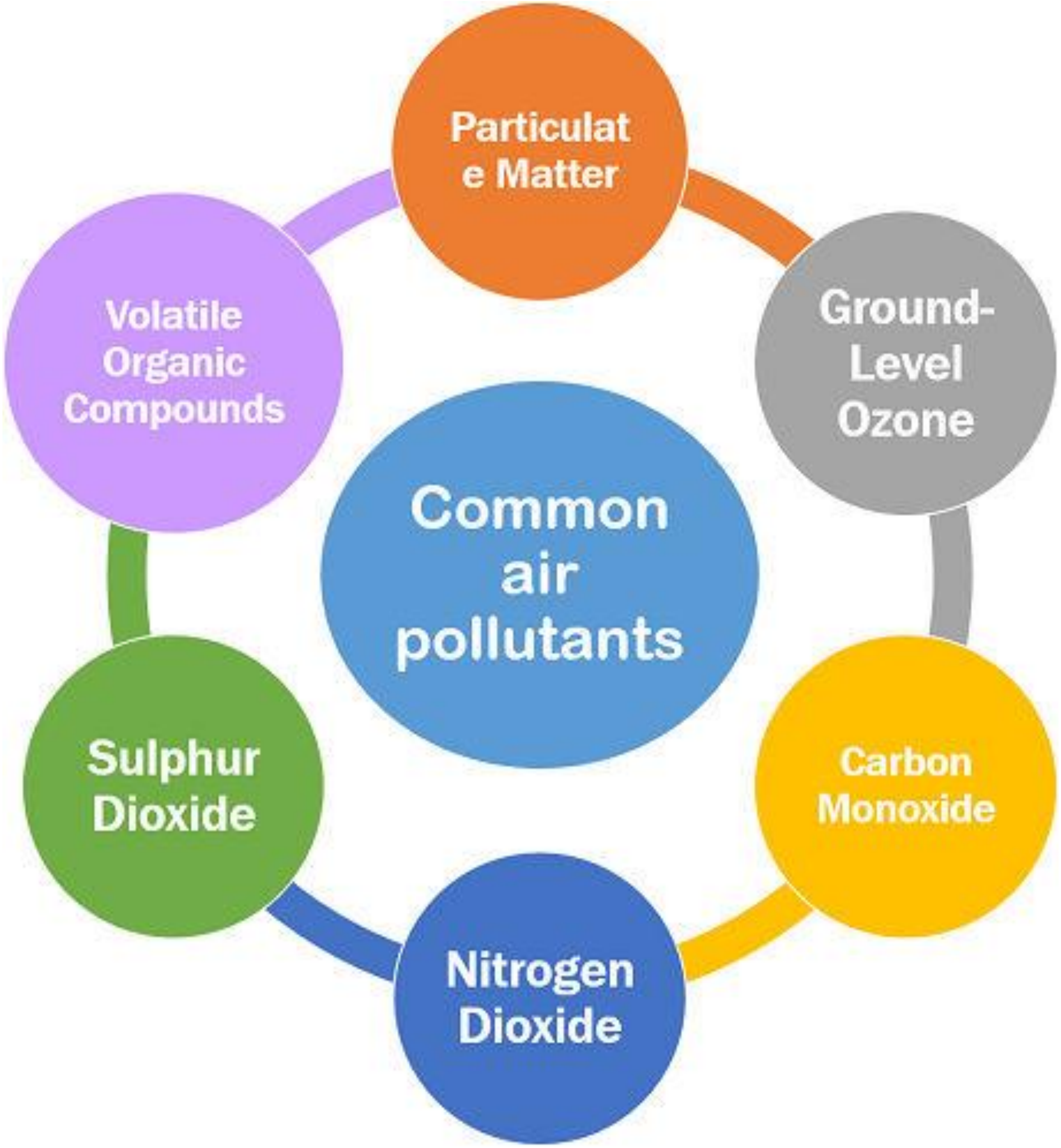
In the past many environmental problems were caused by practices that now seem to be totally unacceptable as expressed from the quote in this slide from what was regarded as a reputable book on the American chemical industry in 1954. The result was polluted air, polluted water, dangerous hazardous waste sites, and harm to living organisms.



Dating from around 1970, laws and regulations were implemented to control air and water pollution and to clean up hazardous waste sites. These measures have relied largely upon "end of pipe" controls in which pollutants were generated but were removed before release to the environment. Although costly and requiring constant vigilance to make sure that standards have been met, these measures have been successful in reducing pollution and preventing increases in pollutant releases.



Deeper analysis of atmospheric pollution

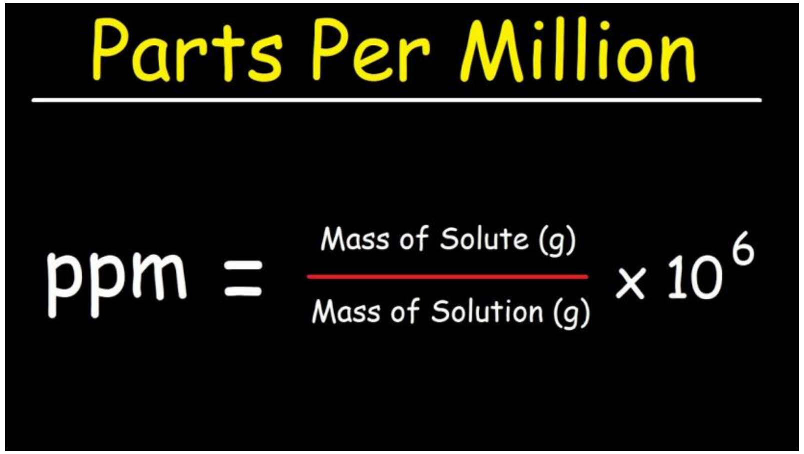


Air quality measurement are commonly reported in terms of:

– micrograms per cubic meter ($\mu g/m^3$)

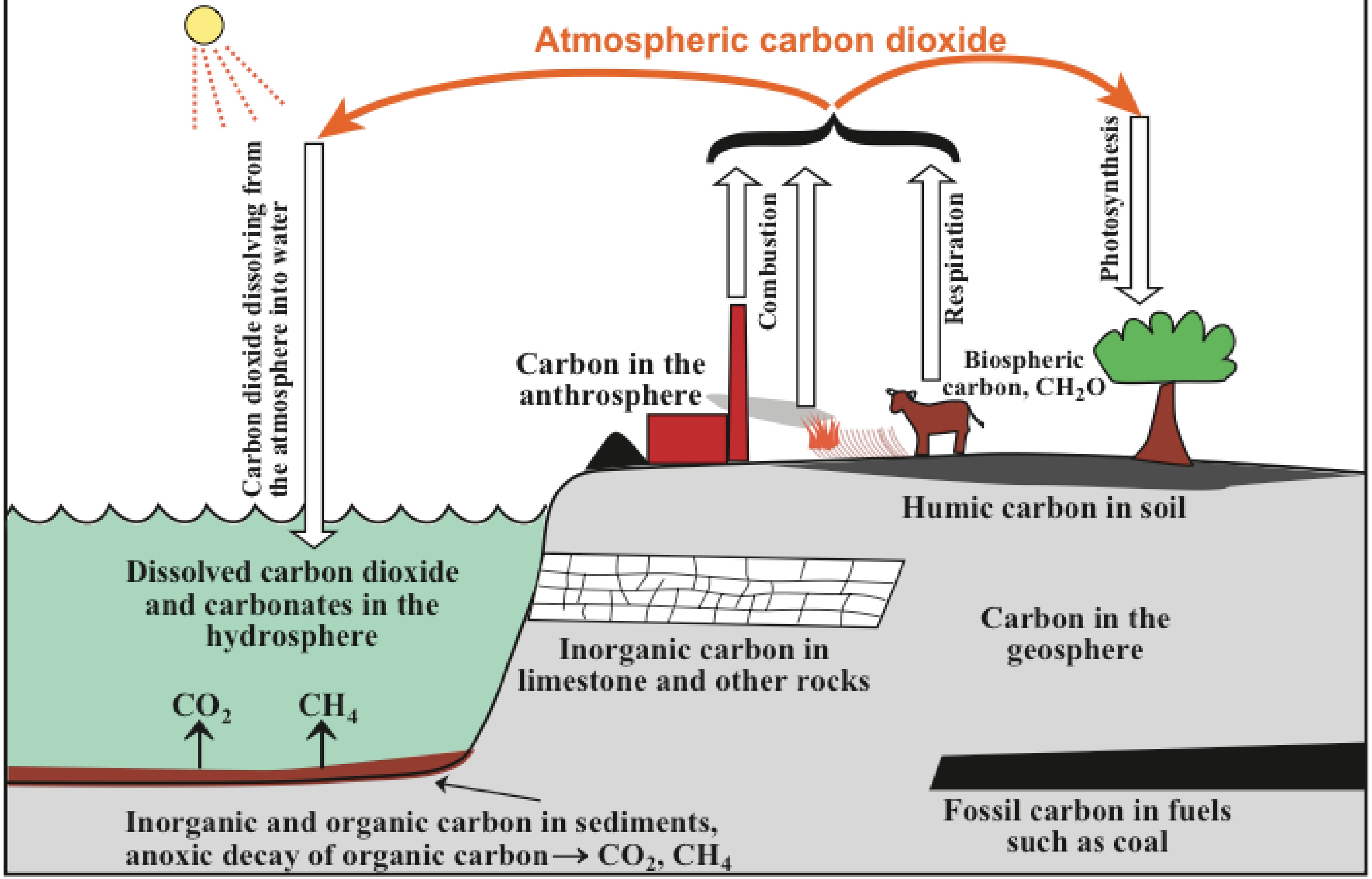
– parts per million (ppm) or parts per billion (ppb)

- For particulate matter, sizes are expressed in micron or micrometer.



Biogeochemical Cycles Are Important in Environmental Chemistry

The Carbon Cycle is Particularly Relevant to Climate Change



Analysis of air and air pollutant

- **Analytical measurements from the foundation on which our understanding of the atmosphere is built**
- **In atmospheric chemistry one of the most fundamental measurement is the most difficult.**
- **What is composition of air?**
- **Nitrogen gas represents more than 78% of the atmosphere whereas reactive species such as ozone are present in ppm level. The range in concentration of atmospheric constituents is extremely wide as large as 10^4**

Two different measurement Techniques:

In situ: It means the sample of the atmospheric gases must be placed inside the device (spectrometer) that is making

Remotely: (Remote sensing Technique): In this case by passing a beam of energy that originates on a satellite, an aircraft, the space shuttle or the ground through a portion of the atmosphere that is to be studied.

Although these measurement techniques involve different instrumentation, the underlying principles are same.

Analysis of air and air pollutant

- **Automobile smoke stack emission are major sources of anthropogenic pollutants into the atmosphere, both of which are regulated by the Environmental Protection Agency (EPA). Measurement of these gases emitted from auto mobiles and smoke stacks are difficult to make because the exhaust gases are hot and travelling at a high velocity.**

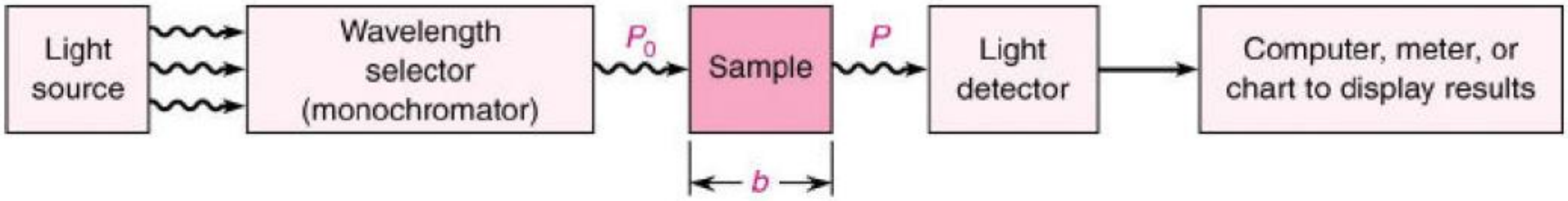
In situ Absorption Measurement

- ***Spectroscopic Measurement*: This method rely on the fact that different chemical compounds absorbs electromagnetic radiation at different wave lengths. When a molecule absorbs a photon of electromagnetic radiation, the energy of the molecule increases.**
- For example, when a molecule absorbs a microwave radiation, which is EMR of a relatively low energy, it only stimulate the rotational motion of the molecule.
- IR radiation which has higher energy than microwaves, stimulate vibrations of the molecules that absorbs it. UV radiation which has even higher energy than IR., causes electrons in the molecules absorbing it to be promoted into higher energy orbitals; the molecule is said to be in the excited state. The lowest energy state of the molecule is called ground state.

In situ Absorption Measurement

- Very high energy EMR such as X-ray has enough energy to break chemical bonds and ionize molecules.
- When the sample absorbs a beam of EMR radiation, the irradiance of the beam is decreased. The irradiance (P) which is some times intensity or radiant power is the energy per second per unit area of the light beam.
- EMR is passed through a monochromator (a prism) to select one wave length of EMR. The light of the single wave length is called monochromatic which means "one color".
- The monochromatic light with irradiance P_0 passes into a sample b. The irradiance of the beam emerging from the other side of the sample is P. Some of the light may be absorbed by the sample and thus $P_0 \geq P$.

Instrumentation

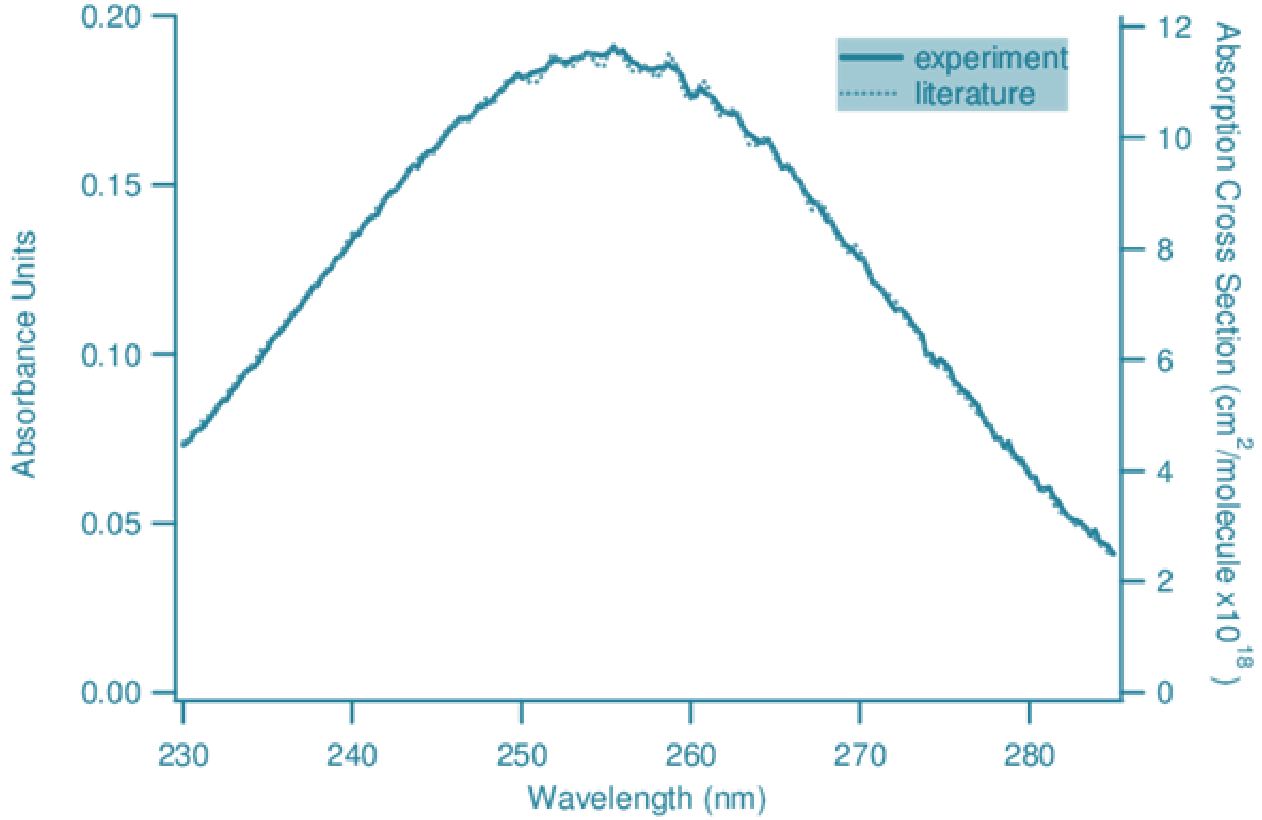


In situ Absorption Measurement

- Transmittance (T): it is defined as the fraction of the original light that has passed through the sample.
- $T = \frac{P}{P_0}$ T has the range of 0 to 1. The percentage of transmittance is 100 T and has a range from 0% to 100%.Absorbance (A) is defined as follows:
- $A = \log\left(\frac{P_0}{P}\right) = -\log T$; When no light is absorbed $P = P_0$ and $A = 0$
- Absorbance is important because it is directly proportional to concentration (C) of the absorbing molecules in the sample. A is dimensionless.
- The Beer-Lambert or simply Beer's Law:
- $A = \varepsilon . b . C$ (b = path length cm or m etc, C = concentration moles/L, ppm, ppb etc)
- ε = molar absorptivity or extinction coefficient. It is the characteristics of the molecule that indicates how much light it will absorb at a particular wave length.

In situ Ozone measurement

- *Ultraviolet* absorption has been used to measure the condensation of ozone in stratospheric air. The figure shows that ozone has a strong absorption in the UV region. Other atmospheric gases such as O_2, N_2 and H_2O do not absorb UV radiation and thus do not have to be removed from the air sample as they do not interfere with the ozone measurement.

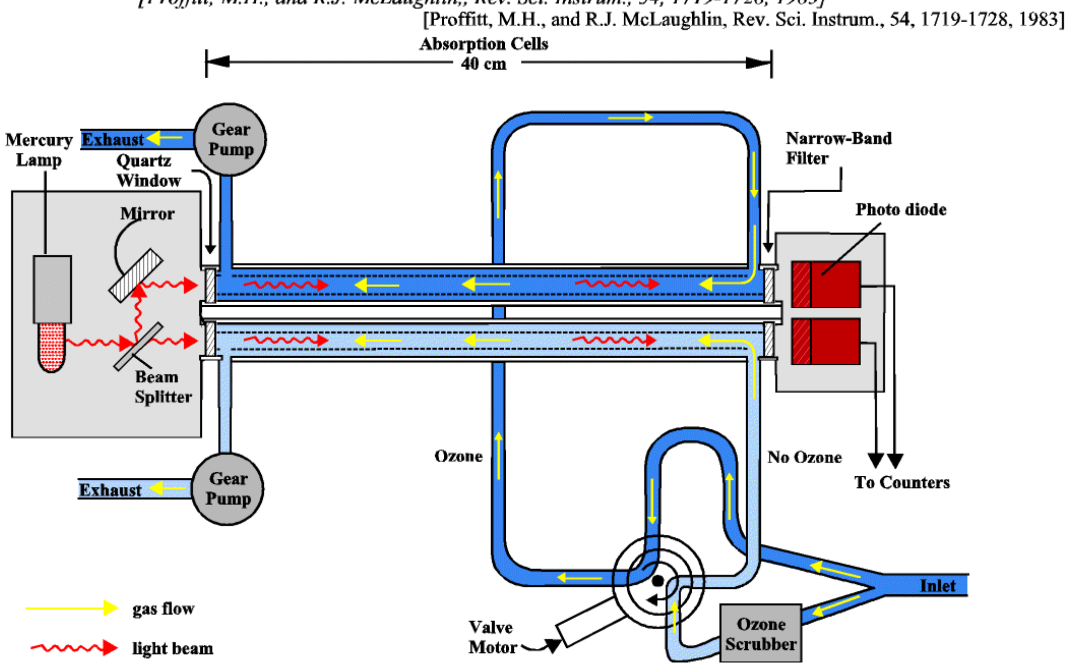


In situ Ozone measurement

- The concentration of ozone in the stratosphere is less than 10 ppm, so the spectrophotometer that is used to make the measurement must be capable of measuring a small absorbance. This is most easily done by making the sample cell very long. Because Beer's law tells that absorbance is propositional to the sample path length and because we can get a lot of sample easily, a long sample path length will greatly improve our ability to measure ppm level of Ozone.

Ozone:Dual Beam UV-Photometer

[Proffitt, M.H., and R.J. McLaughlin,, Rev. Sci. Instrum., 54, 1719-1728, 1983]



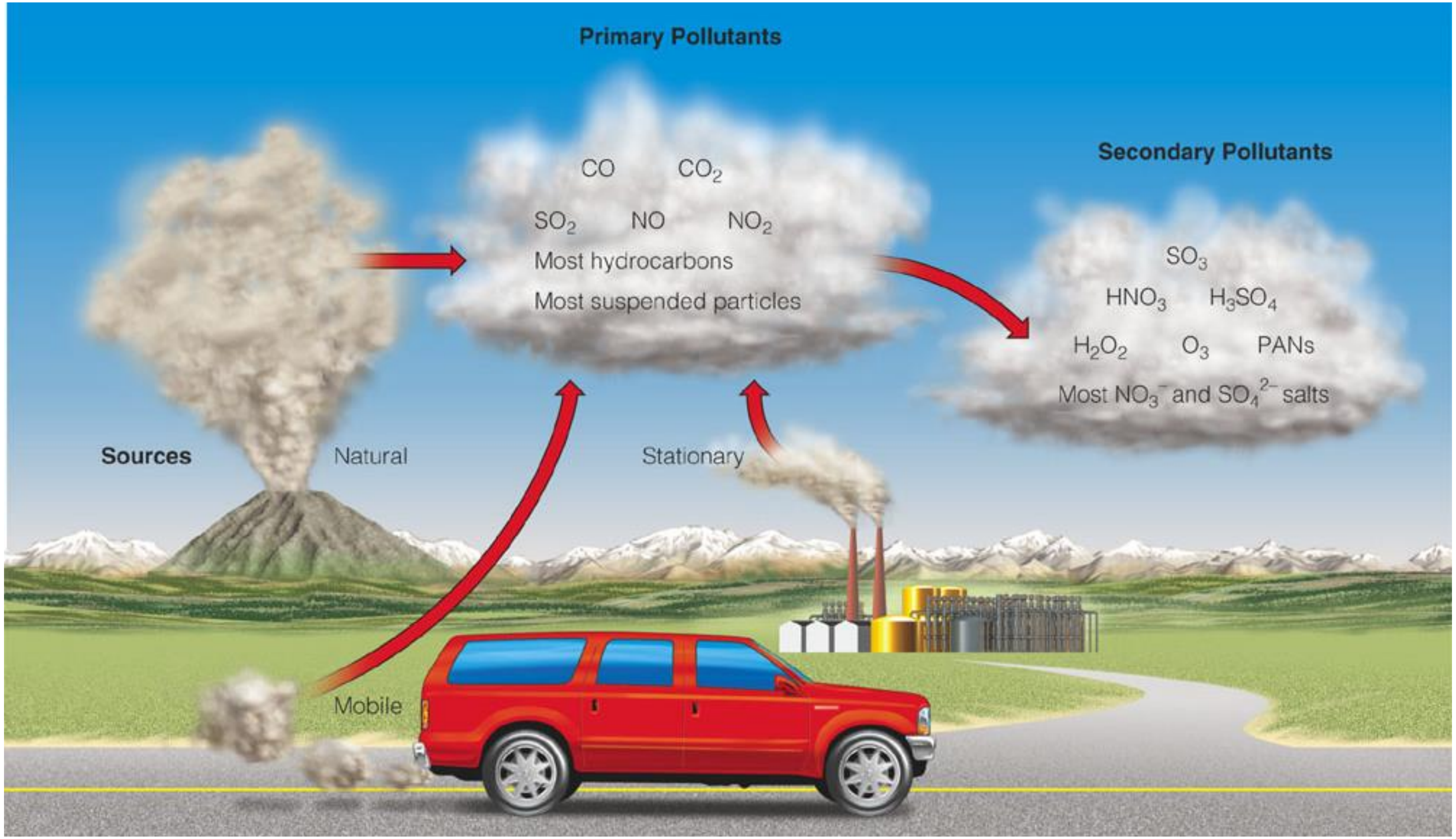
Basic Pollutants

Basic Pollutants

Pollutant	Abbreviation	Type
Carbon Monoxide	CO	Primary
Sulfur Dioxide	SO_2	Primary
Ozone	O_3	Secondary
Nitrogen Dioxide	NO_2	Secondary
Hydrocarbon Compounds (also called VOCs – volatile organic compounds)	HC	Primary & Secondary
Particulate Matter	PM	Primary & Secondary
Lead	Pb	Primary & Secondary

Types of Pollutants

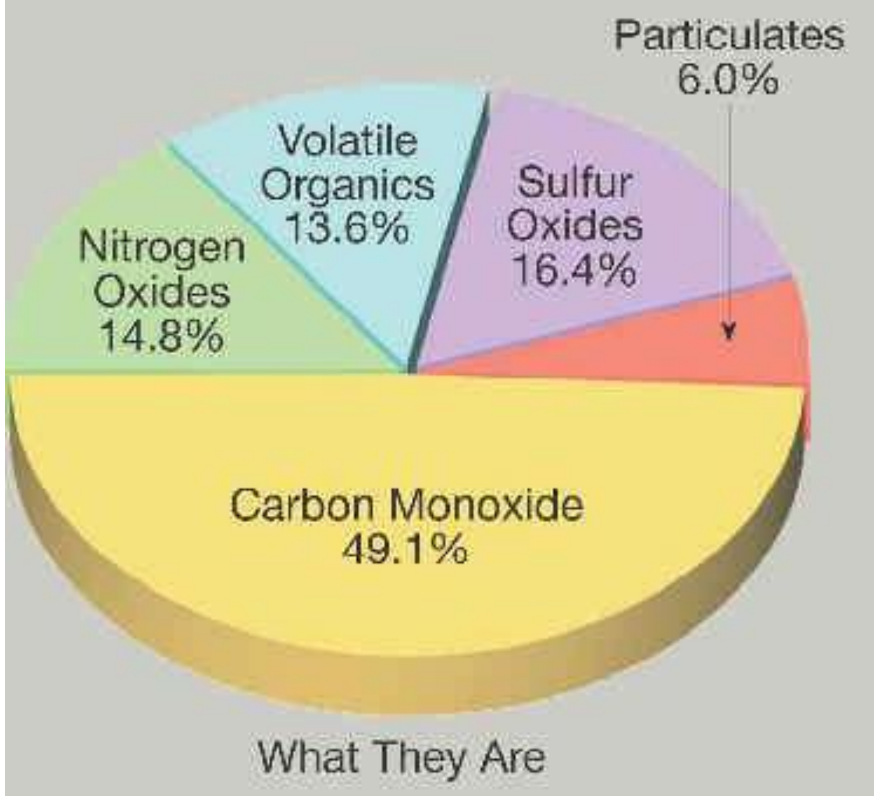
Primary pollutants | Secondary Pollutants

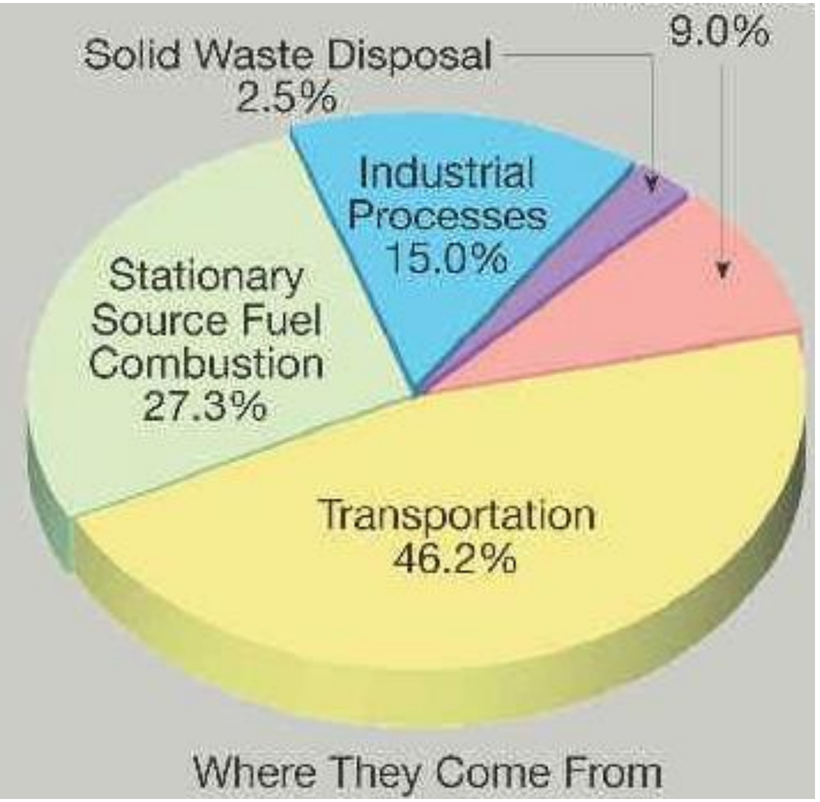


Types of Pollutants

Primary pollutants are those gases or particles that are pumped into the air to make it unclean. They include carbon monoxide from automobile (cars) exhausts and sulfur dioxide from the combustion of coal. Primarily air pollutants can be caused by primary sources or secondary sources. **The pollutants that are a direct result of the process can be called primary pollutants.**

A classic example of a primary pollutant would be the sulfur-dioxide emitted from factories.





Chemistry of Troposphere

- **Air Pollutant**

- An air pollutant is defined as the substance that is present in the atmosphere at a concentration that is sufficient to cause harm to human, other animals, vegetations or materials
- Approx 90% of all air pollution is caused by these primary air pollutant

1. Carbon monoxide (CO)
2. Sulfur dioxide (SO_2)
3. Nitrogen Oxides (NOx)
4. Volatile Organic Compounds (VOCs)
5. Mostly Hydrocarbons (HCs)
6. Suspended particles

- In addition, Secondary pollutants are also present
- Harmful substances produces by chemical reactions between primary pollutant and other constituent of the atmosphere. e.g. H_2SO_4, HNO_3; SO_4^{2-} and NO_3^- contribute to the acid rain

Ozone and other photochemical oxidants contribute to photochemical smog

Chemistry of Troposphere

❖ Carbon Monoxide

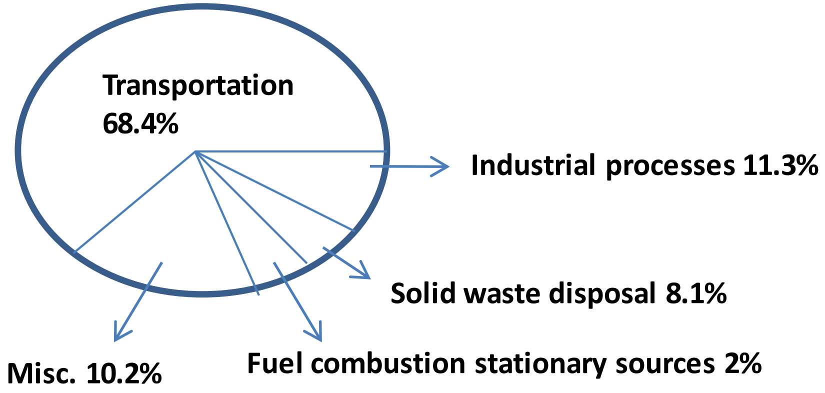
➢ Source of Carbon monoxide

➢ Main anthropogenic source of CO is the combustion of gasoline in automobile engines

1. Gasoline is a complex mixture of hydrocarbons (HCs)
2. If this is ignited in an adequate supply of oxygen; the products are CO_2 and H_2O

$$2\ C_8H_{18} + 25\ O_2 \longrightarrow 18\ H_2O + 16CO_2$$

1. In the confined space of the internal combustion of engine O_2 supply is limited and combustion is incomplete. Thus CO is formed and released to the atmosphere in auto mobile exhaust
2. $2\ C_8H_{18} + 17\ O_2 \longrightarrow 18\ H_2O + 16\ CO$



❖ **However, the introduction of catalyst converter reduce the CO emissions**

❖ **Natural source of CO into the atmosphere is CH_4 gas**

$$2\ CH_4 + 3\ O_2 \longrightarrow 2\ CO + 4\ H_2O$$

Methane is also produced in the stomach in the cattle and sheep and finally released into the atmosphere