Aerosol and chemistry of troposphere

Kirpa Ram

Chapter #4 and 6

4. **Chemistry of Troposphere:** Tropospheric chemistry of reactive gases, sources and inventories; Oxidation-reduction reactions; Oxidizing capacity of the atmosphere; Heterogeneous and homogenous chemical reactions and processes; Atmospheric photochemical reactions; Atmospheric effects- pollution, air quality, fog, smog, visibility, acid rain and precipitation chemistry

6. **Aerosols:** Atmospheric aerosols: source, sinks, removal mechanism; Size distribution, carbonaceous aerosols; Black carbon, brown carbon; SOA formations: chemistry and mechanisms; radiative impact of aerosols

Books

J. Glynn Heney and Gary W. Heinke, *Environmental Science and Engineering (2nd Edition)*, Chapter 13: *General book*

Seinfeld & Pandis, *Atmospheric Chemistry and Physics, (2nd Edition)*: *Most advanced level book*

Finlayson-Pitts & Pitts, *Chemistry of the Upper and Lower Atmosphere*: *Best book if you want to work in Atmospheric Chemistry*

Prerequisites for the course

- Basic Chemistry

  (Organic, Inorganic, physical, analytical)

- Expressing concentration and units conversions

1. Mole, mole fraction, %, ppm, ppb and ppt
2. No. of molecules or moles per m^3
3. $\mu g\ m^{-3}$

These units can be converted into others. Which of these are SI units?
(Mole, mole fraction, ppm, ppb and ppt)

What are various types of pollutions?
How we define and why do we study Air pollution?

Scientific Bodies who looks for such things:
CPCB, SPCB (India), NGOs, Govt and autonoumnus bodies etc..

The United States *Environmental Protection Agency* (*EPA* or sometimes USEPA)

In this lecture, we will be focusing on Air pollution, their sources and impact

Overview of the Lecture

- Atmospheric composition
- Types and Sources of Air Pollution
  - Major Classes of Air Pollutants
  - Sources of Outdoor Air Pollutants
  - Urban Air Pollution
- Effects of Air Pollution (a couple of examples)
- Controlling Air Pollution

What is air pollution?

The result of emission into the air of hazardous substances at a rate that exceeds the capacity of natural processes in the atmosphere to convert, deposit, or dilute them…

Air pollutants=> hazardous substances in the atmosphere which can adversely affect human health, animals, plants or microbial life.

…will require essentially total elimination of anthropogenic aerosols and gaseous pollutants!

clean day

moderately polluted day

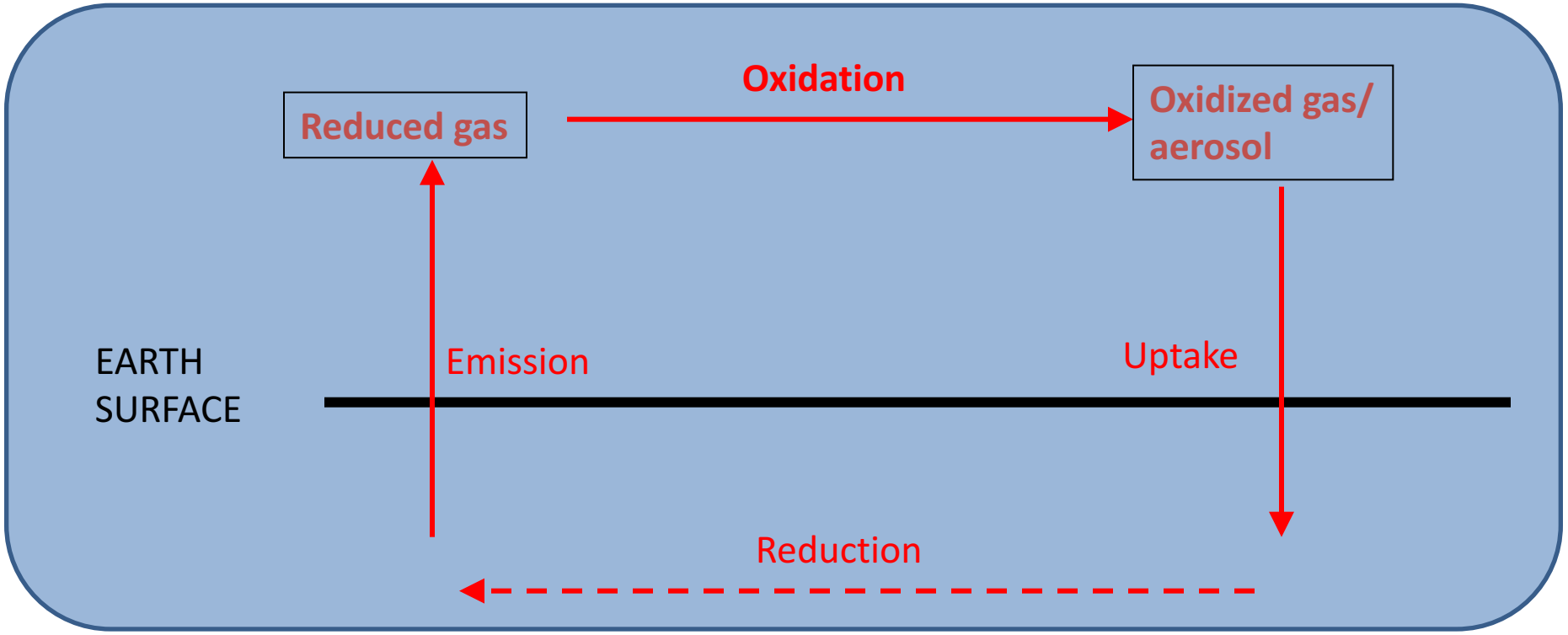
Acadia National Park

http://www.hazecam.net/

The atmosphere: An oxidizing medium in global biogeochemical cycle

Atmospheric oxidation is critical for removal of many pollutants, e.g.

- **methane (major greenhouse gas)**
- **CO (toxic pollutant)**
- **HCFCs (Cl_x sources in stratosphere)**
- **VOCs, NOx and SO2 gases**
- **And many more…..**



Factors that affect air pollution

- Emissions (traffic, industrial, domestic)
- Geography (terrain)
- Weather conditions (rain, winds, humidity)
- Season
- Time of day (diurnal variabilty)
- Population density
- Indoor vs outdoor

Types and Sources of Air Pollution

- Air Pollution (mostly anthropogenic)
  - Chemicals added to the atmosphere by natural events or human activities in high enough concentrations to be harmful

Natural air pollutants are rare, except dust storms:

Smoke from wild fires
Methane released from live stock
Volcanic eruptions

Two categories:

Primary Air Pollutant

Harmful substance that is emitted directly into the atmosphere

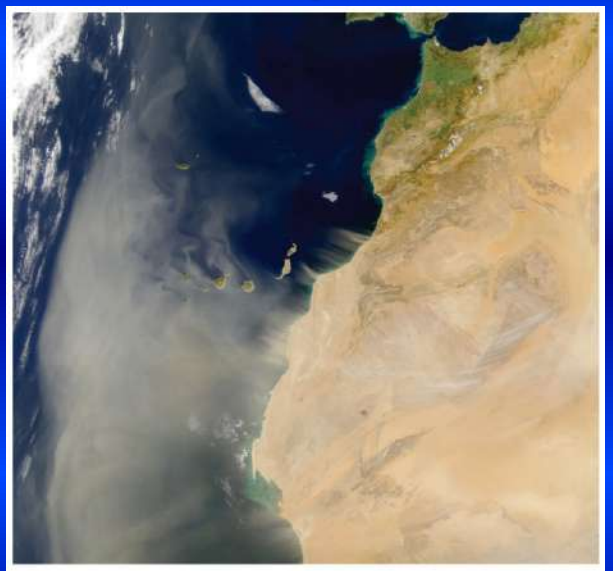
Secondary Air Pollutant

Harmful substance formed in the atmosphere when a primary air pollutant reacts with substances normally found in the atmosphere or with other air pollutants

Natural sources: dust storms

- Terrestrial Sources.
  - Unsustainable farming and grazing, erosion and desertification
- Volcanoes
- Fires
  - Clearing forests for agriculture

Kīlauea



(a) Dust storm off west coast of Africa

(b) Mount Saint Helens eruption, 1980

Types of air pollution

- Aerosols ($PM_{2.5}$ and PM_{10})
  - Particulates solid phase
    - Dust
    - Ash
    - Fumes
    - Carbonaceous materials
  - Solid and liquid
    - Smoke (from combustion)
    - Coastal aerosols
  - Liquid
  - Aggregate gases (sulfate, nitrate)

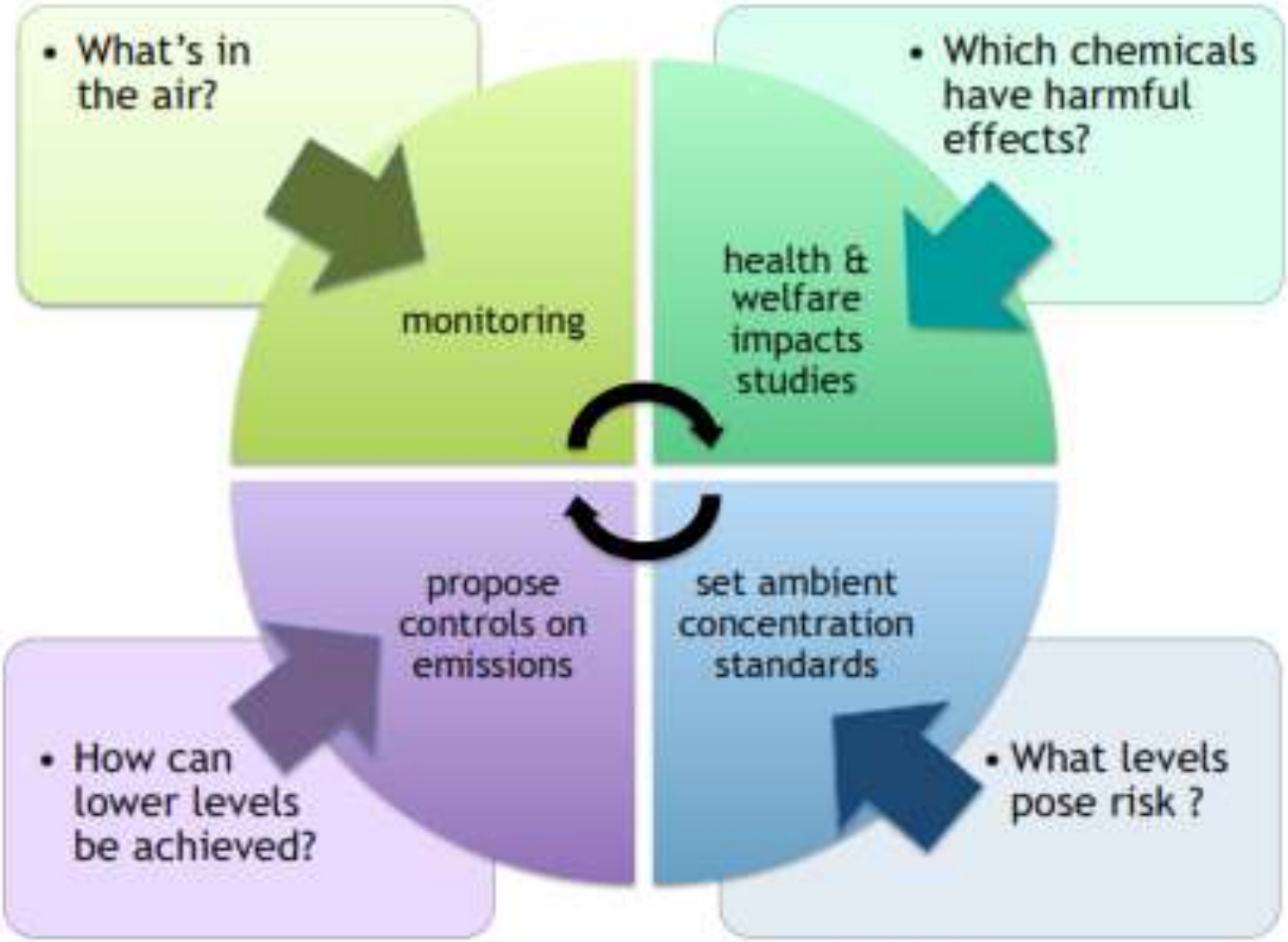
- Gases
  - COx
  - SOx
  - NOx
  - PAH
  - VOCs

Major Air Pollutants

Table 20.1 Major Air Pollutants

Pollutant	Composition	Primary or Secondary	Characteristics
Particulate matter			
Dust	Variable	Primary	Solid particles
Lead	Pb	Primary	Solid particles
Sulfuric acid	H_2SO_4	Secondary	Liquid droplets
Nitrogen oxides			
Nitrogen dioxide	NO_2	Primary	Reddish-brown gas
Sulfur oxides			
Sulfur dioxide	SO_2	Primary	Colorless gas with strong odor
Carbon oxides			
Carbon monoxide	CO	Primary	Colorless, odorless gas
Carbon dioxide*	CO_2	Primary	Colorless, odorless gas
Hydrocarbons			
Methane	CH_4	Primary	Colorless, odorless gas
Benzene	C_6H_6	Primary	Liquid with sweet smell
Ozone	O_3	Secondary	Pale blue gas with acrid odor
Air toxics			
Chlorine	Cl_2	Primary	Yellow-green gas

* Discussed in Chapter 21.
Source: Environmental Protection Agency.


• What's in the air?
monitoring
• Which chemicals have harmful effects?
health & welfare impacts studies
propose controls on emissions
set ambient concentration standards
• How can lower levels be achieved?
• What levels pose risk ?

Gaseous pollutant features

Gaseous Pollutant
Carbon Monoxide (CO_2)
Sulfur Dioxide (SO_2)
Nitrogen Dioxide (NO_2)
Ozone (O3)
Ammonia (NH_3)
Benzene (C_6H_6)

- Chemical reactivity (ozone)
- Solubility in water
  - Soluble
    - Ambient (NOx, SOx)
    - Occupational (Hydrochloric acid, Ammonia)
    - CO_2 and dissolution in sea water, ocean acidification
  - Less soluble
    - H_2S, ozone

NAAQ Standards /criteria for Gaseous pollutants

Pollutant	Primary Stds. µg/m3		Averaging Time
	Industrial	Eco Sensitive	
Carbon Monoxide	2000	2000	8-hour
	4000	4000	1-hour
Sulfur Dioxides	50	20	Annual
	80	80	24 hrs
Nitrogen Dioxide	80	30	Annual
	80	80	24 hrs
Ozone	100	100	8-hour
	180	180	1-hour
NH3	100	100	Annual
	400	400	24 hrs
Benzene	5	5	Annual

Source: http://cpcb.nic.in/National_Ambient_Air_Quality_Standards.php

INTRODUCTION: Particulate Material (or aerosol)

- **Aerosols are tiny solid or liquid particles suspended in air/gas medium**
- Air is Dispersion medium and sols (solid particles) as dispersed phase
- They are also called aerocolloids / aerodisperse system
- **Size: 1 nm -100 µm**
- **Classification of aerosols: fine (<2.5 µm; $PM_{2.5}$) & coarse (>2.5 µm) mode**
- **Sources: Natural as well as anthropogenic emissions**
- **Sinks: Dry and wet deposition**

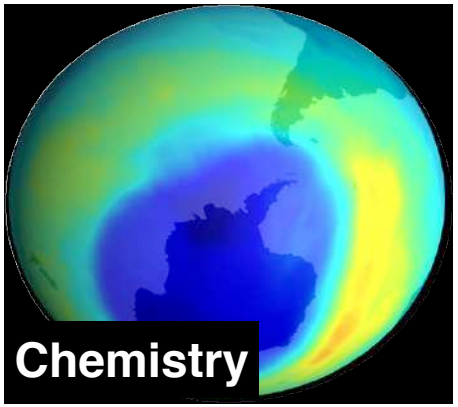
Introduction---ctd..

- Thousands of different solid or liquid particles suspended in air
  - Includes: soil particles, soot, lead, asbestos, sea salt, and sulfuric acid droplets, carbonaceous materials etc..

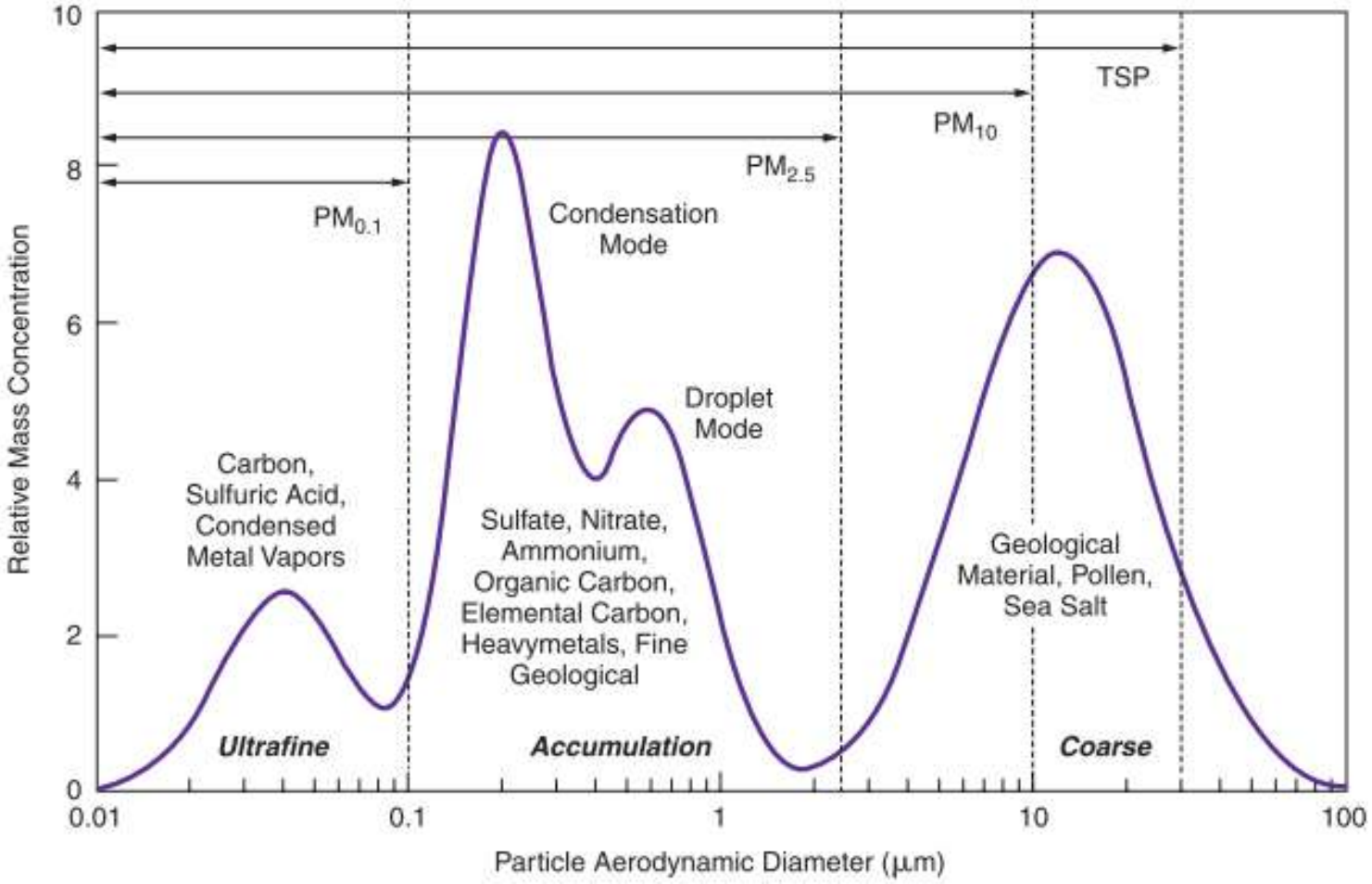
- Dangerous
  - May contain materials with toxic or carcinogenic effects
  - Extremely small particles can become lodged in lung

  - But also good for many reasons:

Why do we care about atmospheric aerosols?



Particle Size Distribution



Source: Judith Chow, Desert Research Institute, USA. Chow, J.C. (1995)

http://www.esmap.org/esmap/node/1159

Tropospheric Chemistry

- **OH, O_3 and NO_x radicals are important oxidizing species.**
- **They can oxidize reactive gases and compounds present in atmosphere and can form new aerosols**
- **These newly formed species can be incorporated in haze or cloud formation**

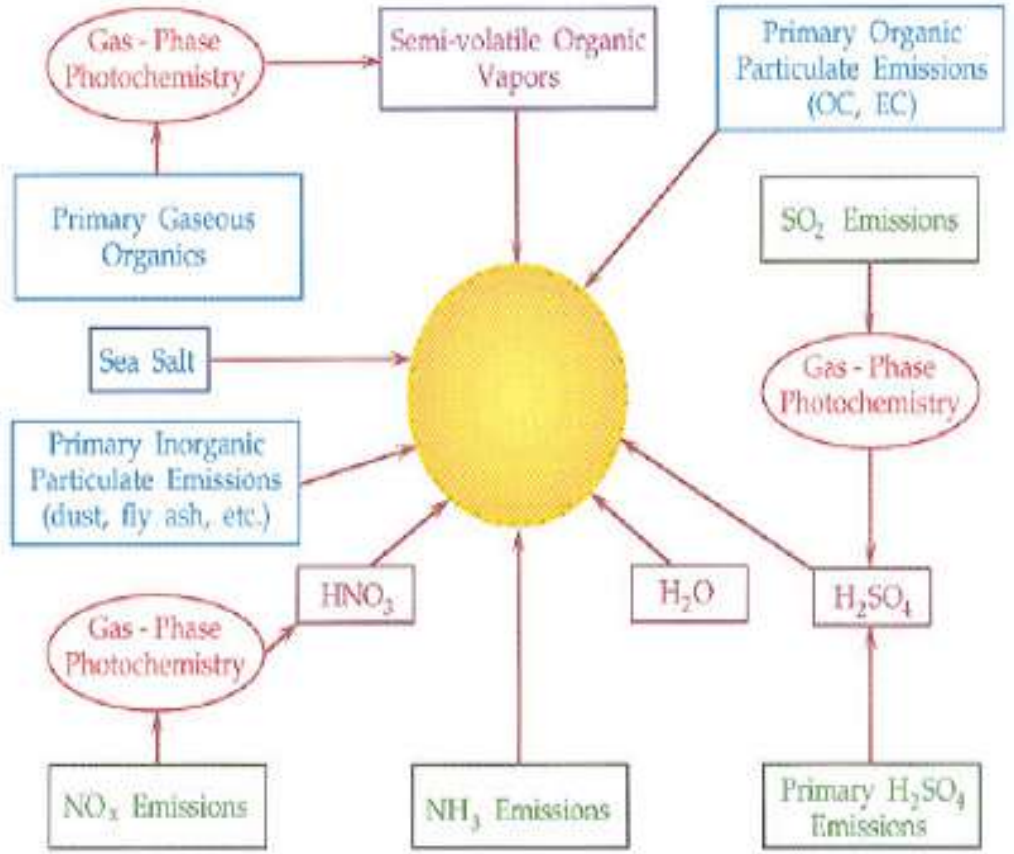
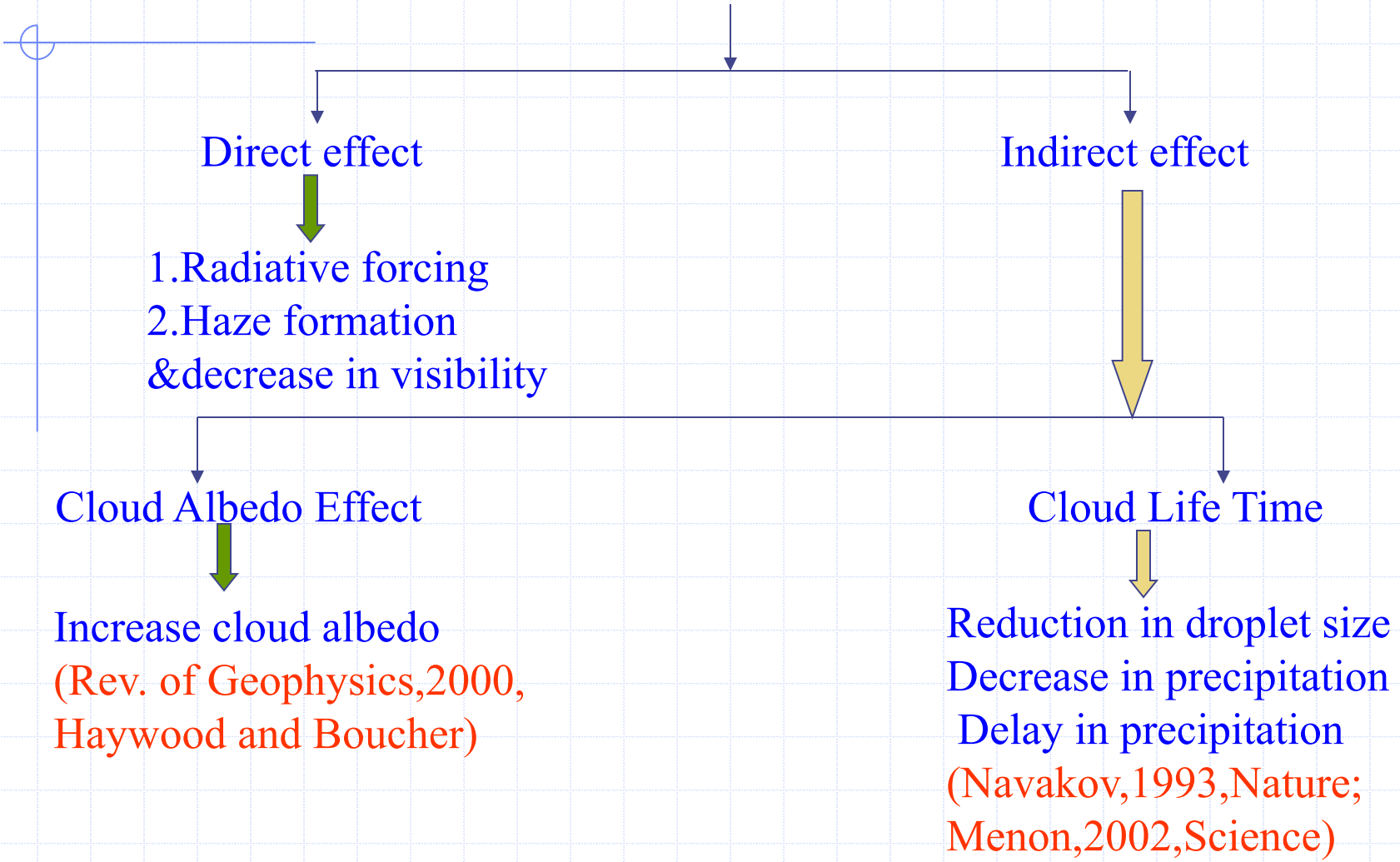


Fig. Routes of incorporation of chemical species into atmospheric particulate matter. OC and EC denote organic and elemental carbon

Impact of aerosols on climate



Particulate air pollutants

- Particulate Matter: TSP, PM_{10} and $PM_{2.5}$
  - respiratory disorders
- Lead: Pb
  - cause learning disabilities in children , toxic to liver, kidney, blood forming organs
  - tetraethyl lead – anti knocking agent in gasoline
    - leaded gasoline has been phased out
- Benzo (a) Pyrene (Particulate phase)
- Arsenic (As)
- Nickel (Ni)

National Ambient Air Quality Standards (for India ug/m^3 or ppm)

Particulate Matter (PM_{10})	60	60	Annual
	100	100	24 hrs
Particulate Matter ($PM_{2.5}$)	40	40	Annual
	60	60	24 hrs
Lead (Pb)	0.5	0.5	Annual
	1	1	24 hrs
Benzo (a) Pyrene (Particulate phase)	1 ng/m3	1 ng/m3	Annual
Arsenic	6 ng/m3	6 ng/m3	Annual
Nickel	20 ng/m3	20 ng/m3	Annual

Source: http://cpcb.nic.in/National_Ambient_Air_Quality_Standards.php

Volatile Organic Pollutants (VOCs)

- Sources: Petroleum emissions, fuel combustion, incineration, biomass burning
- Account for ~14% of all air pollution
- Important factor of indoor air pollution
- Types
  - Aliphatic
  - Alcohols (ethylene glycol, MTBE)
  - Aldehydes (formaldehyde)
  - Aromatic (benzene, toluene, xylene)
  - Halogenated (Tetracholroethene, TCE, Perchloroethene, Methylene Chloride)
  - Polycyclic aromatic hydrocarbons (PAHs)
  - Other (Carbon disulfide)

Other air pollutants - HAPs

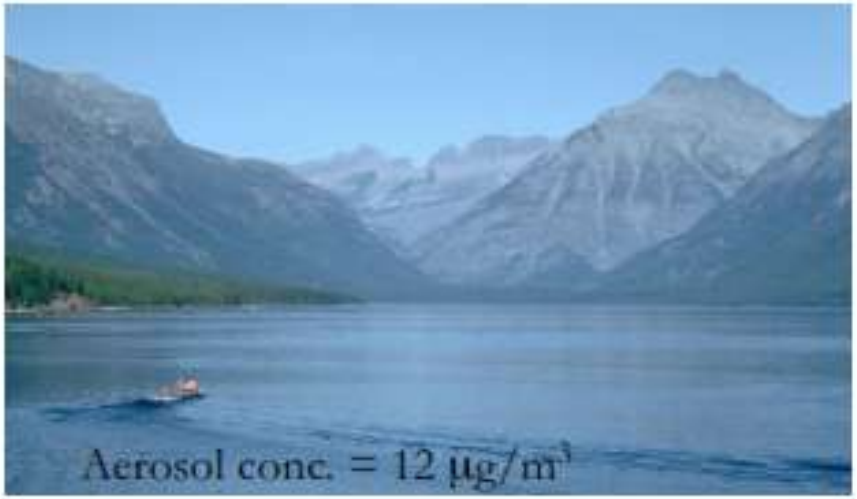
- Hazardous air pollutants (HAPs)
  - Not included in the 6 criteria air pollutants
- Include
  - Organic chemicals (acrolein)
  - Minerals (asbestos)
  - PAH (benzo[a]pyrene)
  - Metals (Hg, Be)
  - Pesticides (carbaryl, parathion)
- Some are carcinogenic

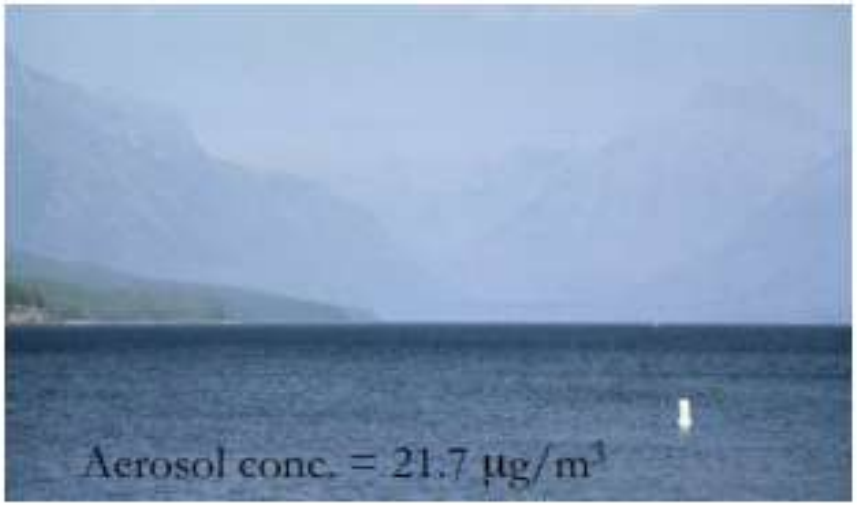
Consequences of Air pollution

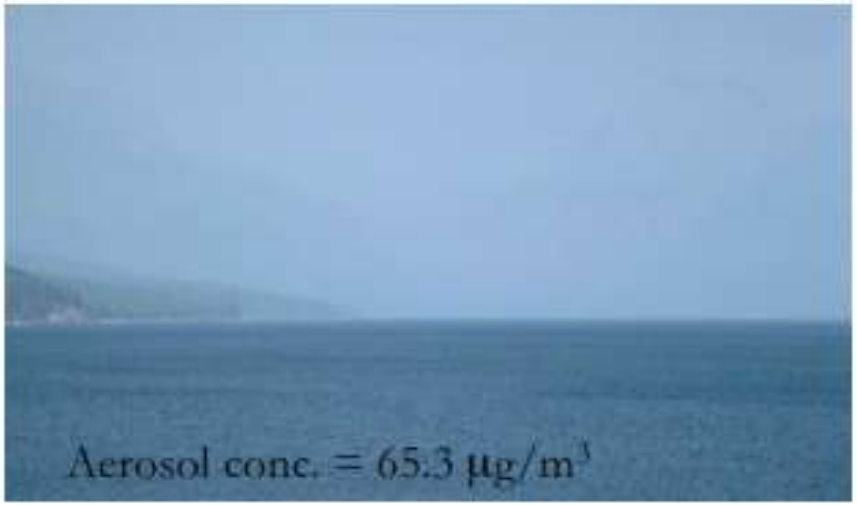
Examples:

1. Poor air-quality and visibility
2. Photochemical smog
3. Acid Rain
4. Climate change

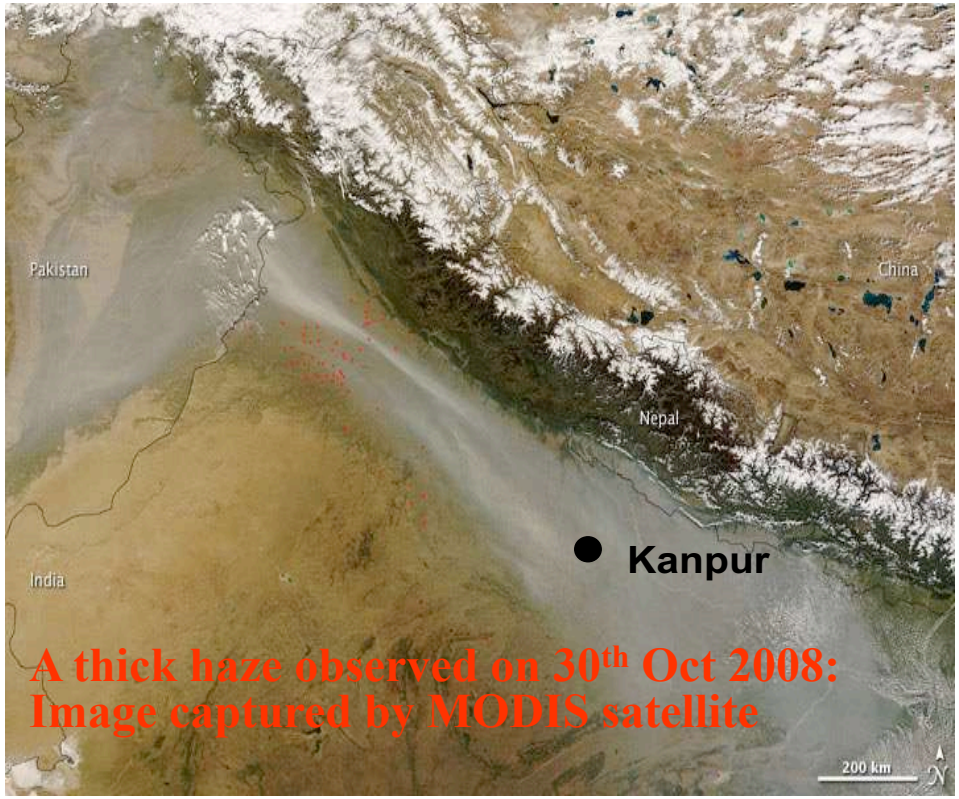
Particles affect visibility







1. A case study: Fog-haze formation over IGP during wintertime



A thick haze observed on 30th Oct 2008: Image captured by MODIS satellite

- **Emission sources and meteorological conditions?**

1. **Relative humidity (RH)**
2. **Boundary layer dynamics**

- **Chemical composition**

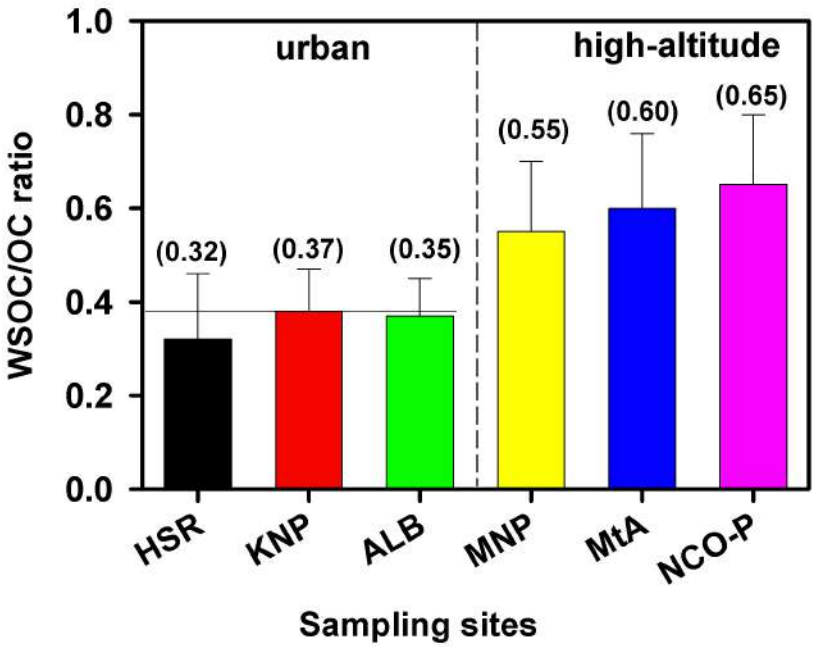
Chemical analysis suggest that ~80% of aerosol mass is composed of carbonaceous and inorganic aerosols.

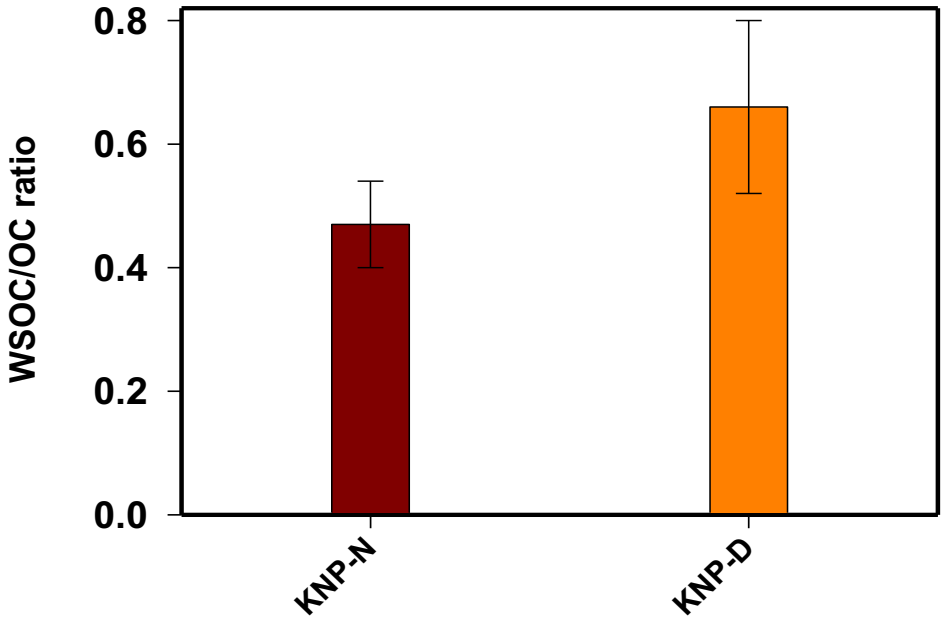
TCA (=1.6*OC+EC) ~60% and water-soluble inorganic species (WSIS) ~20% of aerosol mass

- **Primary aerosols: Less soluble and less hygroscopic in nature**
- **Emission strength is higher and boundary layer height is lower: results in trapping of aerosols.**

- **Secondary aerosols: More hygroscopic in nature and the growth of secondary aerosols increases scattering under high RH condition. Thus, could be a probable reason for haze events.**

Do we have any evidence of SOA formation over IGP

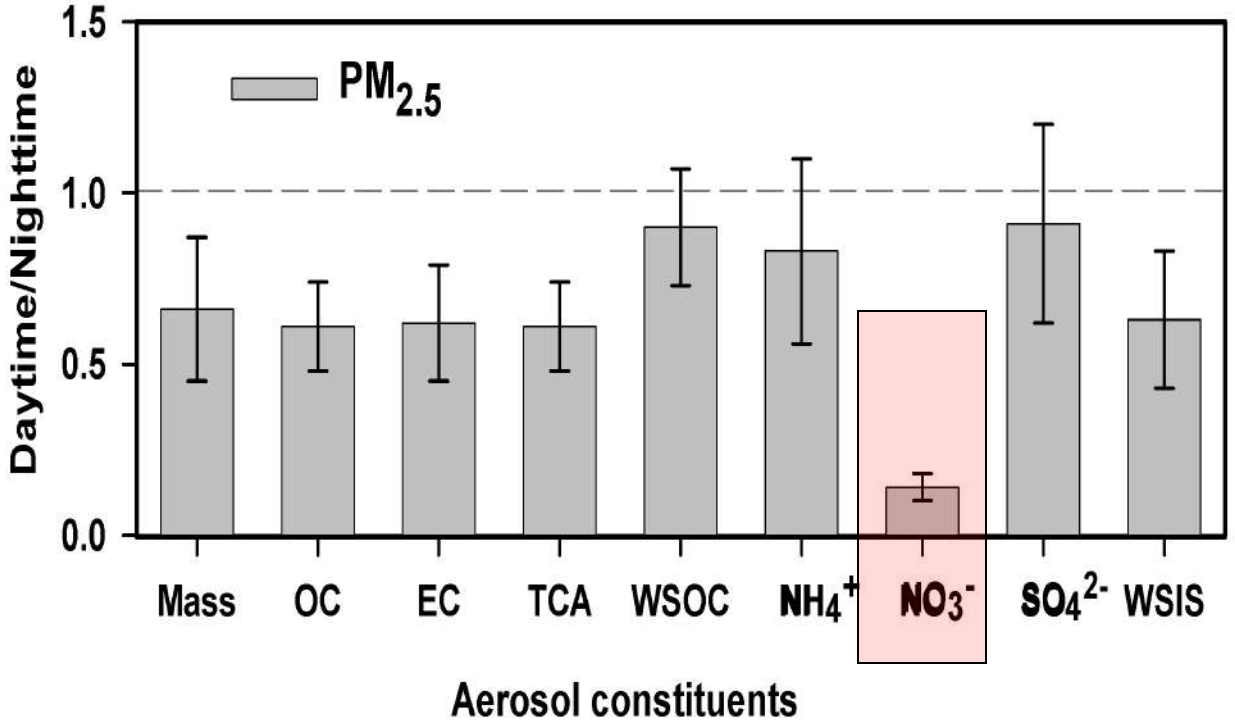




- Average $(OC/EC)_{Day}$=6.7; $(OC/EC)_{Night}$=5.6
- Average ratios: $(WSOC/OC)_{Day}$=0.66; $(WSOC/OC)_{Night}$=0.46, $(WSOC/OC)_{winter}$=0.30-0.40
- Relatively higher WSOC/OC ratios suggest enhanced SOA formation during daytime.

Ram and Sarin, Atmos. Environ. (2011)

Secondary inorganic aerosol (SIA) formation

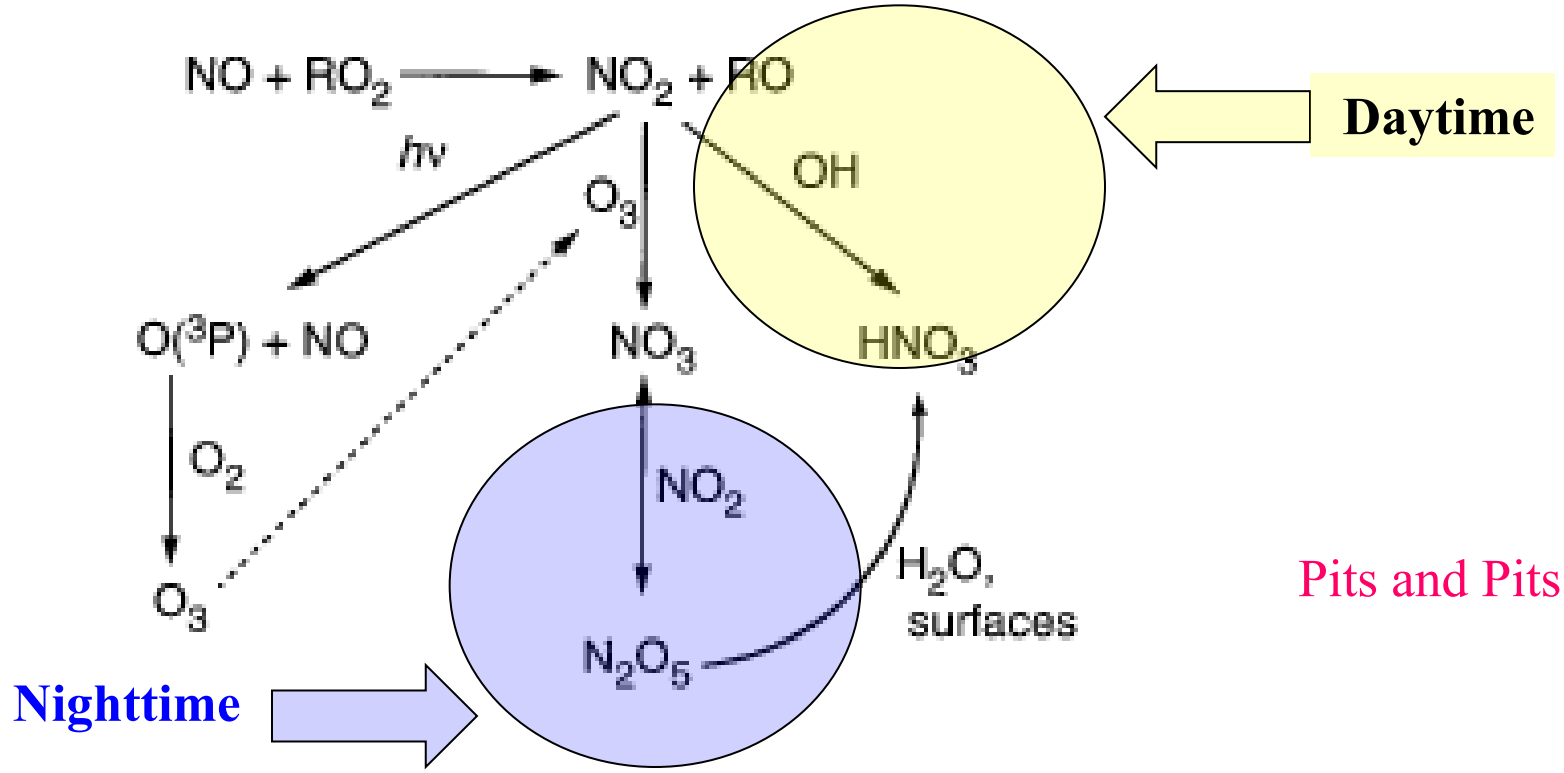


- NO_3^- increases by a factor of 5 during night-time: secondary formation from the hydrolysis of N_2O_5 via heterogeneous reaction.

- Concentrations of SIAs (NH_4^+, NO_3^- and SO_4^{2-}) show 2 to 4 fold increase during the haze events.

Ram and Sarin, Atmos. Environ. (2011)

NOx tropospheric chemistry



Pits and Pits, Science, 1997

- ✓ **Day and night chemistry: major pathways of removal of NOx from atmosphere**
- ✓ **NO_3 radical is unstable in daytime and dissociate back to NO_2**
- ✓ **Nighttime: Heterogeneous hydrolysis of N_2O_5**

2. Photochemical (brown air) smog

(b) Photochemical smog over Mexico City

Delhi Smog on 8 November 2012

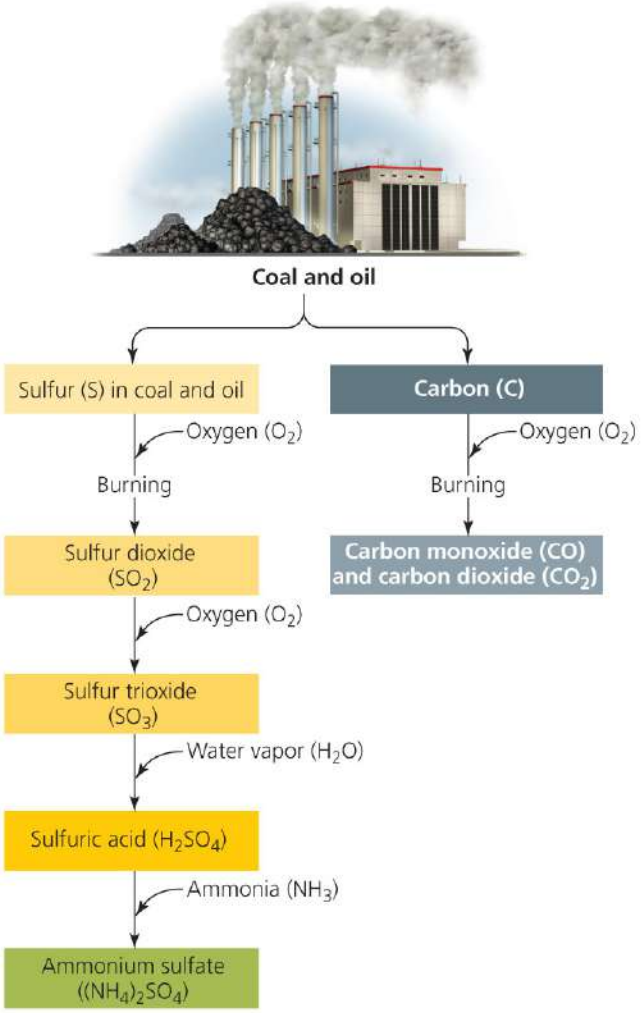
- Produced by a series of reactions
  - Light-driven reactions of primary pollutants and normal atmospheric compounds
  - Hot, sunny, windless days in urban areas
  - Morning traffic exhaust releases pollutants.
  - Irritates eyes, noses, and throats
  - Vehicle inspection programs in the U.S. have decreased smog.

SMOG
(Sulfurous vs. Photochemical Pollution)

Example: London (also Eastern US)
- smoke + fog
- SO_2
- characterized by inversions, cool weather, coal burning

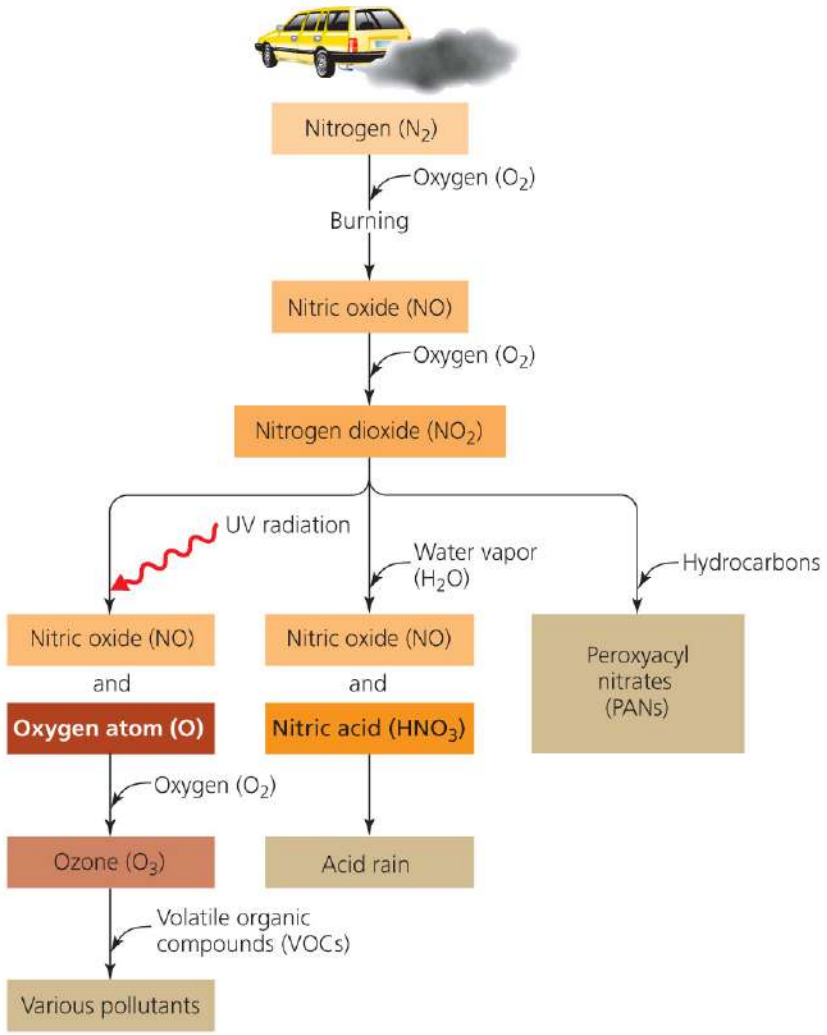
Example: LA
- UV, hydrocarbons, NOx
- characterized by hot dry sunny weather, reduced visibility and high oxidant levels

Industrial smog



(a) Burning sulfur-rich oil or coal without adequate pollution control technologies

Photochemical smog



(a) Formation of photochemical smog

GREAT LONDON SMOG OF 1952

Smog = fog intensified by smoke

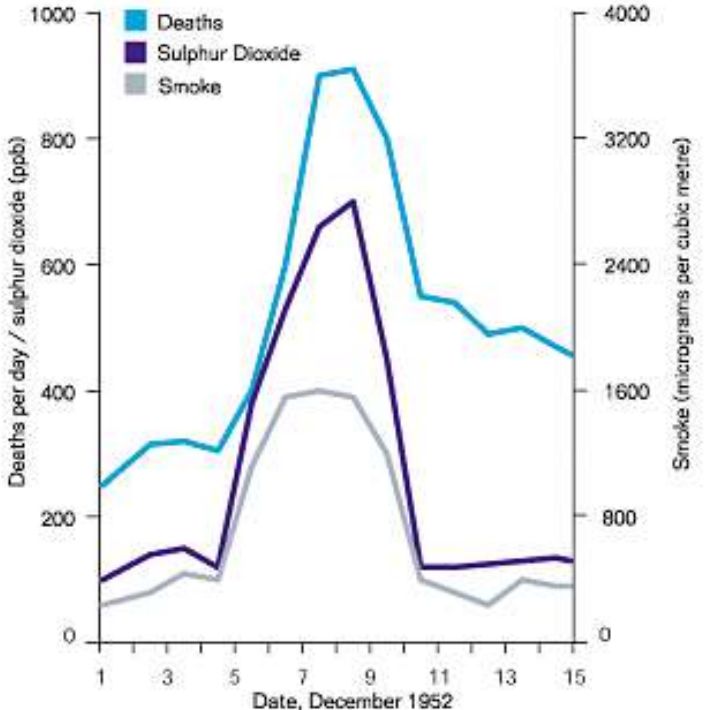
(Henry Antoine Des Voeux, who first used it in 1905 to describe British urban areas)

http://www.martinfrost.ws/htmlfiles/great_smog.html

Dec 5-9, 1952

- **Cold fog + (high sulfur) coal + diesel buses = "pea souper (killer fog)"**
- **Killed 4000 people (young & elderly), and over 8000 died subsequently**
- **Clean Air Acts of 1956 and 1968 and City of London Act of 1954.**

Monet painting showing Victorian smog (1900)
[Baker and Thornes, 2006]

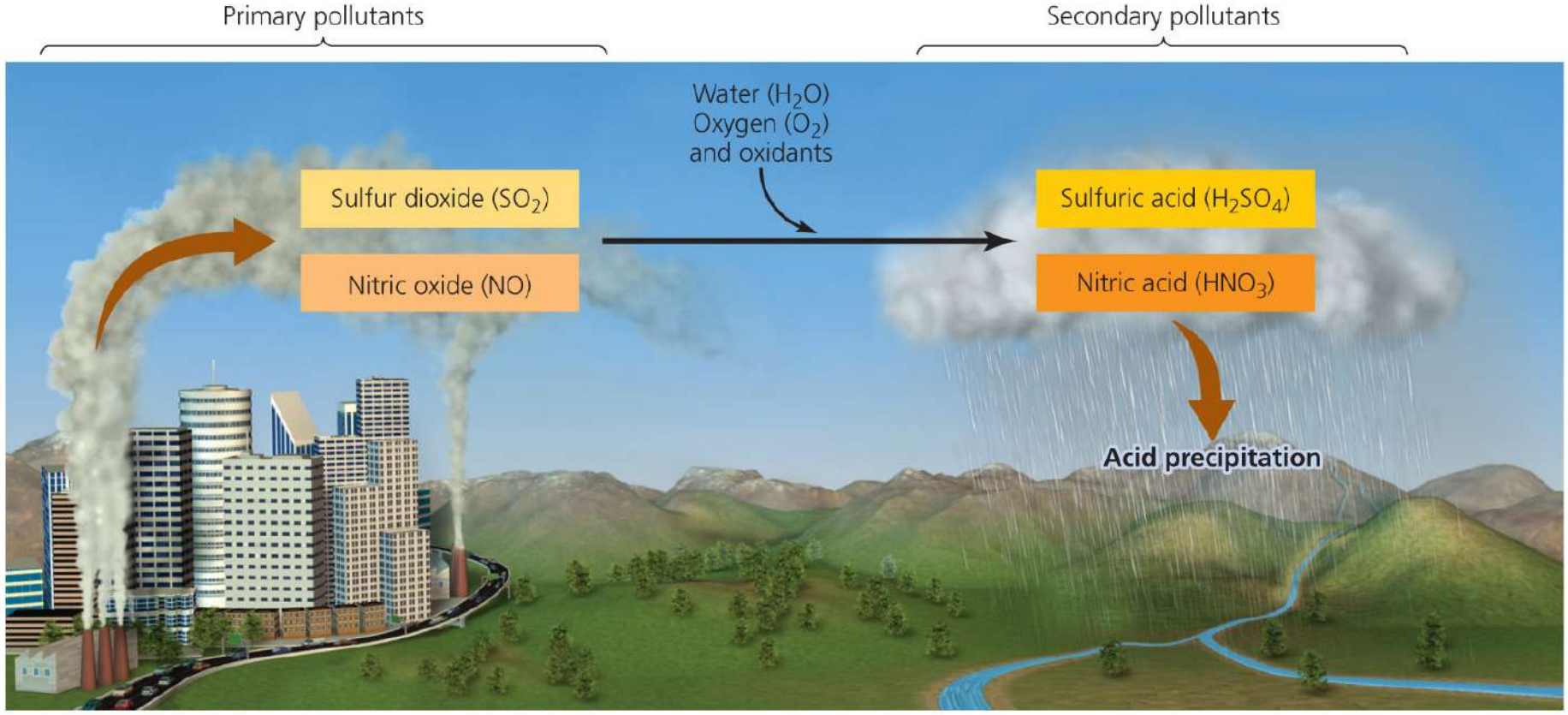


3. Acid deposition (pH <5.5.)

- **Acidic deposition**: the deposition of acid, or acid-forming pollutants, from the atmosphere onto Earth's surface
  - **Acid rain**: precipitation of acid
  - **Atmospheric deposition**: the wet or dry deposition on land of pollutants

Sources of acid deposition

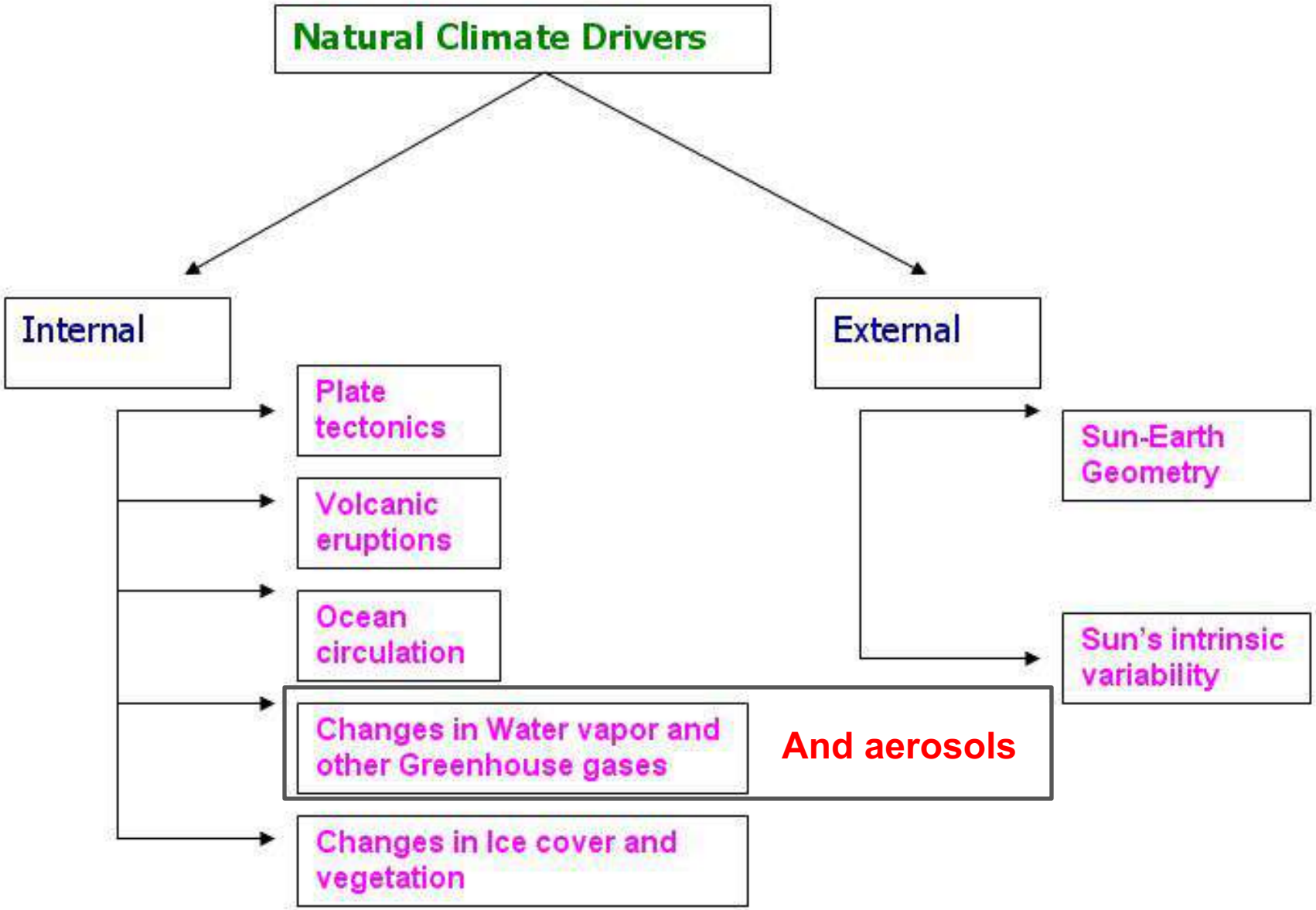
- Originates from burning fossil fuels that release sulfur dioxide and nitrogen oxides
  - These compounds react with water to form sulfuric and nitric acids.



Effects of acid deposition

- Nutrients are leached from topsoil.
- Metal ions (aluminum, zinc, etc.) are converted into soluble forms that pollute water.
- Damages agricultural crops
- Affects surface water and kills fish
- Widespread tree mortality
- Erodes stone buildings, corrodes cars, erases writing on tombstones
- New technologies such as scrubbers have helped, but deposition's effects are worse than predicted.

4. Deriver of Climate on longer time scale



Air pollutants and climate change

Increase in NO_x leads to

- **decreased lifetime of CH_4 and HFCs (via OH): ↓ radiative forcing**
- **increase in O_3: ↑ radiative forcing**
- **increased N deposition → fertilization → CO_2 uptake: ↓ radiative forcing**

Net effect not yet clear, but significant impacts on radiative forcing expected for 2100 (IPCC TAR, 2001)

A multi-pollutant/multi-effect problem extended towards radiative forcing

	SO_2	NO_x	NH_3	VOC	Primary PM+BC	CH_4	CO_2+ GHGs
Acidification	√	√	√				
Eutrophication		√	√				
Ground-level ozone		√		√		√	
Health impacts *via sec. aerosols*	√	√	√	√	√		
Radiative forcing						√	√
via aerosols	√	√	√	√	√		
via OH		√		√		√	