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Chemical & Physical Processes Impacting Air Pollution

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Definition of Air Pollution

Buildup in the air of **gases and/or aerosol particles** in concentrations sufficiently high to cause damage to humans, plants, animals, other life forms, ecosystems, structures, or works of art.

Source: Atmospheric Pollution, By Dr. Mark Jacobson

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Air Pollution

The major historic air pollution problem has typically been high levels of smoke and sulfur dioxide arising from the combustion of sulfur-containing fossil fuels such as coal.

The major threat to clean air is now posed by traffic emissions. Gasoline and diesel-powered motor vehicles emit a wide variety of pollutants, principally carbon monoxide (CO), oxides of nitrogen (NO_x), volatile organic compounds (VOCs) and particulates (PM_{10}), which have an increasing impact on urban air quality.

In addition, photochemical reactions resulting from the action of sunlight on nitrogen dioxide (NO_2) and VOCs from vehicles leads to the formation of ozone, a secondary long-range pollutant, which impacts in rural areas often far from the original emission site.

Acid rain is another long-range pollutant influenced by vehicle NO_x emissions. In all except worst-case situations, industrial and domestic pollutant sources, together with their impact on air quality, tend to be steady-state or improving over time. However, traffic pollution problems are worsening world-wide.

Sulfur Dioxide SO_2
Carbon Monoxide CO
Nitrogen Oxides NO_x
Lead Pb
Hydrocarbons/VOCs
Particulate Matter

Ozone

Smog

Acid Rain

Toxic Organics

CO_2???

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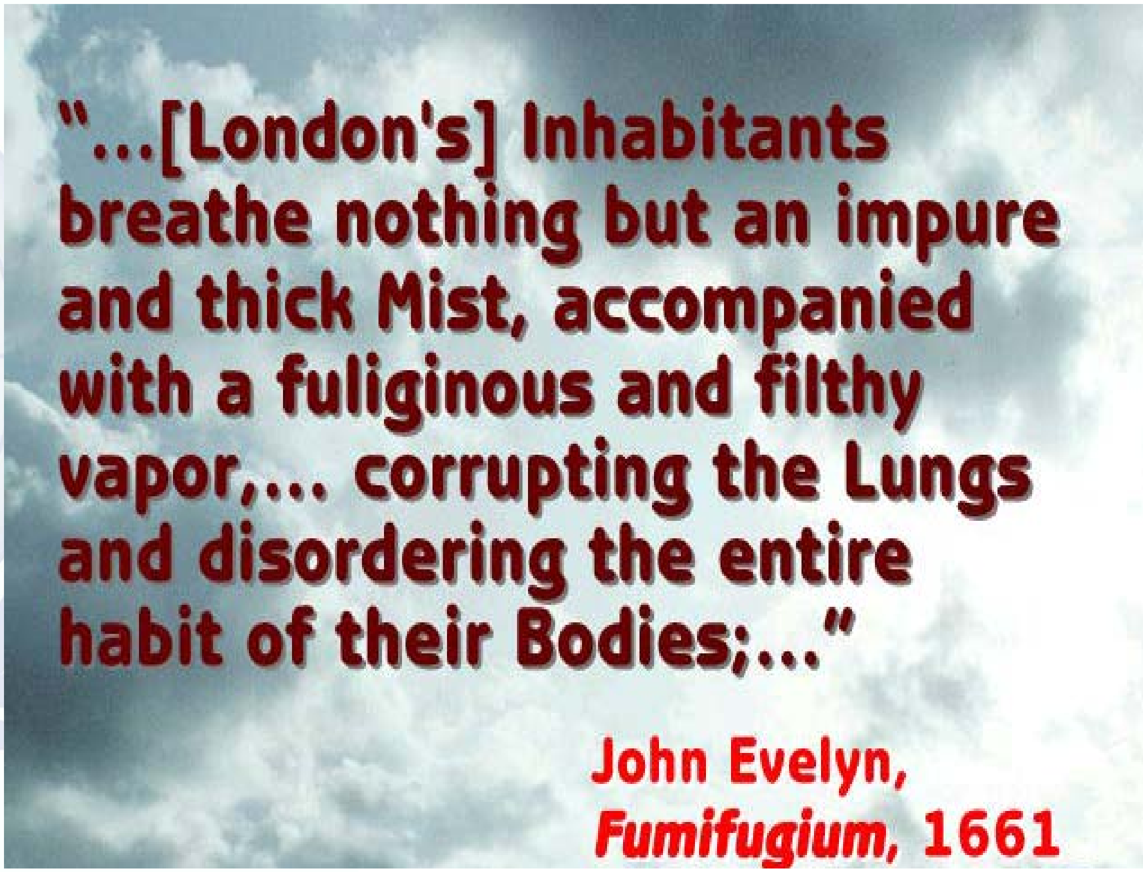
A Brief History of PM/Smog



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Reading, Pennsylvania (c. 1909)

Library of Congress Prints and Photographs Division, Washington, D. C.

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Youngstown, Ohio (c. 1910)

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Gary, Indiana (c. 1912)

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London-Type Smog

Smog

Harold Antoine Des Voeux of London’s Coal Smoke Abatement Society, introduced word in 1905 to describe combination of smoke and fog visible in several cities in Great Britain.

London-type smog:

Arises from coal- and chemical-combustion smoke in presence of fog or low-lying temperature inversion.

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Air Pollution Disasters

1930 Meuse River Valley, Belgium

A three-day episode of severe air pollution makes 6,000 ill and kills 63.

1948 Denora, PA

Oct. 26 to 31: air pollution episode leaves 20 dead out of 14,000 persons.

Donora, PA at noon on Oct. 29, 1948

1952 London, England

Dec. 4 to 9: “Killer Fog” leaves three to four thousand people dead.

London buses are escorted by lantern at 10:30 in the morning.

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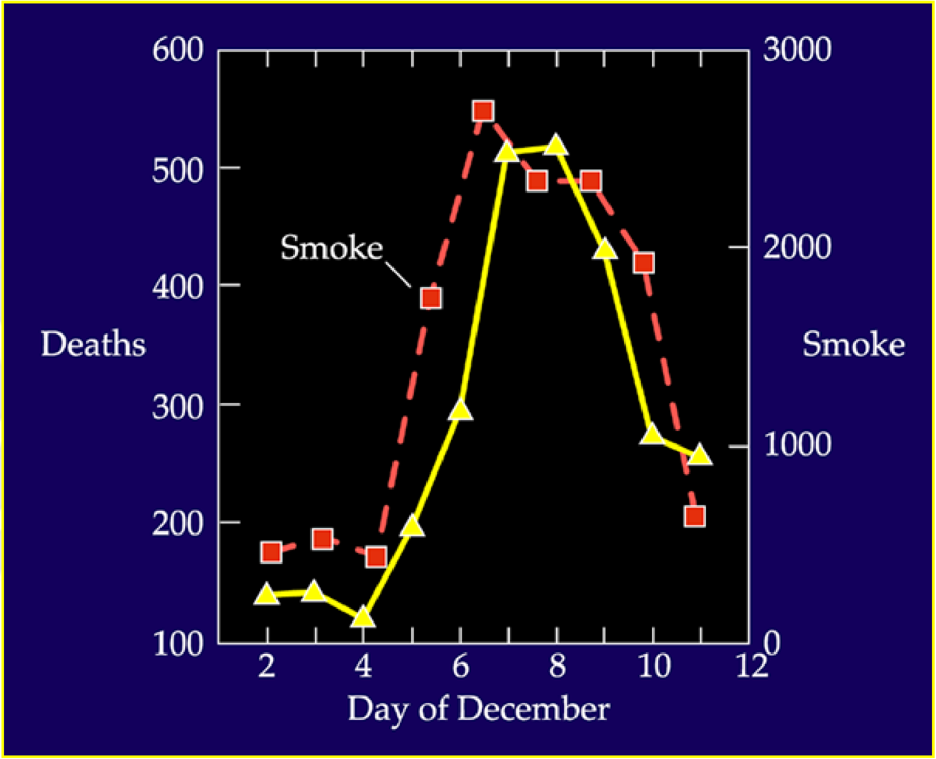
Mortality attributed to London Smog



Schwartz, 1994

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Smog Bothers Pedestrians, Los Angeles (1950s)

Hollywood Citizens News Collection, Los Angeles Public Library

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Backyard Incinerator Ban

Herald-Examiner Photo Collection, Los Angeles Public Library

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Los Angeles (July 23, 2000)

Mark Z. Jacobson

A cloud of pollution envelops Hong Kong making outdoor physical exertion dangerous – BBC September 15th, 2004

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Delhi (November, 2008)

BBC

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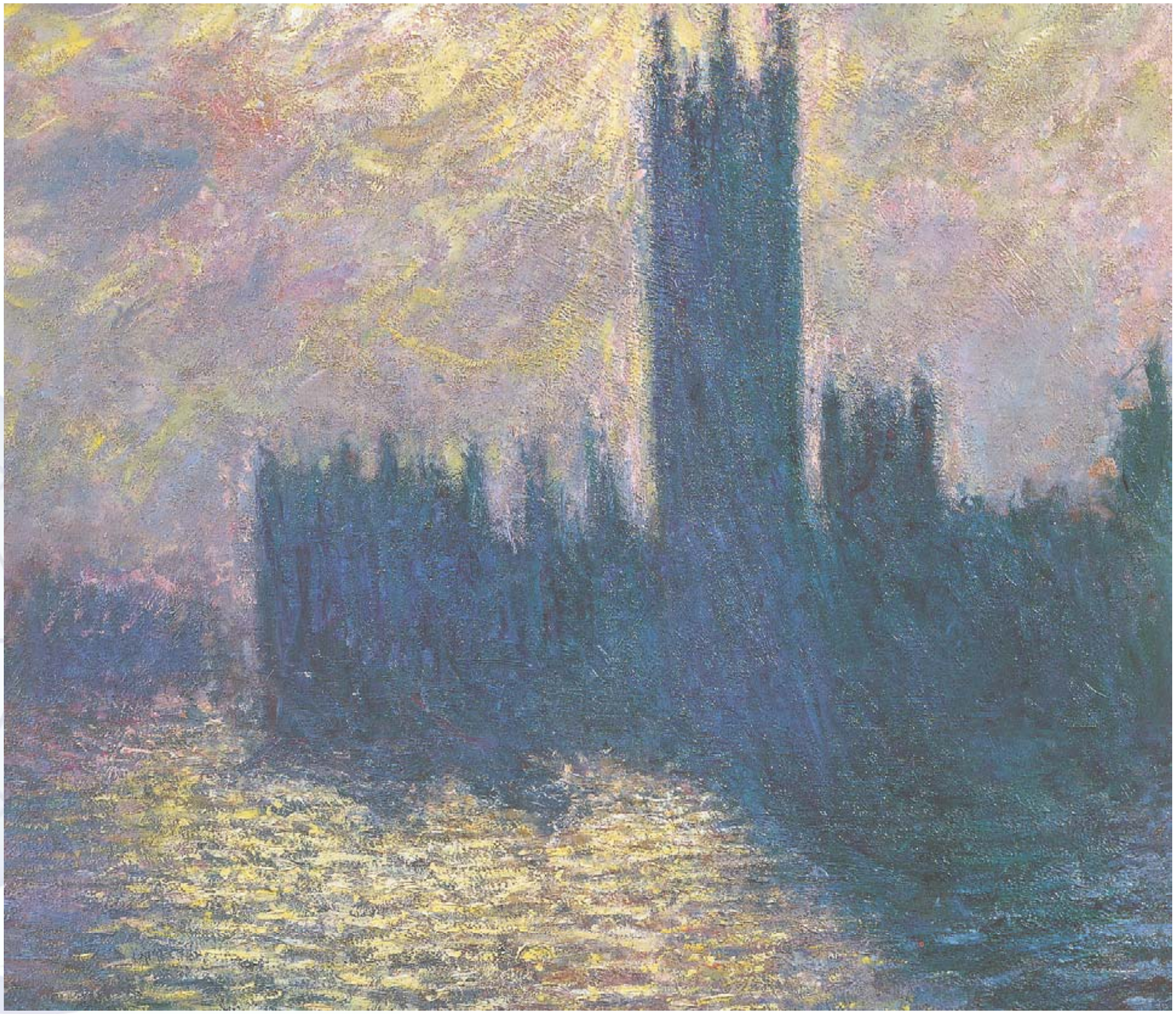

The Houses of Parliament, Stormy Sky

Claude Monet, 1904

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Basic Pollutants (1 of 2)

Categories of pollutants

- Primary – emitted directly from a source
- Secondary – formed in the atmosphere from a reaction of primary pollutants
- Precursors – primary pollutants (gases) that participate in the formation of secondary pollutants

Pollutants originate from

- Combustion of fossil fuels and organic matter
- Evaporation of petroleum products or compounds used in commercial products, services, and manufacturing
- Natural production of smoke from fires, dust from strong winds, and emissions from the biosphere and geosphere

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Basic Pollutants (2 of 2)

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

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Emissions

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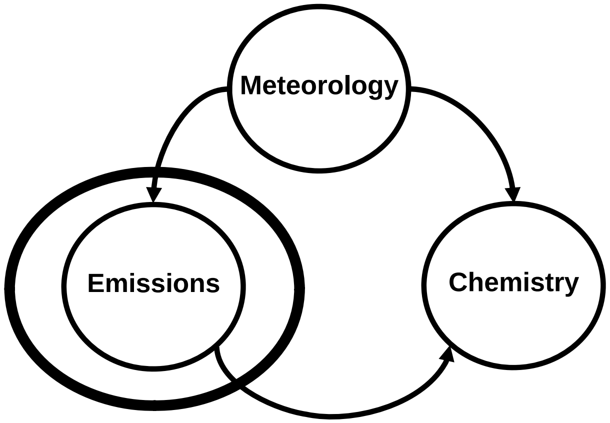
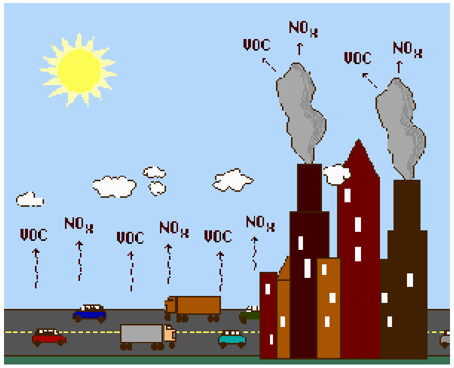
Ozone Precursor Emissions

- Man-made sources
  - Oxides of nitrogen (NO_x) through combustion
  - VOCs through combustion and numerous other sources
- Natural sources (biogenic)
  - VOCs from trees/vegetation
  - NO_x from soils (Midwest fertilizer)
- Concentration depends on
  - Source location, density, and strength
  - Meteorology





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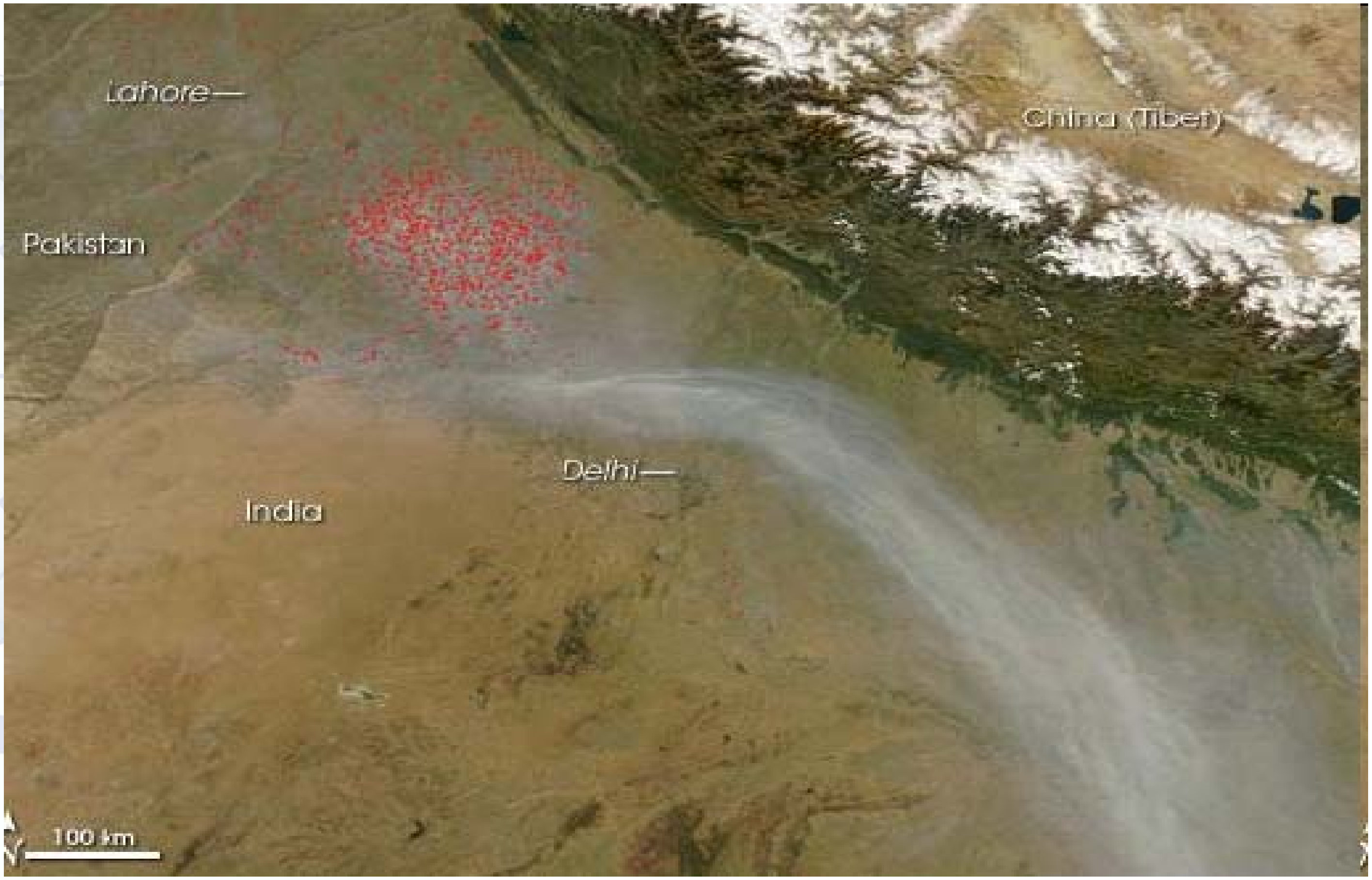
Haze (November, 2008)



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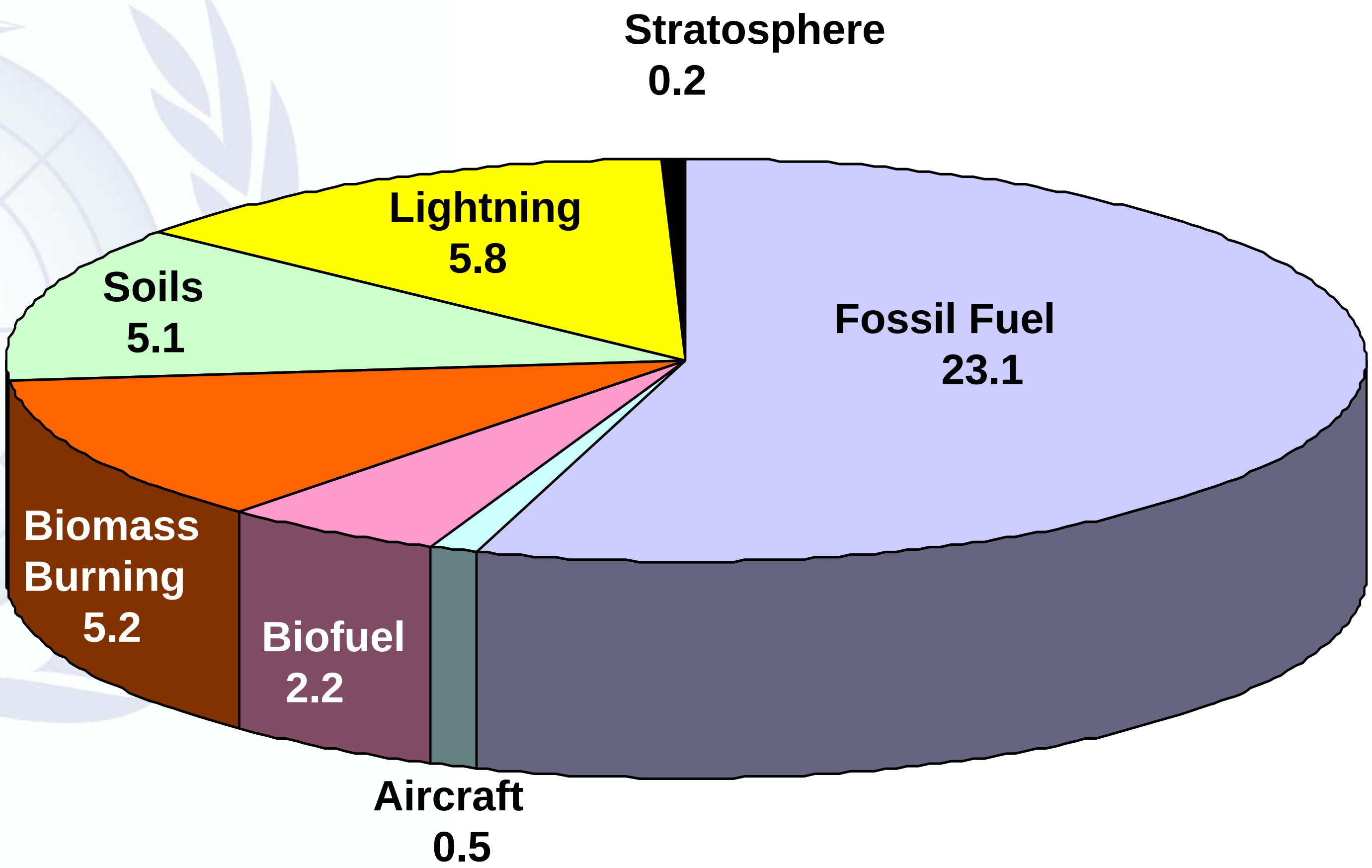
NO_x Emissions (Tg N yr^{-1}) To Troposphere



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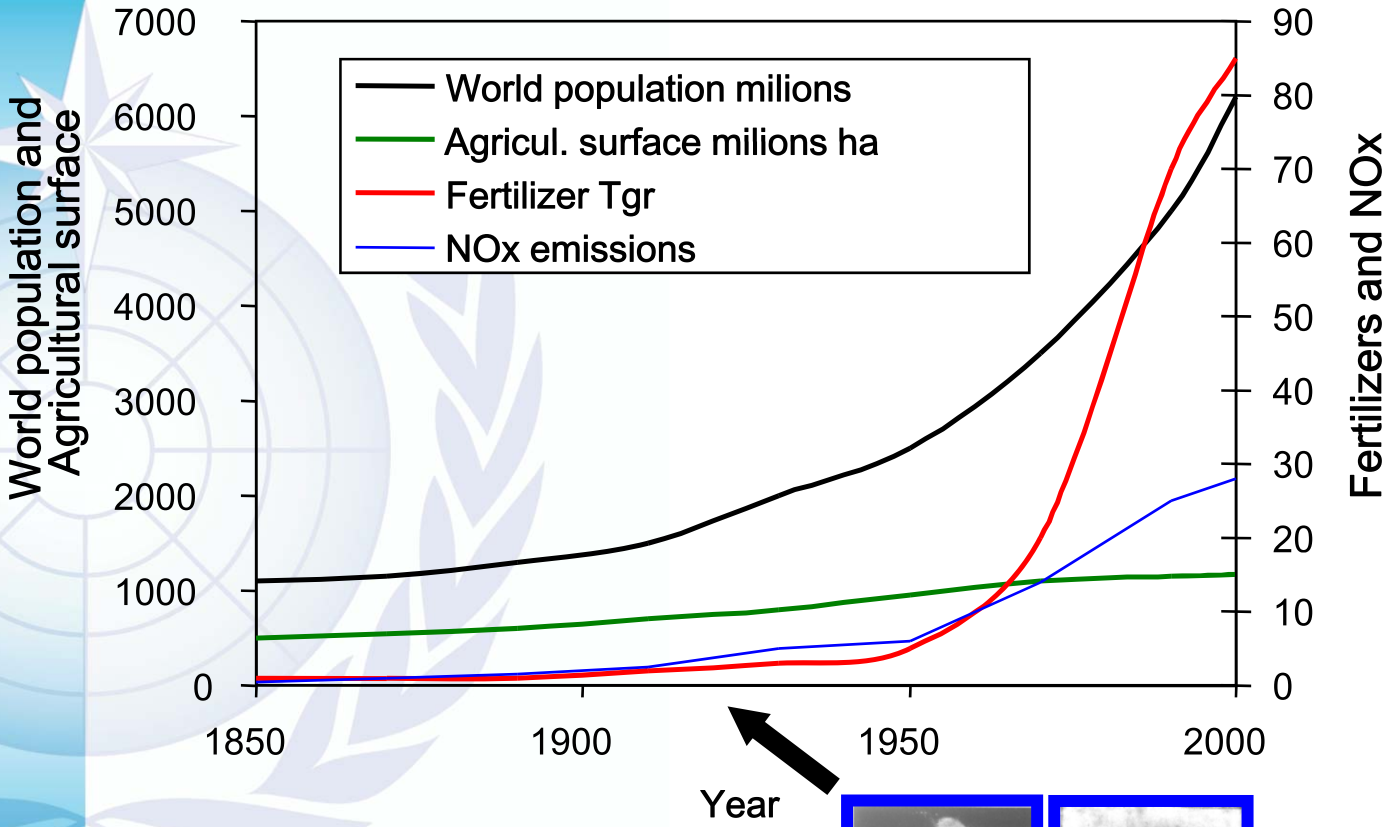
N = food; energy = N



Carl Bosch **Fritz Haber**

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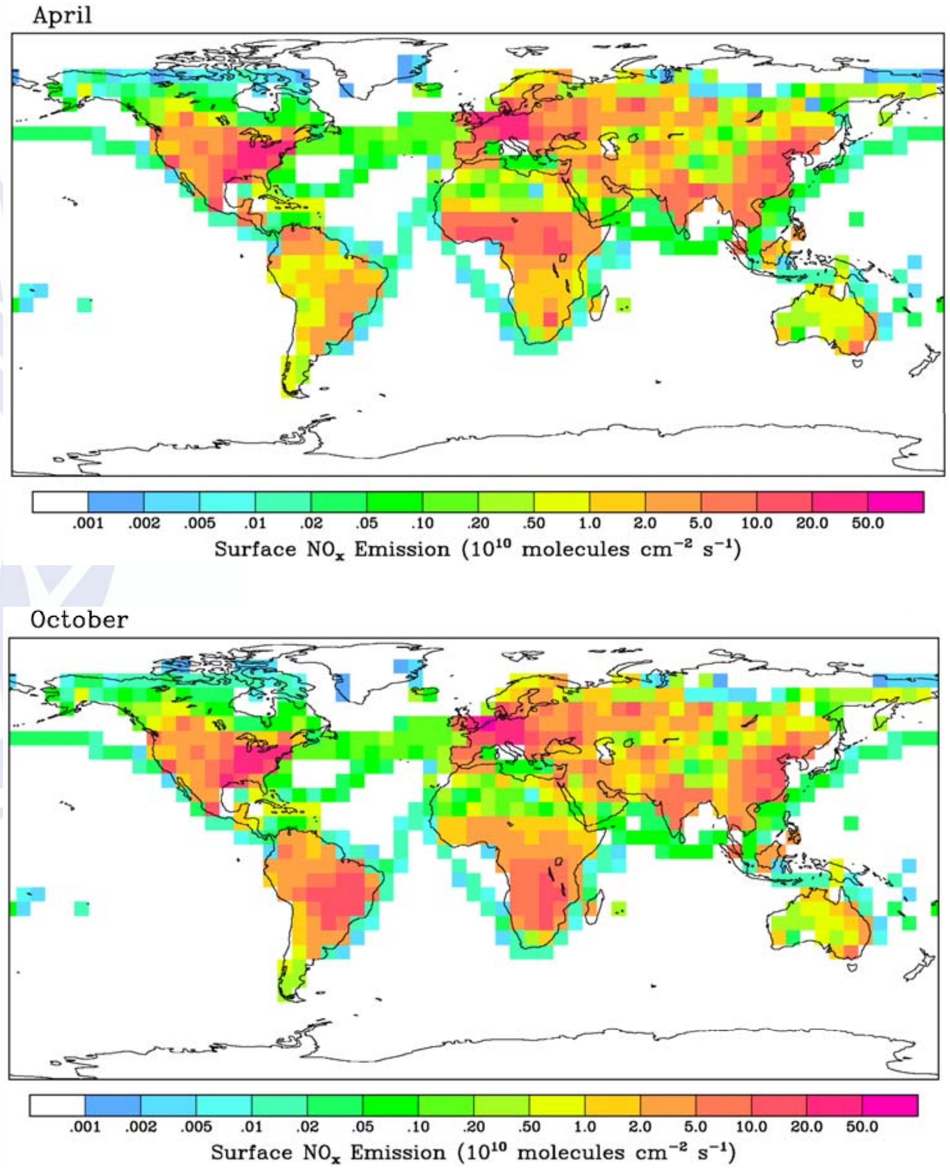
An example of gridded NO_x emissions



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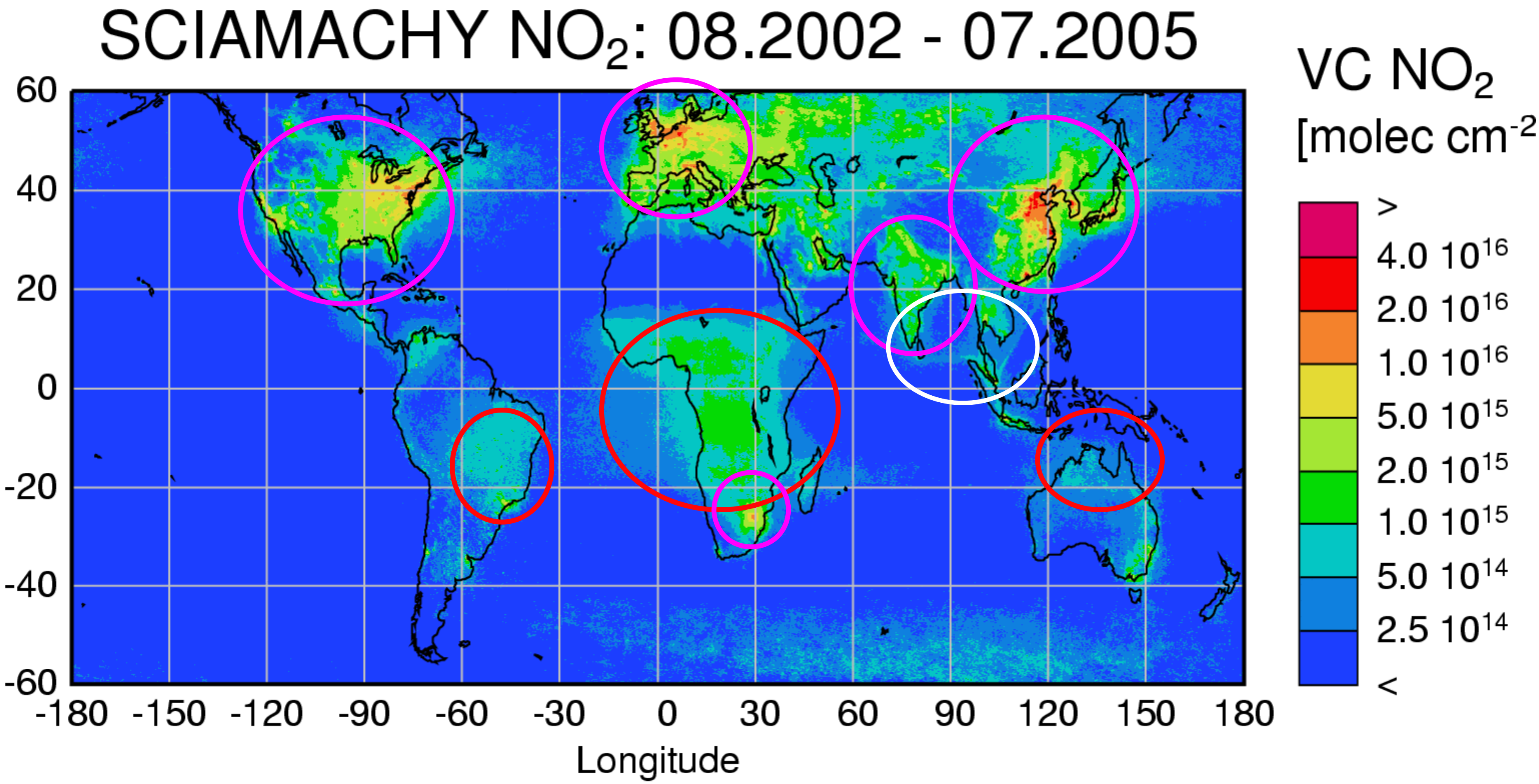
SCIAMACHY Tropospheric NO_2



pollution

biomass burning

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Global Budget of CO

	Range of estimates (Tg CO yr^{-1})
Sources	1800–2700
Fossil fuel combustion/industry	300–550
Biomass burning	300–700
Vegetation	60–160
Oceans	20–200
Oxidation of methane	400–1000
Oxidation of other hydrocarbons	200–600
Sinks	2100–3000
Tropospheric oxidation by OH	1400–2600
Stratosphere	~ 100
Soil uptake	250–640

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Most Important Gases in Smog in Terms of Ozone Reactivity and Abundance

1. *m*- and *p*-Xylene
2. Ethene
3. Acetaldehyde
4. Toluene
5. Formaldehyde
6. *i*-Pentane
7. Propene
8. *o*-Xylene
9. Butane
10. Methylcyclopentane

Table 4.4

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Lifetimes of ROGs Against Chemical Loss in Urban Air

ROG Species	Phot.	OH	HO_2	O	NO_3	O_3
n-Butane	---	22 h	1000 y	18 y	29 d	650 y
trans-2-butene	---	52 m	4 y	6.3 d	4 m	17 m
Acetylene	---	3 d	---	2.5 y	---	200 d
Formaldehyde	7 h	6 h	1.8 h	2.5 y	2 d	3200 y
Acetone	23 d	9.6 d	---	---	---	---
Ethanol	---	19 h	---	---	---	---
Toluene	---	9 h	---	6 y	33 d	200 d
Isoprene	---	34 m	---	4 d	5 m	4.6 h

Table 4.3

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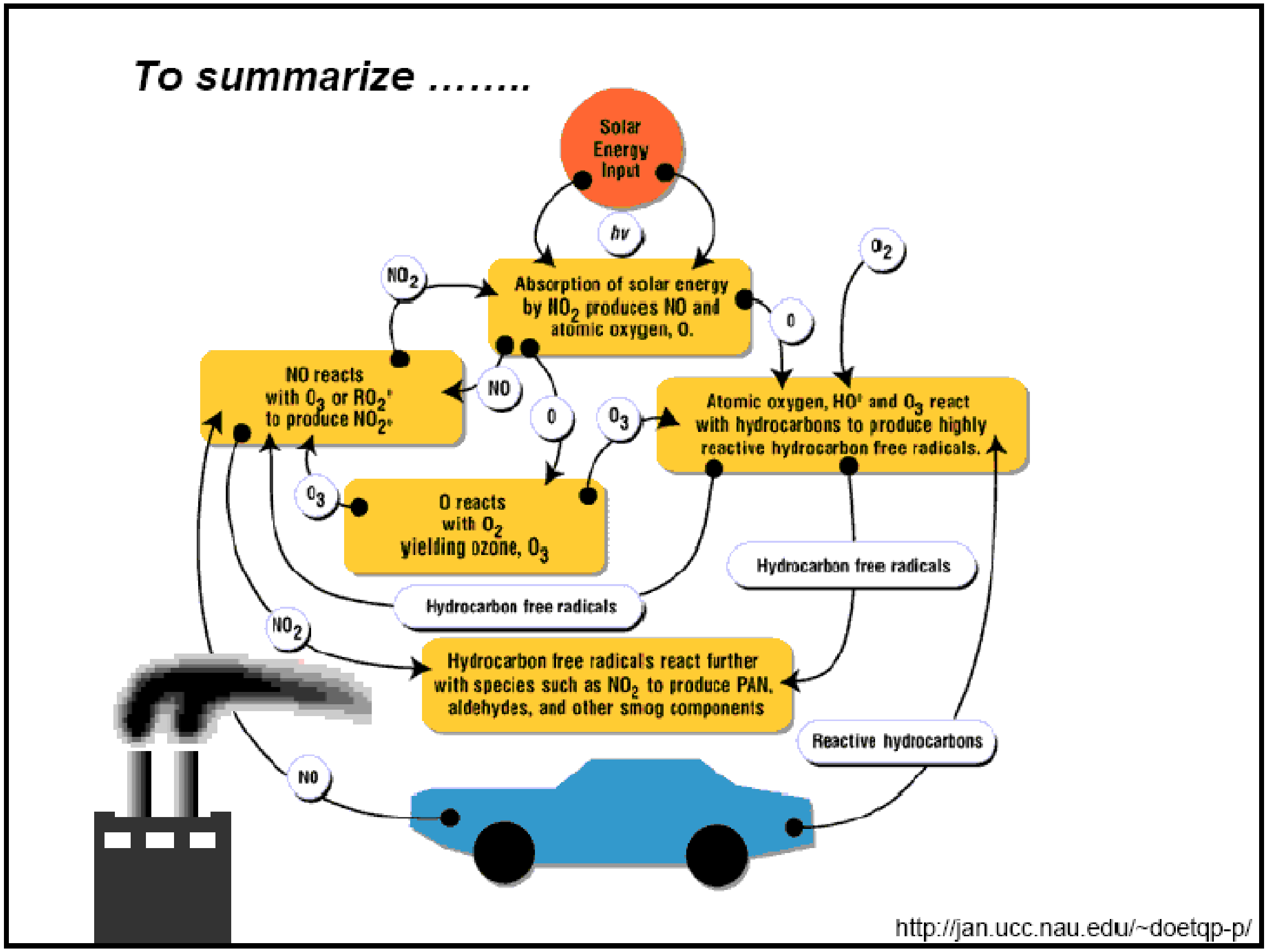
Summary



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Ozone

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Ozone

- Colorless gas
- Composed of three oxygen atoms
  - Oxygen molecule (O_2)—needed to sustain life
  - Ozone (O_3) —the extra oxygen atom makes ozone very reactive
- Secondary pollutant that forms from precursor gases
  - Nitric oxide – combustion product
  - Volatile organic compounds (VOCs) – evaporative and combustion products

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Solar radiation and chemistry

- The reaction that produces ozone in the atmosphere:

$$O + O_2 + M \equiv O_3 + M$$

- Difference between stratospheric and tropospheric ozone generation is in the source of atomic O
- For solar radiation with a wavelength of less than 242 nm:

$$O_2 + hv \equiv O + O$$

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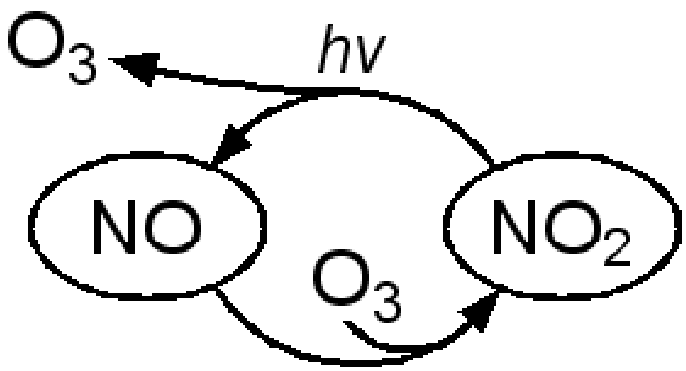
Solar radiation and chemistry

- Photochemical production of O_3 in troposphere tied to NO_x (NO + NO_2)
- For wavelengths less than 424 nm:

$$NO_2 + h\nu \equiv NO + O$$

- But NO will react with O_3

$$NO + O_3 \equiv NO_2$$



- Cycling has no net effect on ozone

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Nitrogen Oxides

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Nitrogen Oxides

- Nitrogen oxides, or NO_x, is the generic term for a group of highly reactive gases, all of which contain nitrogen and oxygen in varying amounts.
- Nitrogen dioxide is most visually prominent (it is the yellow-brown color in smog)
- The primary man-made sources of NO_x are motor vehicles; electric utilities; and other industrial, commercial, and residential sources that burn fuels
- Affects the respiratory system
- Involved in other pollutant chemistry
  - One of the main ingredients in the formation of ground-level ozone
  - Reacts to form nitrate particles, acid aerosols, and NO_2, which also cause respiratory problems
  - Contributes to the formation of acid rain (deposition)

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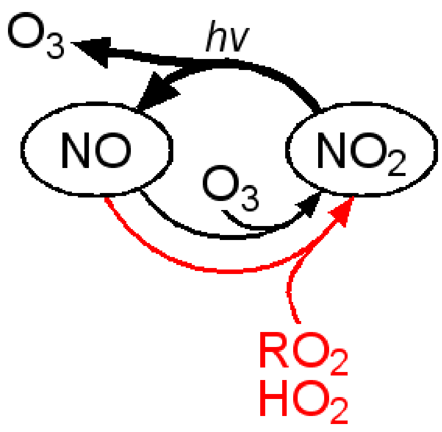
Must make NO_2

- To make significant amounts of ozone must have a way to make NO_2 without consuming ozone
- Presence of peroxy radicals, from the oxidation of hydrocarbons, disturbs O_3-NO-NO_2 cycle

$$NO + HO_2\cdot \equiv NO_2 + OH\cdot$$

$$NO + RO_2\cdot \equiv NO_2 + RO\cdot$$

  – leads to net production of ozone



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The Hydroxyl Radical

- produced from ozone photolysis
  - for radiation with wavelengths less than 320 nm:

$$O_3 + h\nu \equiv O(^1D) + O_2$$

followed by

$$O(^1D) + M \equiv O(^3P) + M\ (+O_2 \equiv O_3) \qquad (\sim 90\%)$$

$$O(^1D) + H_2O \equiv 2\ OH\cdot \qquad (\sim 10\%)$$

- OH initiates the atmospheric oxidation of a wide range of compounds in the atmosphere
  - referred to as ‘detergent of the atmosphere’
  - typical concentrations near the surface ~10^6 - $10^7 cm^{-3}$
  - very reactive, effectively recycled

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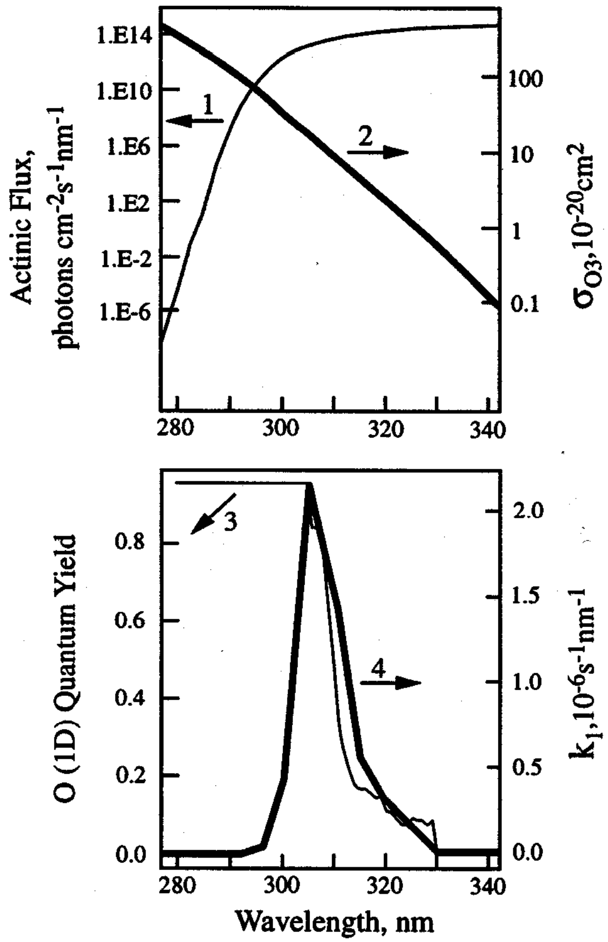
THE OH RADICAL: MAIN TROPOSPHERIC OXIDANT



- Primary source:
    - O_3 + hn → O_2 + O(1D) (1)
    - $O(^1D)$ + M → O + M (2)
    - $O(^1D)$ + H_2O → 2OH (3)
- Sink: oxidation of reduced species –leads to HO2(RO2) production
    - CO + OH → CO_2 + H
    - CH_4 + OH → CH_3 + H_2O
    - HCFC + OH

  } **Major OH sinks**

- Global Mean [OH] = 1.0×10^6 molecules cm^{-3}

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Carbon Monoxide

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Carbon Monoxide

- Odorless, colorless gas
- Caused by incomplete combustion of fuel
- Most of it comes from motor vehicles
- Reduces the transport of oxygen through the bloodstream
- Affects mental functions and visual acuity, even at low levels

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Oxidation of CO - production of ozone

$$CO + OH\cdot \equiv CO_2 + H\cdot$$

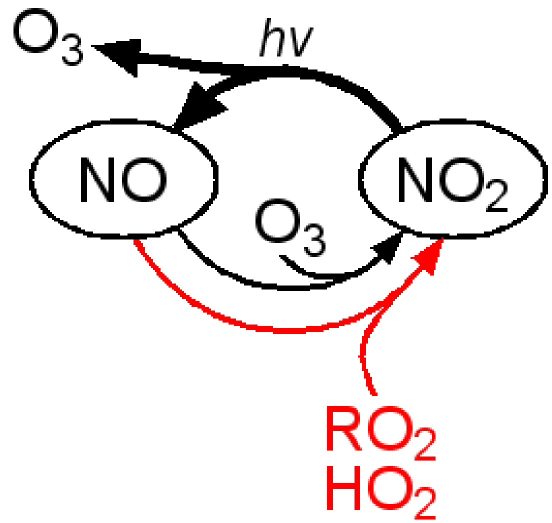
$$H\cdot + O_2 + M \equiv HO_2\cdot + M$$

$$NO + HO_2\cdot \equiv NO_2 + OH\cdot$$

$$NO_2 + h\nu \equiv NO + O$$

$$O + O_2 + M \equiv O_3$$

$$CO + 2\ O_2 + h\nu \equiv CO_2 +$$



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In Summary

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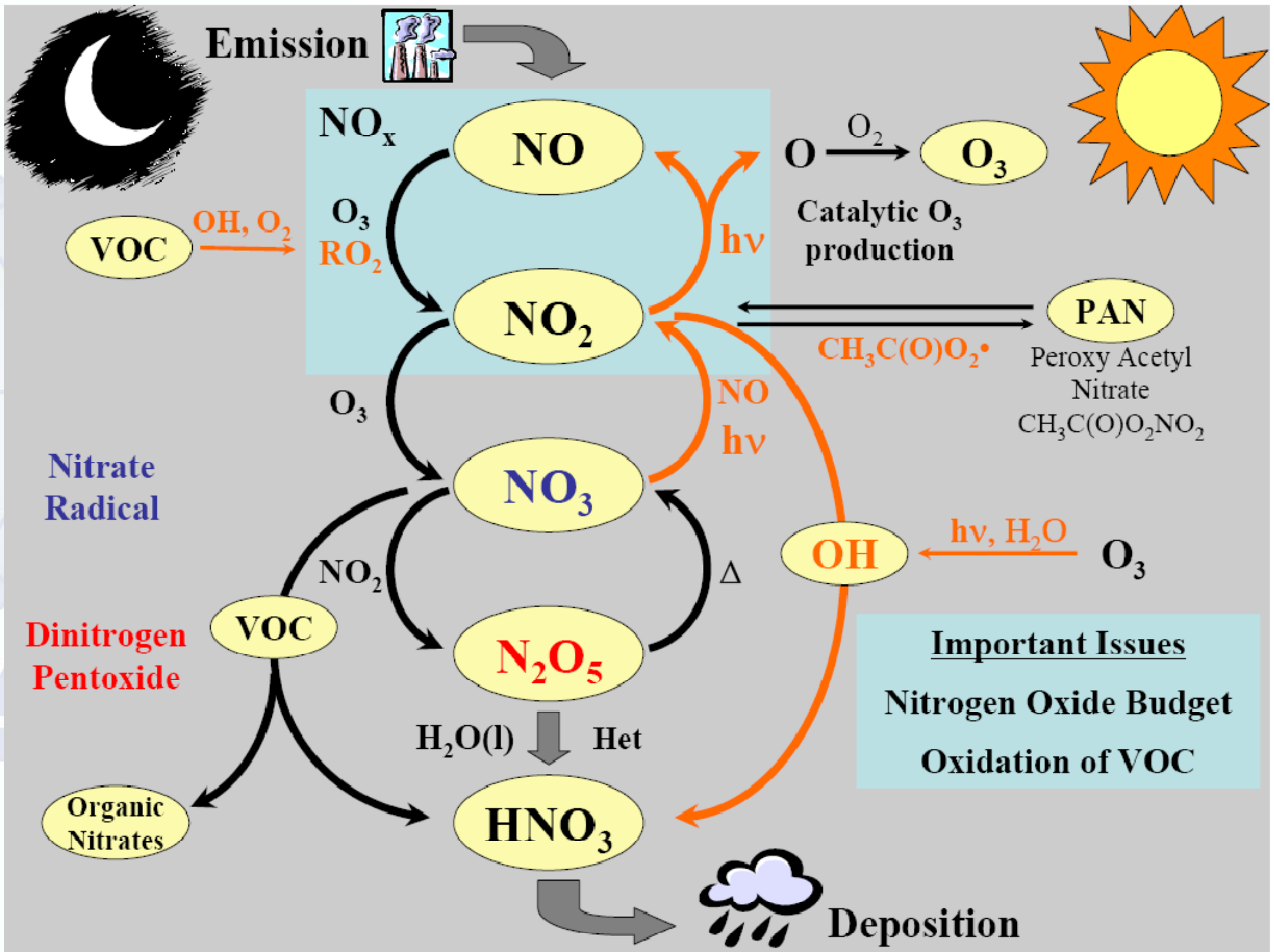
Day <u>and</u> Night Chemistry



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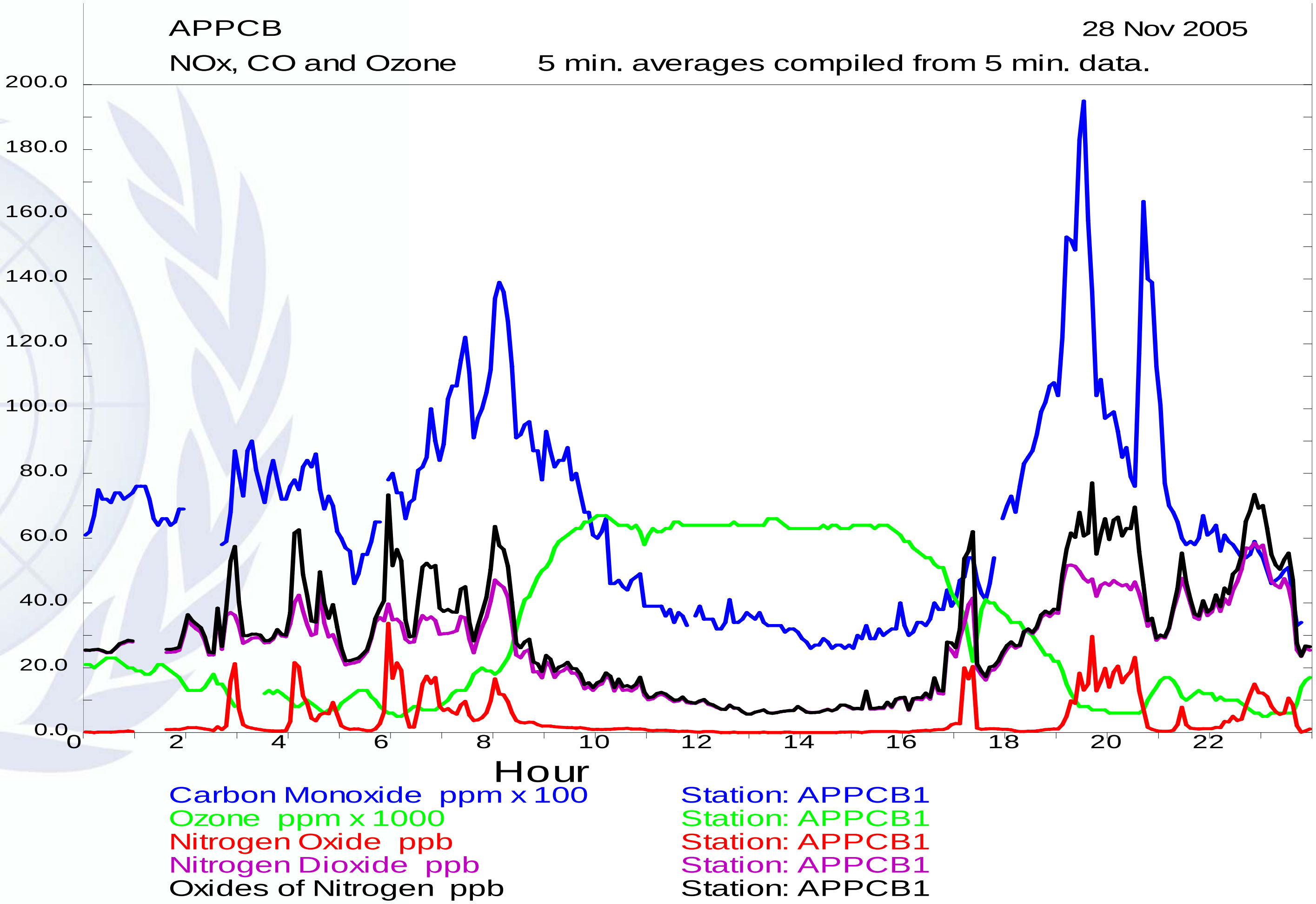
Hyderabad, 2005



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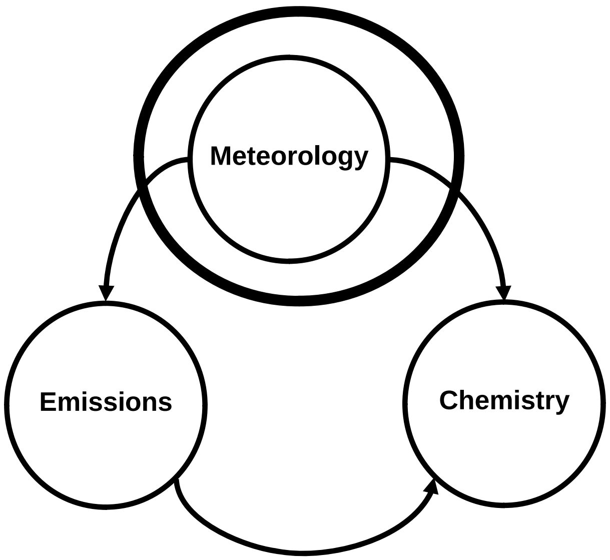
Physical Aspects

Ozone Meteorology – Key Processes

- Dispersion (horizontal mixing)
- Vertical mixing
- Sunlight
- Transport
- Weather pattern
- Geography
- Diurnal
- Season



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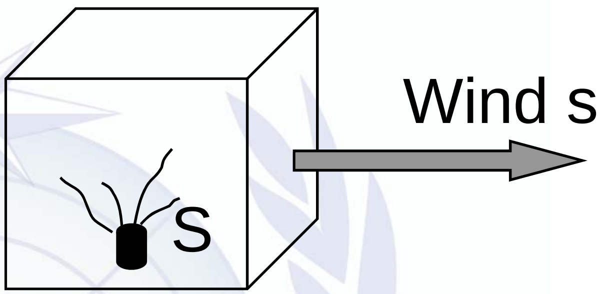
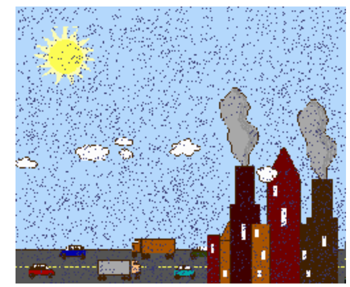
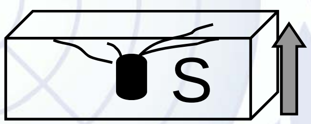
Ozone Precursor Emissions (2 of 2)



Wind speed (WS)

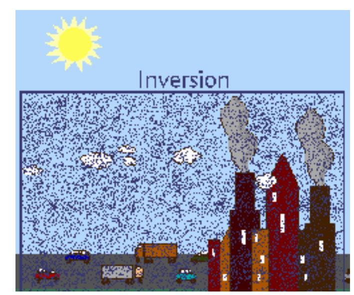
Concentration ∝ S/WS





Vertical mixing (VM)

Concentration ∝ S/VM



Courtesy of New Jersey
Department of Environmental Protection

- Key processes
  - Source location, density, and strength
  - Dispersion (horizontal mixing) - wind speed
  - Vertical mixing - inversion

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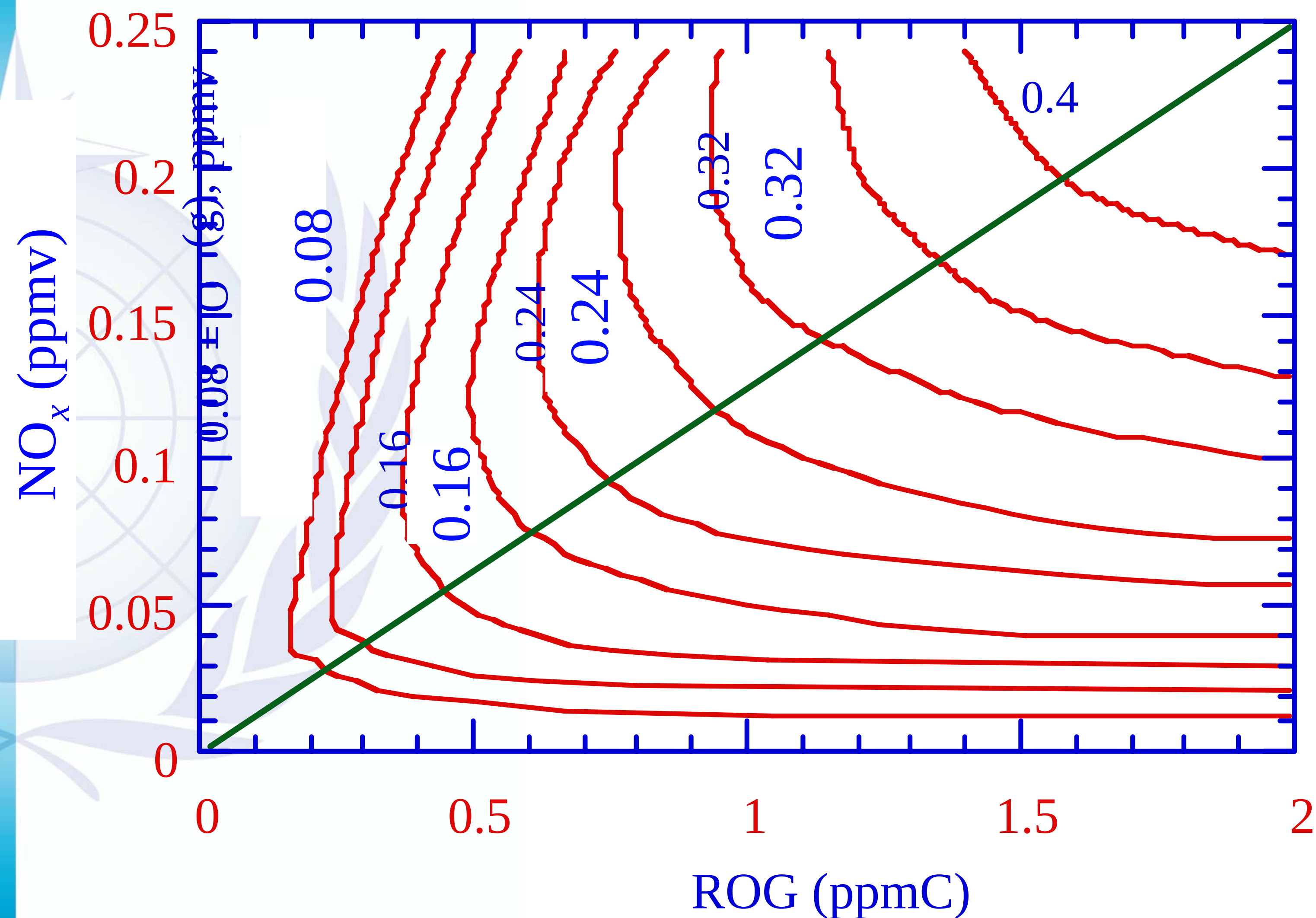
Ozone Isopleth Plot



Contours are ozone (ppmv)

Figure 4.9

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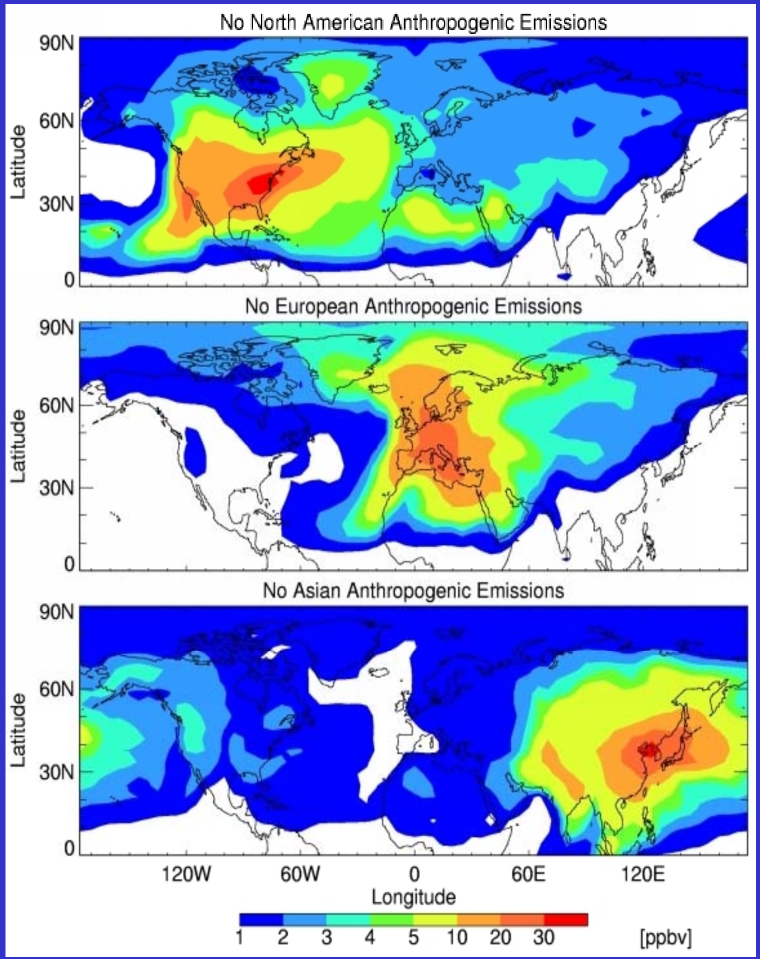
EU/USA LRTAP Long-range Transboundary Air Pollution

Task Force on Hemispheric Transport of Air Pollution

SURFACE OZONE ENHANCEMENTS CAUSED BY ANTHROPOGENIC EMISSIONS FROM DIFFERENT CONTINENTS



GEOS-CHEM model, July 1997

North America

Europe

Asia

Li et al. [2002]

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Particulates

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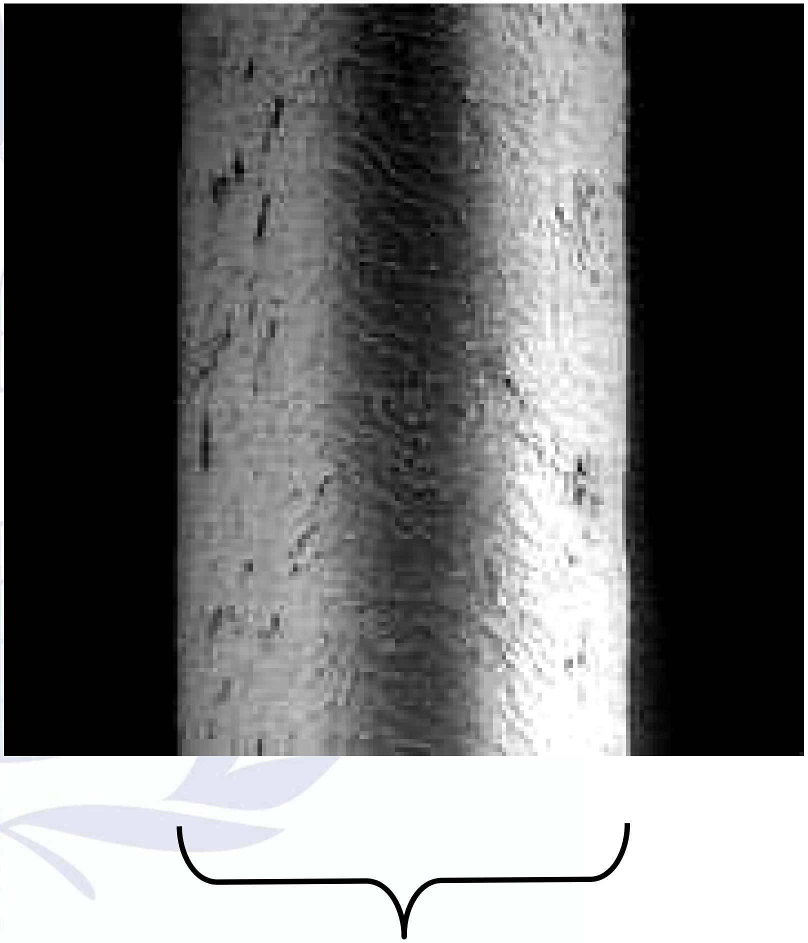
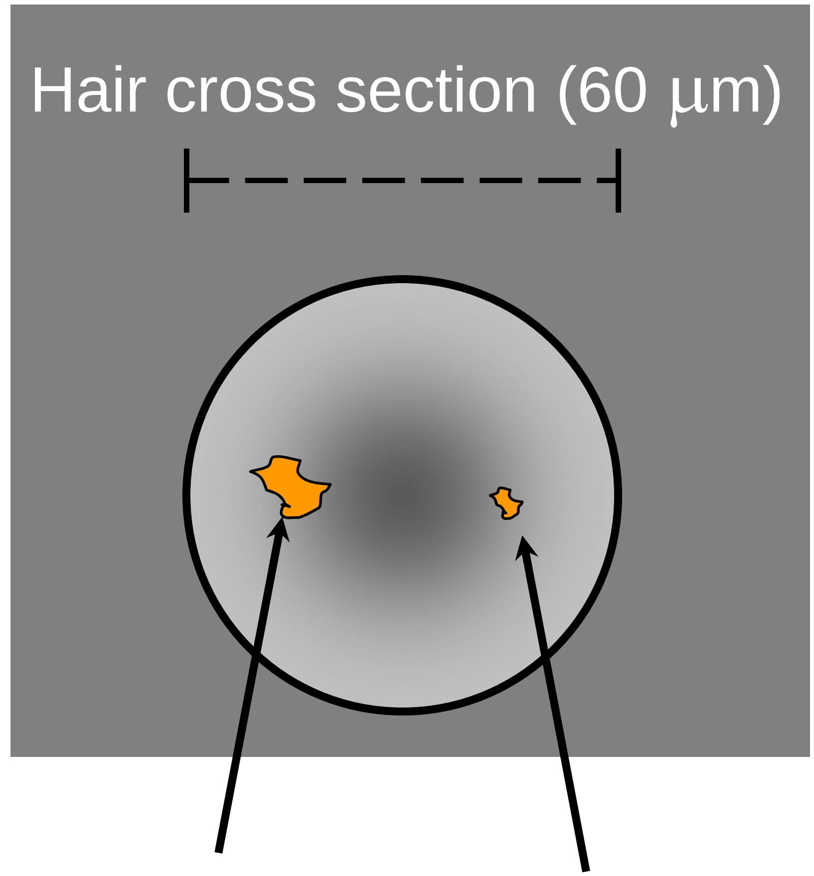
PM relative to hair cross section



Human Hair



PM10 (10 μm)

PM2.5 (2.5 μm)

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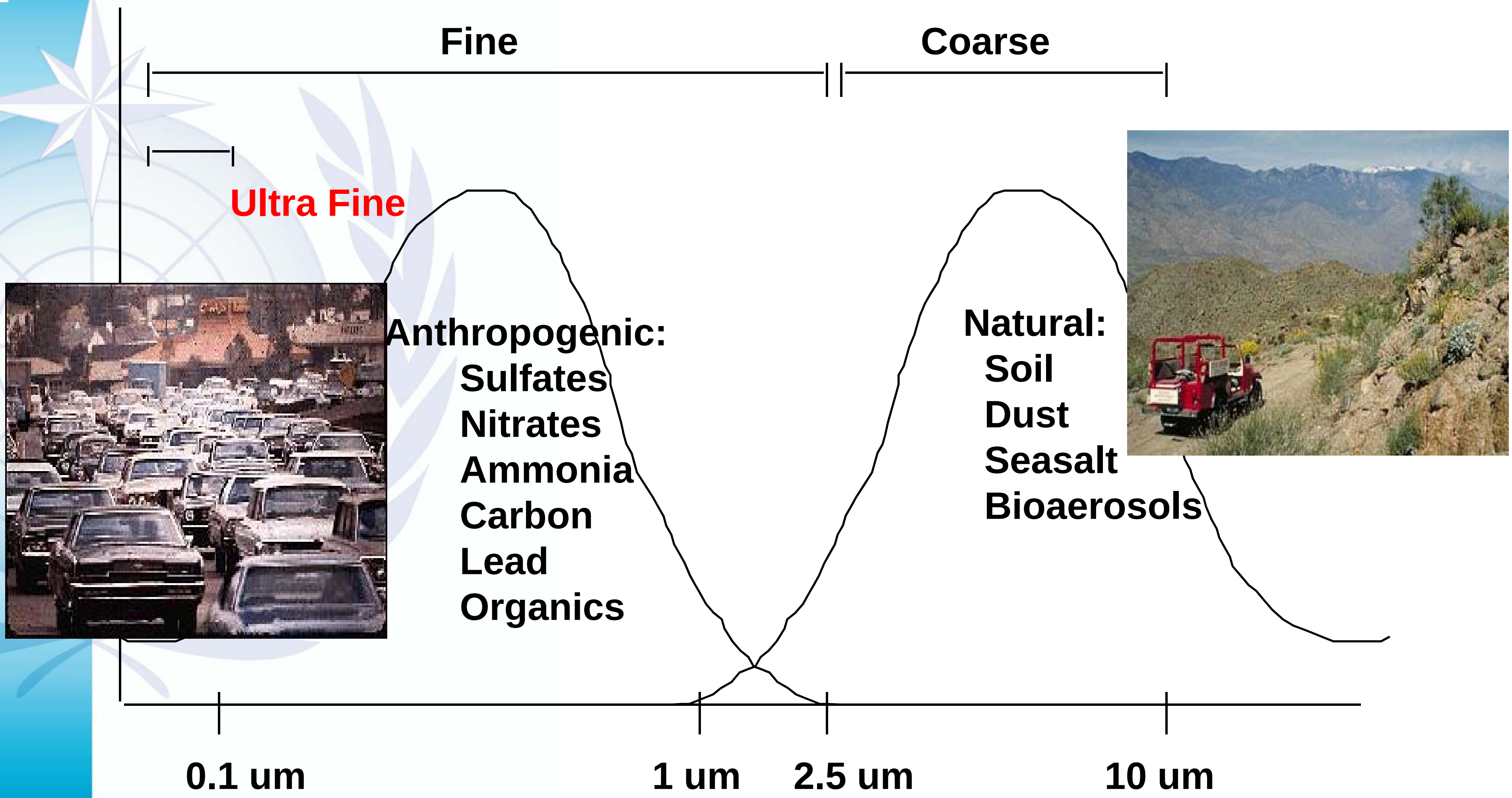
Particulate Matter
Sizes and Composition



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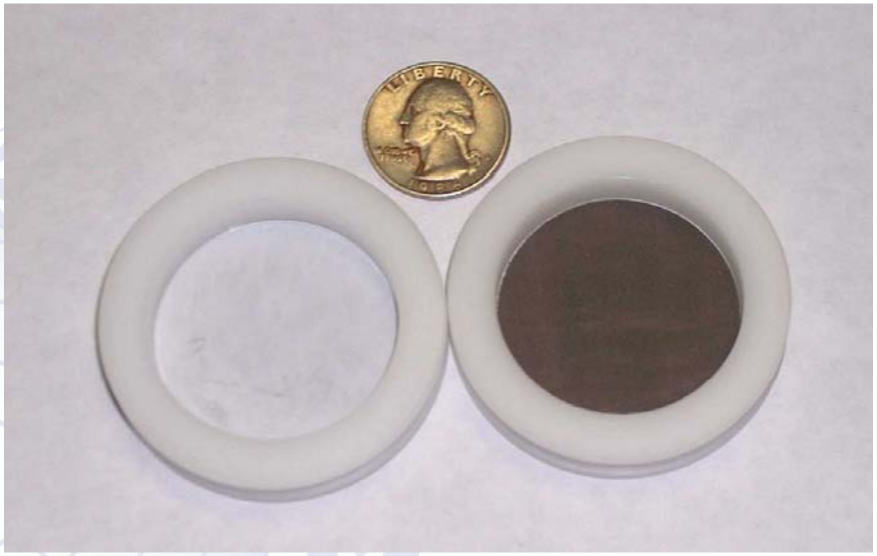
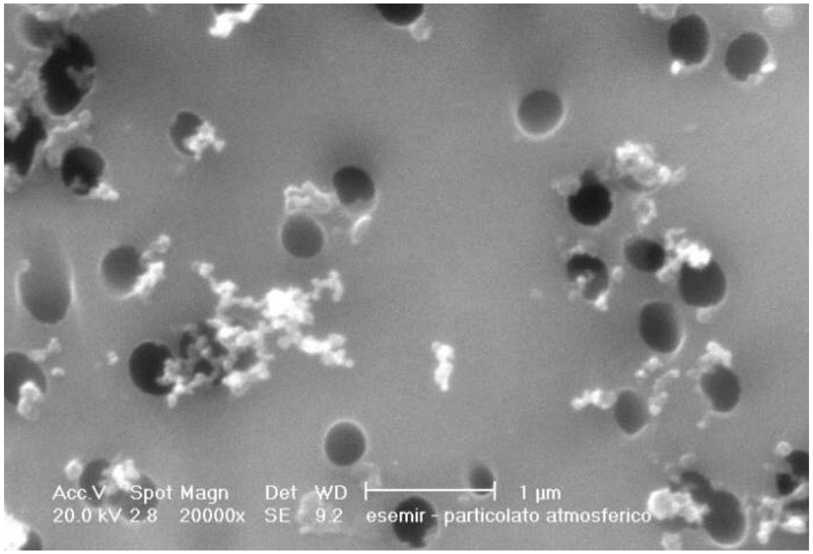
Particulate Matter (3 of 3)



A clear (left) and dirty (right) PM filter



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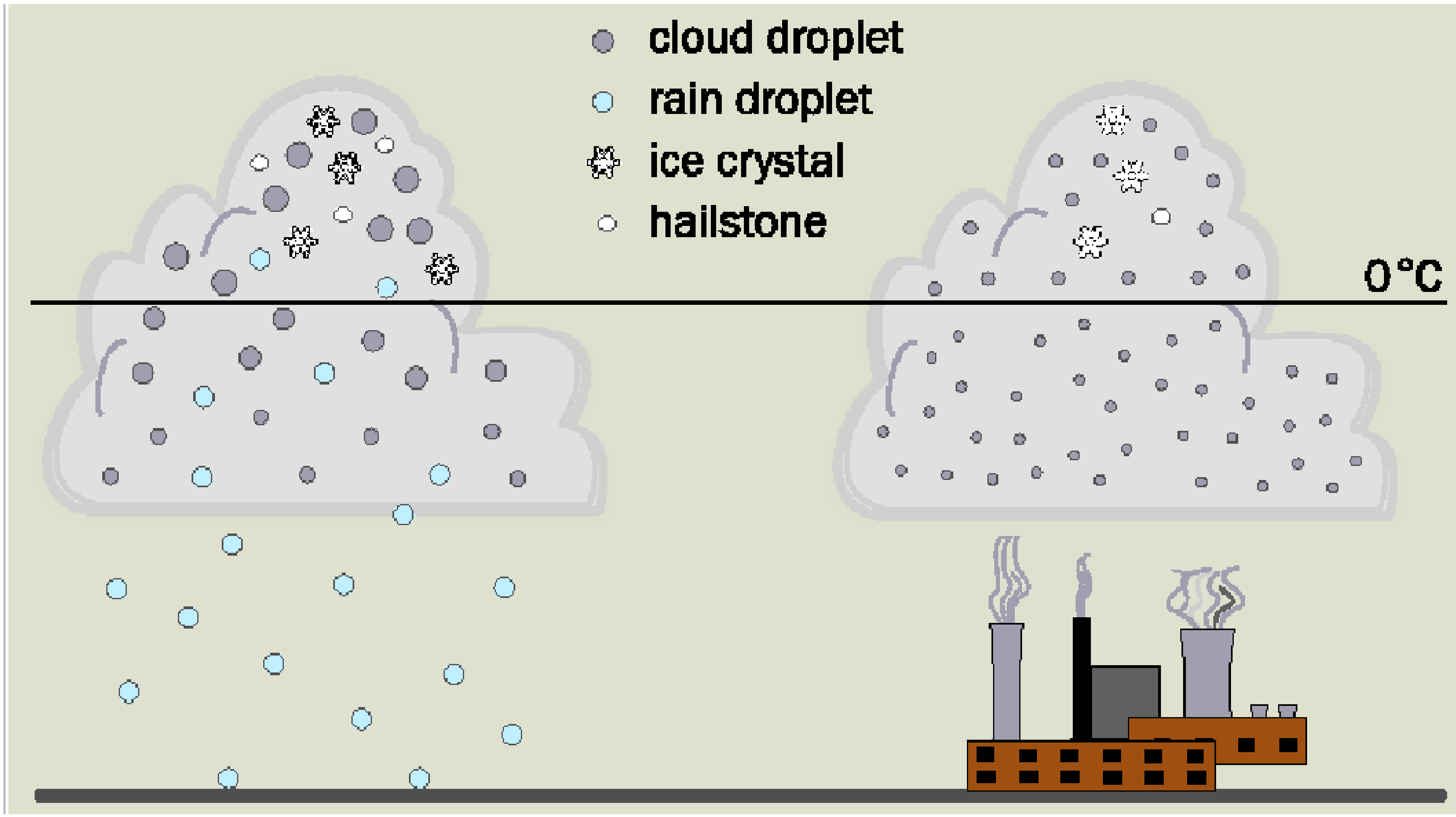
Particles Impact Human Health and MORE

Suppression of Rain and Snow by Urban and Industrial Air Pollution



Courtesy of D. Rosenfeld.

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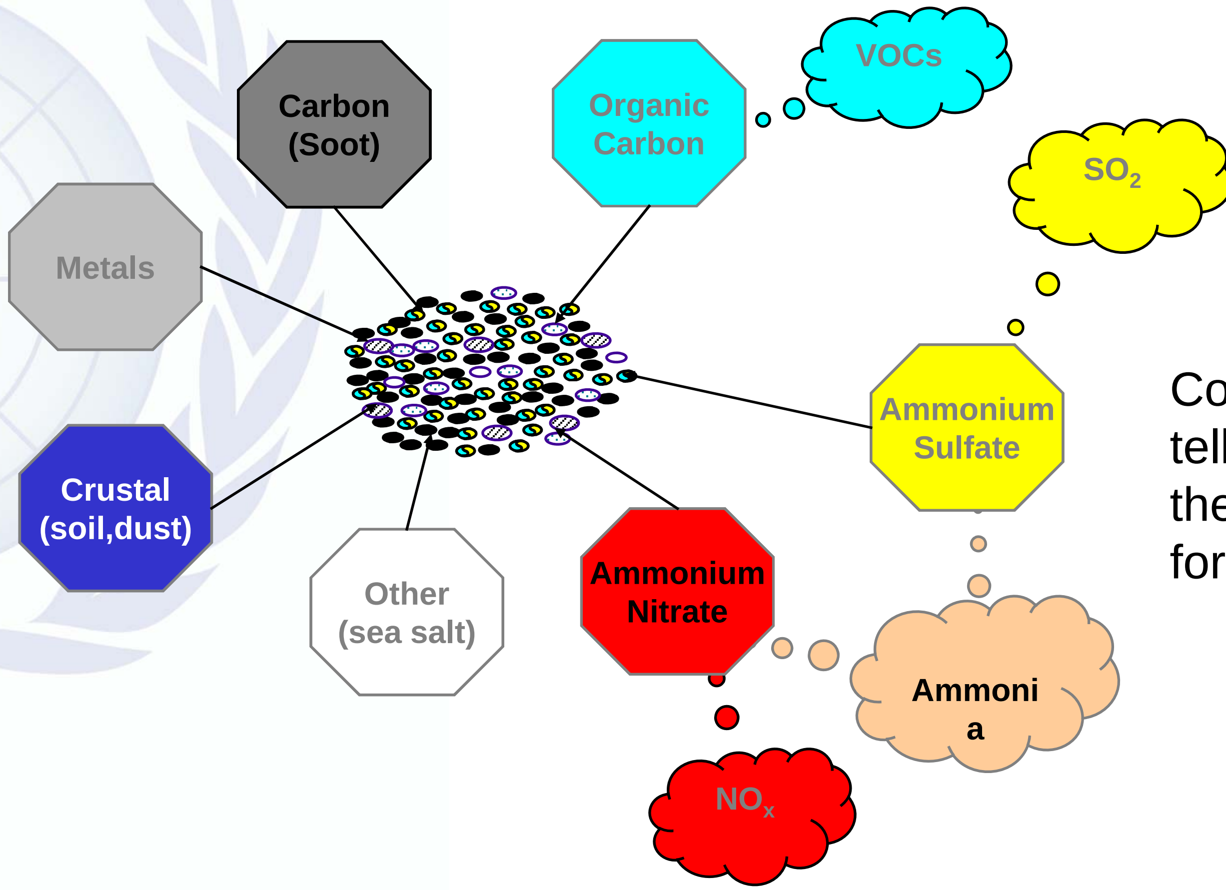
Particulate Matter Composition

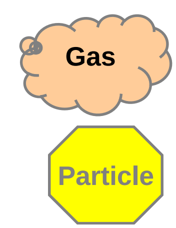
PM contains many compounds

Primary Particles
(directly emitted)

Secondary Particles
(from precursor gases)



Composition of PM tells us about the sources and formation processes



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PM Emissions Sources (1 of 4)

Point – generally a major facility emitting pollutants from identifiable sources (pipe or smoke stack). Facilities are typically permitted.

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PM Emissions Sources (2 of 4)

Area – any low-level source of air pollution released over a diffuse area (not a point) such as consumer products, architectural coatings, waste treatment facilities, animal feeding operations, construction, open burning, residential wood burning, swimming pools, and charbroilers

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PM Emissions Sources (3 of 4)

Mobile

- On-road is any moving source of air pollution such as cars, trucks, motorcycles, and buses
- Non-road sources include pollutants emitted by combustion engines on farm and construction equipment, locomotives, commercial marine vessels, recreational watercraft, airplanes, snow mobiles, agricultural equipment, and lawn and garden equipment

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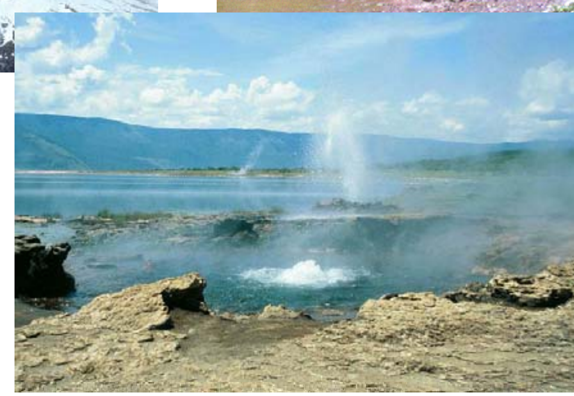
PM Emissions Sources (4 of 4)

Natural – biogenic and geogenic emissions from wildfires, wind blown dust, plants, trees, grasses, volcanoes, geysers, seeps, soil, and lightning







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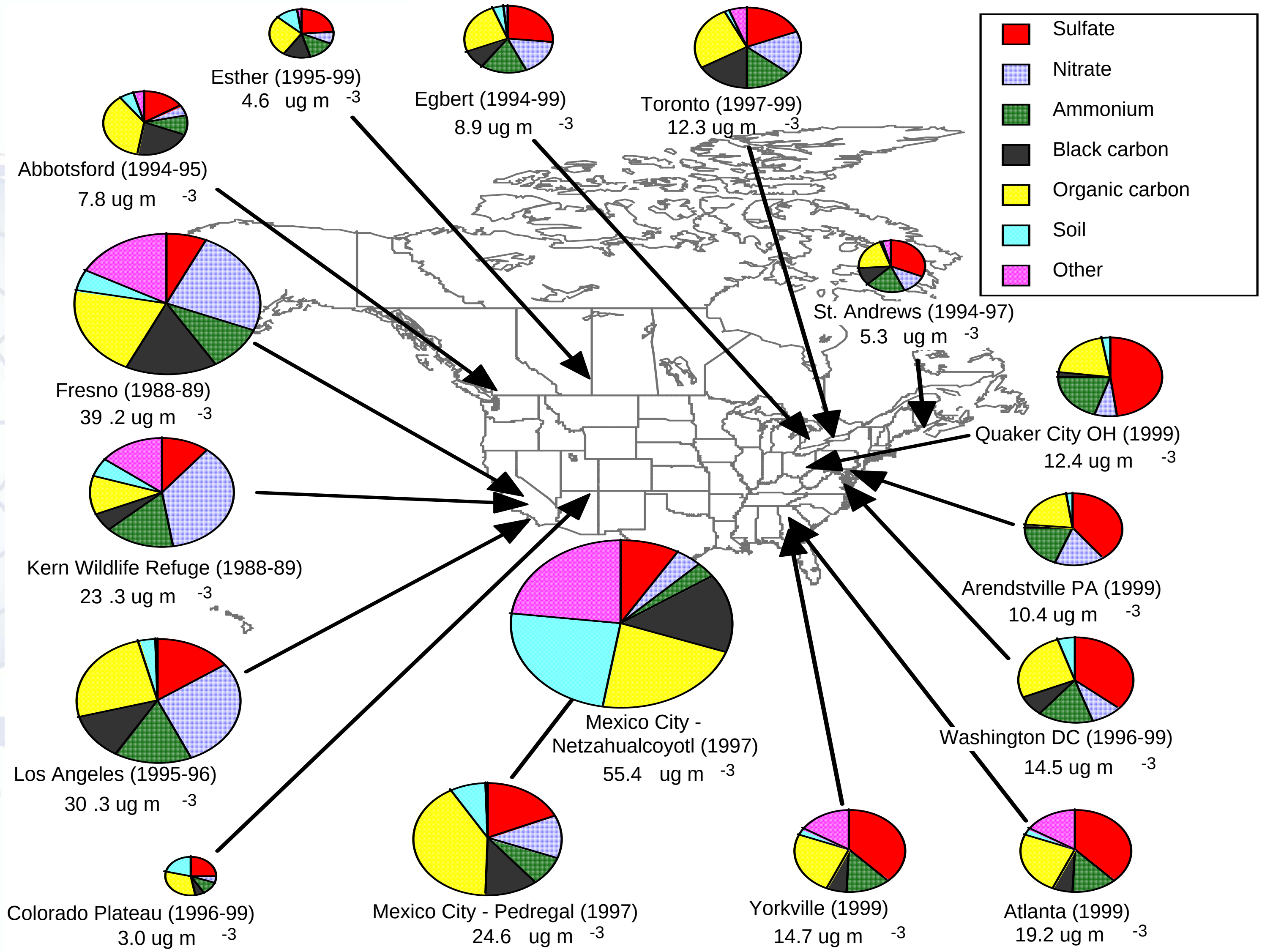
COMPOSITION OF PM2.5 IS HIGHLY VARIABLE (NARSTO PM ASSESSMENT)



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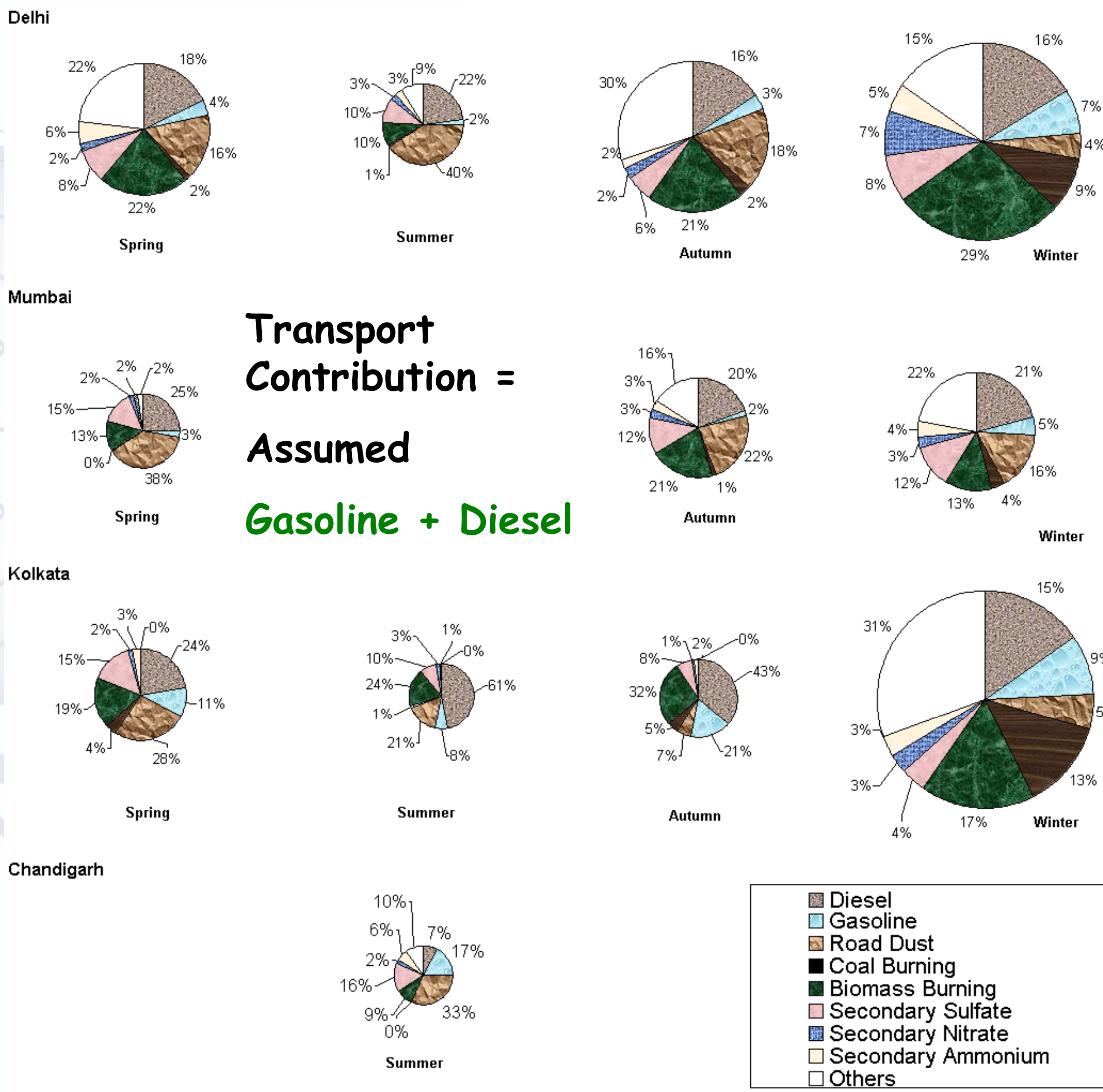
India Case Studies (2001 $PM_{2.5}$)

New Delhi | Mumbai | Kolkata | Chandigarh



Transport Contribution = Assumed Gasoline + Diesel

Spr-Sum-Aut-Win

22-24-19-23

28-*-22-26

35-69-64-24

-24--*

Geogia Tech (USA), 2004

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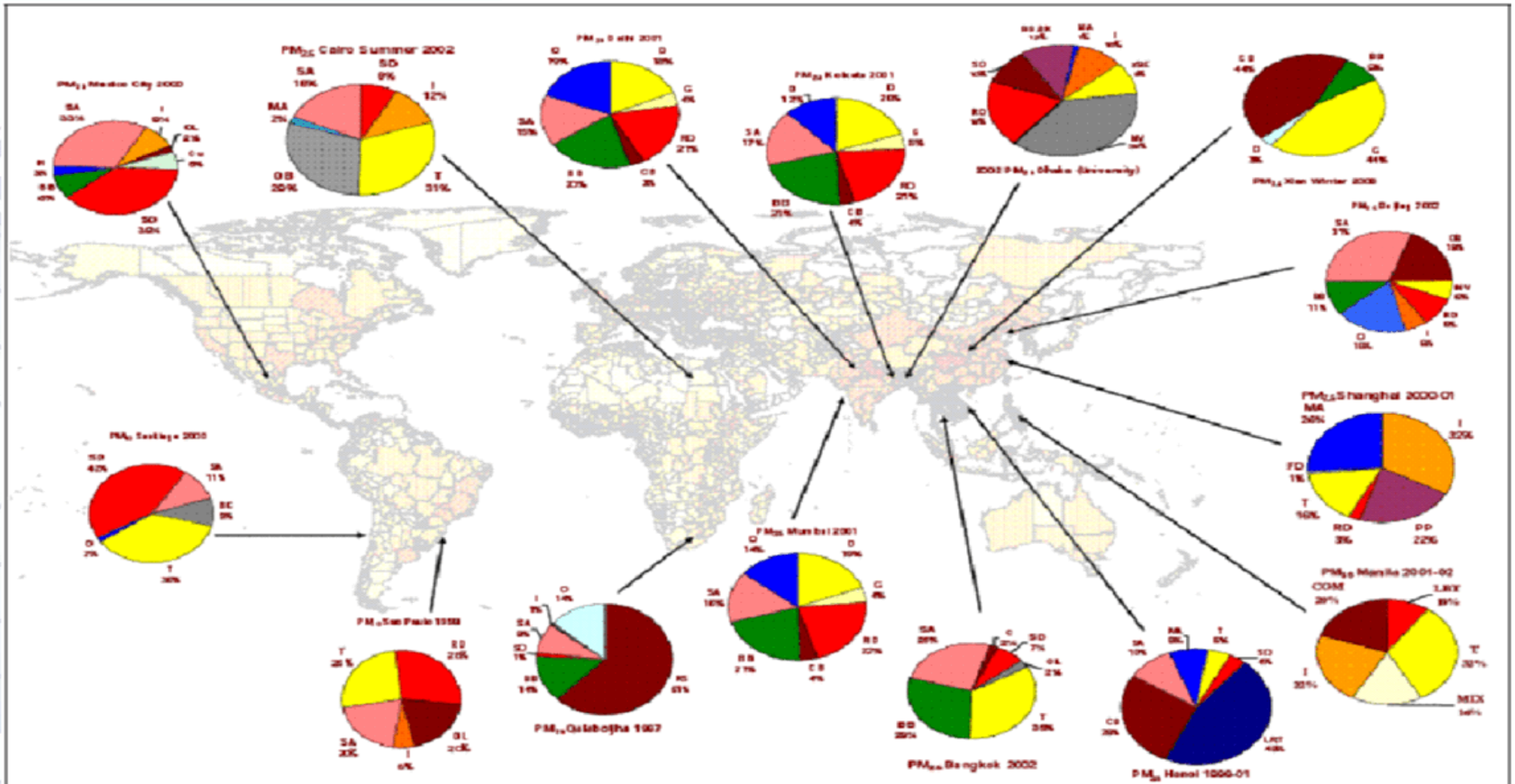
Summary of PMSA Studies



BB=Biomass Burning; CB = Coal Burning; D=Diesel; G=Gasoline; RD=Road Dust; Sa=Secondary Aerosols; O=Others; I=Industry; MV=Motor Vehicles; T=Transport; OL=Oil Burning; SD=Soil Dust; BC=Black Carbon; Cu=Copper; H=Hydrogen; RS=Residential; LRT=Long Range Transport; MA=Marine; PP=Power Plant; FD=Fugitive Dust; 2StE=2-Stroke Engine; BK=Brick Kiln; C=Construction

Guttikunda and Johnson, The World Bank, 2008

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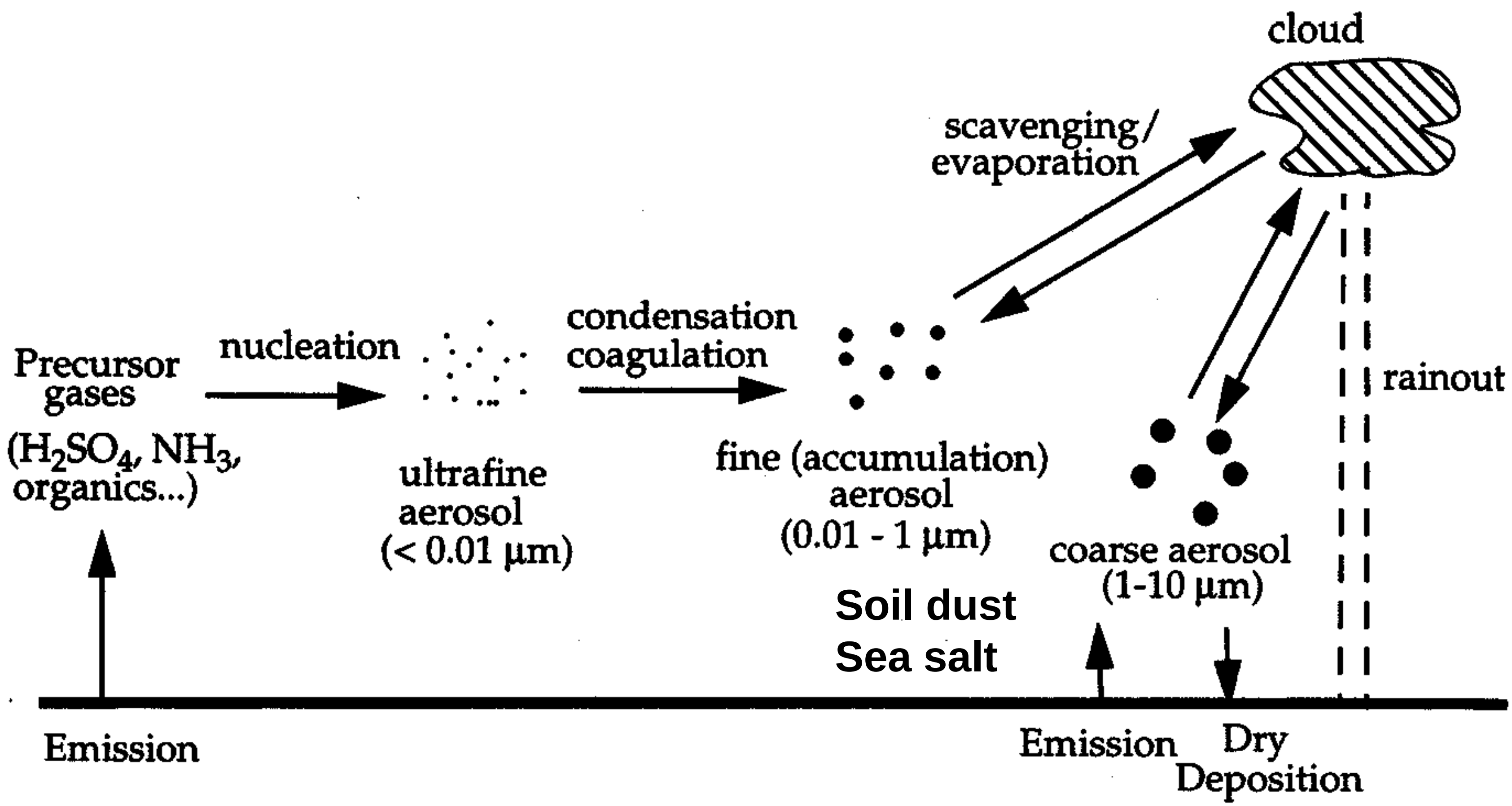
ORIGIN OF THE ATMOSPHERIC AEROSOL

Aerosol: dispersed condensed matter suspended in a gas
Size range: 0.001 μm (molecular cluster) to 100 μm (small raindrop)



Environmental importance: health (respiration), visibility, radiative balance, cloud formation, heterogeneous reactions, delivery of nutrients…

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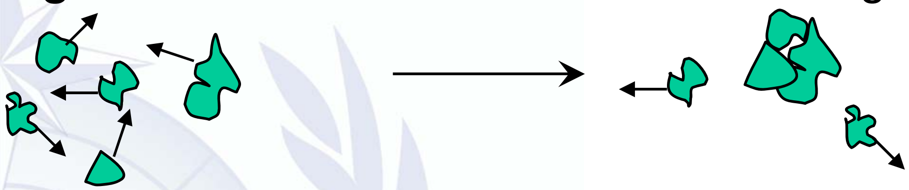
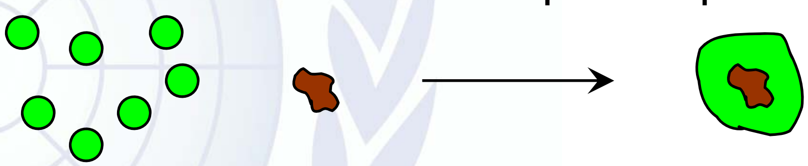
Particulate Matter Chemistry

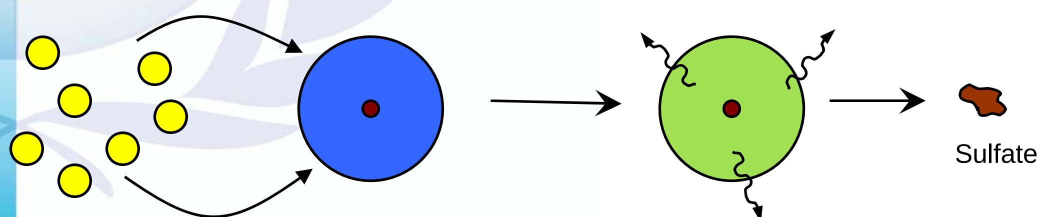
Coagulation: Particles collide and stick together.

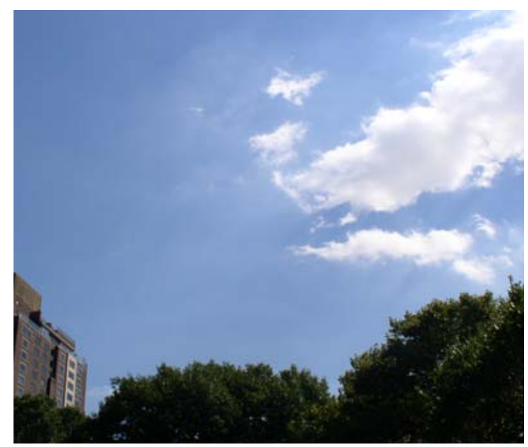


Condensation: Gases condense onto a small solid particle to form a liquid droplet.



Cloud/Fog Processes: Gases dissolve in a water droplet and chemically react. A particle exists when the water evaporates.





Chemical Reaction: Gases react to form particles.

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Sulfur Dioxide

- Sulfur dioxide (SO_2) belongs to the family of sulfur oxide (SO_x) gases.
- Gases are formed when fuel containing sulfur (mainly coal and oil) is burned and during metal smelting and other industrial processes.
- Affects the respiratory system
- Reacts in the atmosphere to form acids, sulfates, and sulfites
- Contributes to acid rain

Impact of low soil pH on agriculture in Victoria

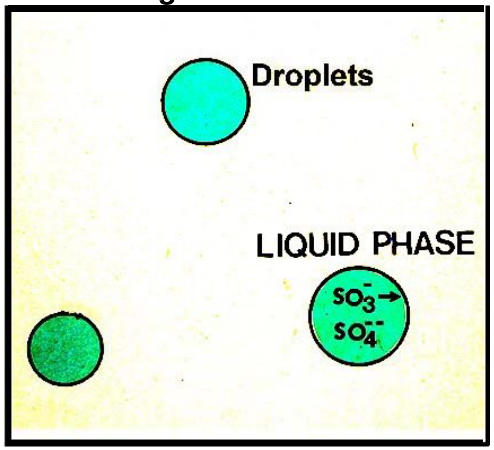
German sandstone statue, 1908, 1969

Low crown density of spruce trees

Particulate Matter Chemistry (2 of 4)

Sulfate Chemistry

Heterogeneous Oxidation



Husar (1999)

- Virtually all ambient sulfate (99%) is secondary, formed within the atmosphere from SO_2 during the summer.
- About half of SO_2 oxidation to sulfate occurs in the gas phase through photochemical oxidation in the daytime. NO_x and hydrocarbon emissions tend to enhance the photochemical oxidation rate.
- At least half of SO_2 oxidation takes place in cloud droplets as air molecules react in clouds.
- Within clouds, soluble pollutant gases, such as SO_2, are scavenged by water droplets and rapidly oxidize to sulfate.
- Only a small fraction of cloud droplets deposit out as rain; most droplets evaporate and leave a sulfate residue or “convective debris”.
- Typical conversion rate 1-10% per hour

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Summary

Sources	Emissions	PM Formation	PM Transport/Loss	Sample Collection

Chemical Processes

Mechanical → **Particles**
- Sea salt
- Dust

Particles
- NaCl
- Crustal

Combustion → **Particles**, **Gases**
- Motor vehicles
- Industrial
- Fires

Particles
- Soot
- Metals
- OC

Gases
- NO_x
- SO_2
- VOCs
- NH_3

Other gaseous → **Gases**
- Biogenic
- Anthropogenic

Gases
- VOCs
- NH_3
- NO_x

gases condense onto particles
cloud/fog processes

condensation and coagulation

photochemical production
cloud/fog processes

transport

sedimentation (dry deposition)

wet deposition

Measurement Issues
- Inlet cut points
- Vaporization of nitrate, H_2O, VOCs
- Adsorption of VOCs
- Absorption of H_2O

Meteorological Processes

Emissions	PM Formation	PM Transport/Loss	Sample Collection
Winds	Clouds, fog	Winds	Temperature
Temperature	Temperature	Precipitation	Relative humidity
Solar radiation	Relative humidity		Winds
Vertical mixing	Solar radiation		

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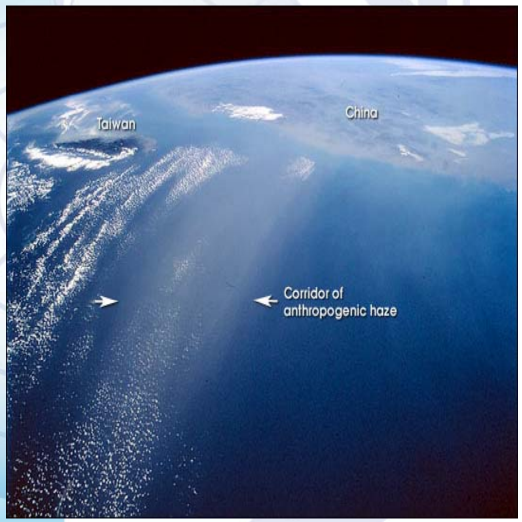
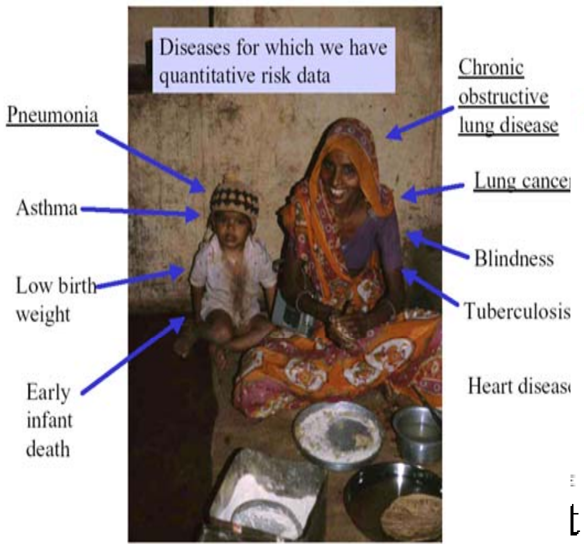
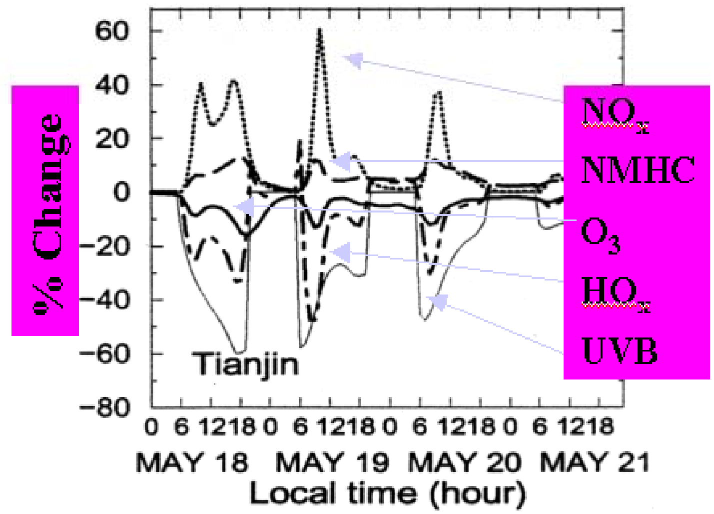
Aerosols Link Air Quality, Health and Climate:
Dirtier Air and a Dimmer Sun







Anderson et al., Science 2003

Smith et al., 2003

He et al., 2002

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Thank you

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