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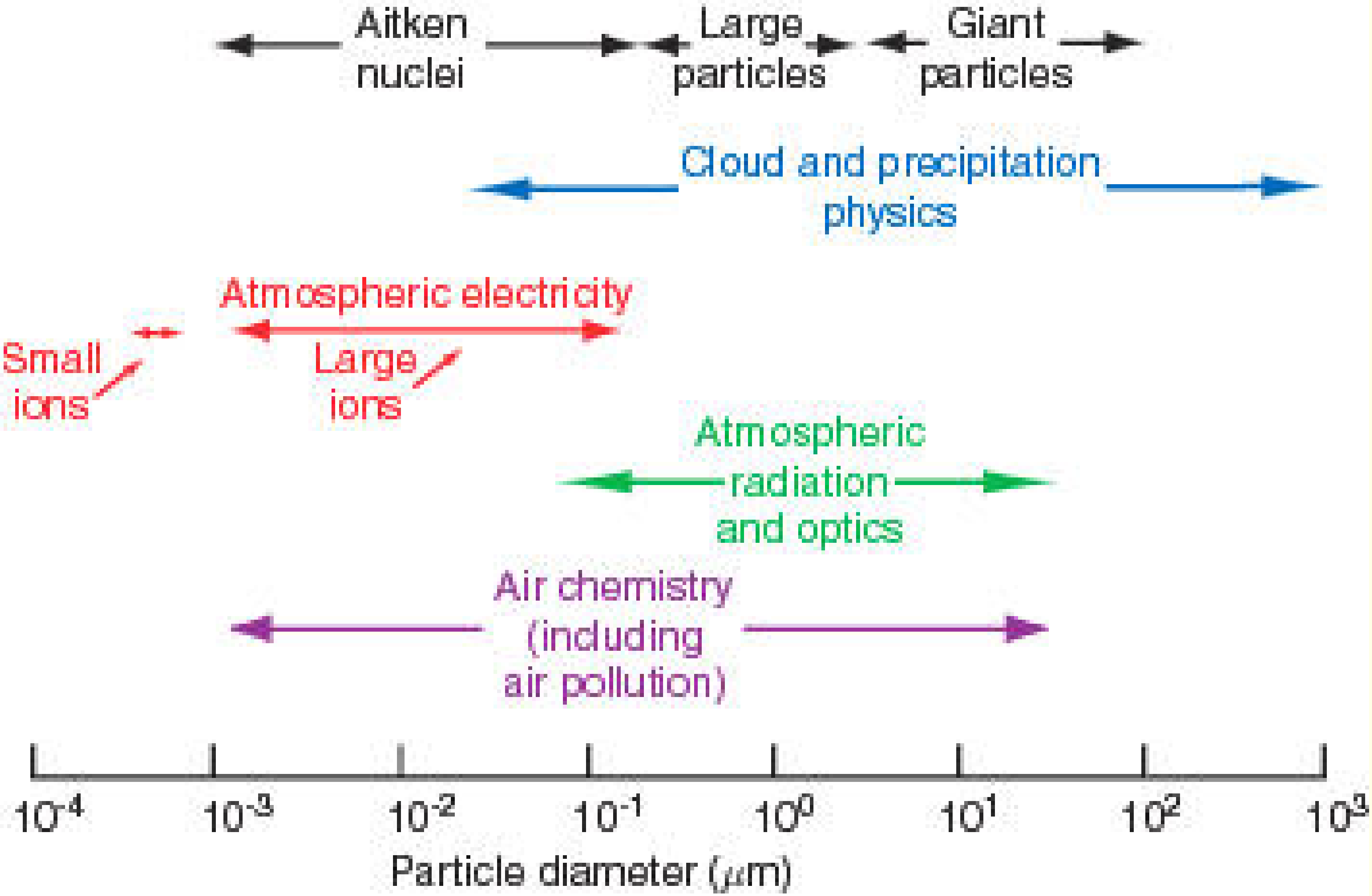
Ions are removed by combining with ions of opposite sign.

The following Figure shows the size ranges of particles that play a role in the atmosphere.



Size range of particles in the atmosphere

$d < 0.2\mu m$: **Aitkin.** $0.2 < d < 0.2\mu m$: **Large.** $d > 2\mu m$: **Giant.**

Concentrations of small ions vary from about 40 to 1500 cm^{-3} at sea level, while concentrations of large ions vary from about 200 cm^{-3} in marine air to a maximum value of about 8×10^5 cm^{-3} in some cities.

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The observed decrease of at least 20% in the electrical conductivity of the air over the North Atlantic Ocean during the 20th century is attributed to a doubling in the concentration of particles with diameters between 0.02 and 0.2 μm, probably due to pollution.

Sources

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a. Biological

Solid and liquid particles are released into the atmosphere from plants and animals. These emissions, which include seeds, pollen, spores, and fragments of animals and plants, are usually 1-250 μm in diameter. Bacteria, algae, protozoa, fungi, and viruses are generally $<1\,\mu$m in diameter.

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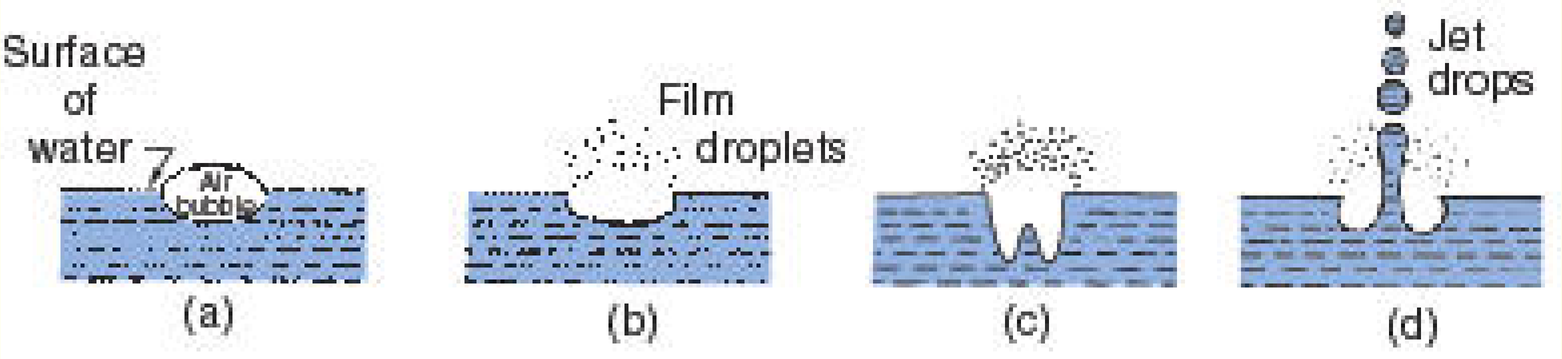
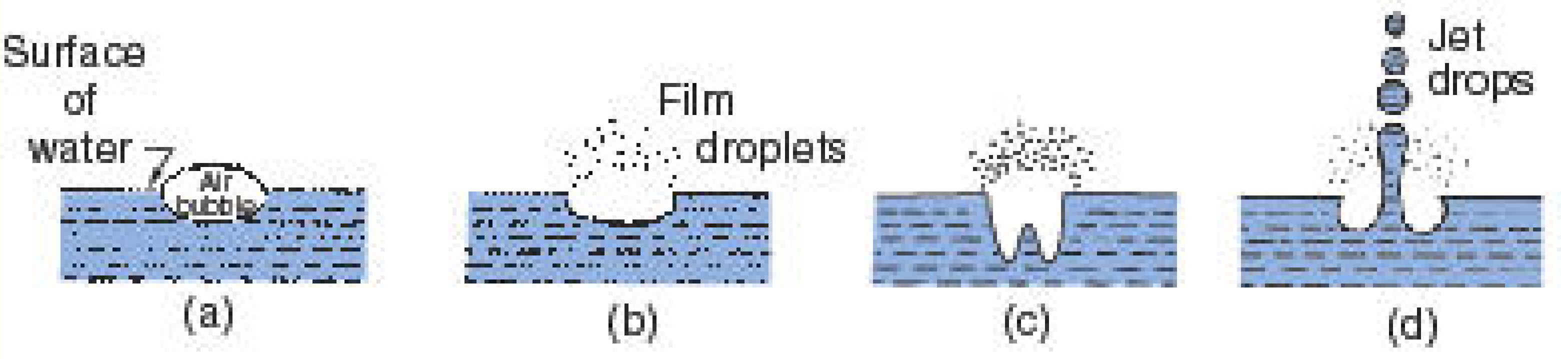
Microorganisms live on skin: when you change your clothes, you can propel $\sim 10^4$ bacteria per minute into the air, with diameters from 1–5 μm.

The oceans are an important source of biogenic aerosols. They are injected into the atmosphere by the bursting of air bubbles and by sea foam.



Production of film droplets and jet drops when an air bubble bursts at the surface of water. The time between (a) and (d) is ∼2 ms.

⋆ ⋆ ⋆



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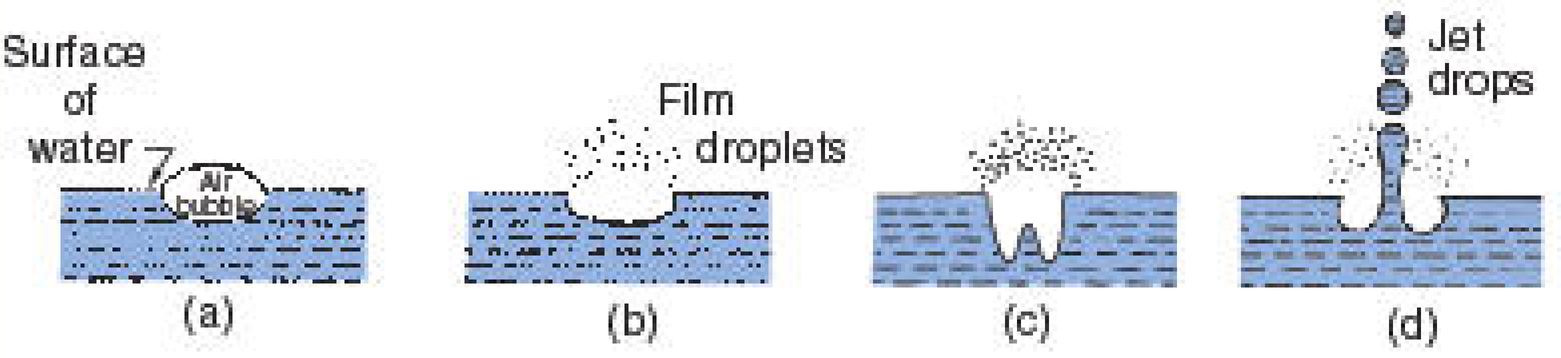

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The number distribution of particles from forest fires peak at ∼0.1 μm diameter, which makes them efficient cloud condensation nuclei. Some biogenic particles (e.g., bacteria from vegetation) may nucleate ice in clouds.

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Volcanoes inject gases and particles into the atmosphere. The large particles have short residence times, but the small particles can be transported globally, particularly if they are blasted to high altitudes.

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It is projected that by 2040, anthropogenic sources of particles could be comparable to those from natural processes.

d. In situ formation

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Summary: Table 5.3 in *Wallace & Hobbs* summarizes the magnitudes of the principal sources of direct emission of particles into the atmosphere and in situ sources.

Chemical Composition

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Nitrate (NO_3^-) occurs in larger sized particles than sulfate in marine air. Since seawater contains negligible nitrate, the nitrate in these particles must derive from the condensation of gaseous HNO_3 by g-to-p conversion.

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Elemental carbon (commonly referred to as "soot") is a common component of organic aerosols in the atmosphere, and is a strong absorber of solar radiation.

For example, in polluted air masses from India, elemental carbon contributes about 10% to the mass of submicrometer sized particles.

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Thus, Saharan dust is transported to the Americas, and dust from the Gobi Desert can reach the west coast of North America.

Sulpher dioxide (SO_2) emitted from power plants in the United Kingdom can be deposited as sulfate far inland in continental Europe.

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Improvements in visibility that frequently follow periods of precipitation are due, in large part, to the removal (i.e., scavenging) of particles by precipitation. It is estimated that, on the global scale, precipitation processes account for about 80–90% of the mass of particles removed from the atmosphere.

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For example, the fall speeds of particles 1 and 10 μm in diameter are $\sim 3 \times 10^{-5}$ and $\sim 3 \times 10^{-3}\,$m s^{-1}, respectively.

Some 10–20% of the mass of particles removed from the atmosphere is by dry fallout.

Concentrations.

One of the oldest and most convenient techniques (which in various forms is still in widespread use) for measuring the concentrations of particles in the air is the Aitken nucleus counter. For details, see *Wallace & Hobbs*.

The concentration of particles measured with this instrument is referred to as the Condensation Nucleus (CN) count.

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Condensation nucleus counts near the Earth's surface vary widely from one location to another, and they can also fluctuate by more than an order of magnitude with time at any one site.

Generally, they range from average values of $\sim 10^3\,\mathrm{cm}^{-3}$ over the oceans, to $\sim 10^4\,\mathrm{cm}^{-3}$ over rural land areas, to $\sim 10^5\,\mathrm{cm}^{-3}$ or greater in urban polluted air.

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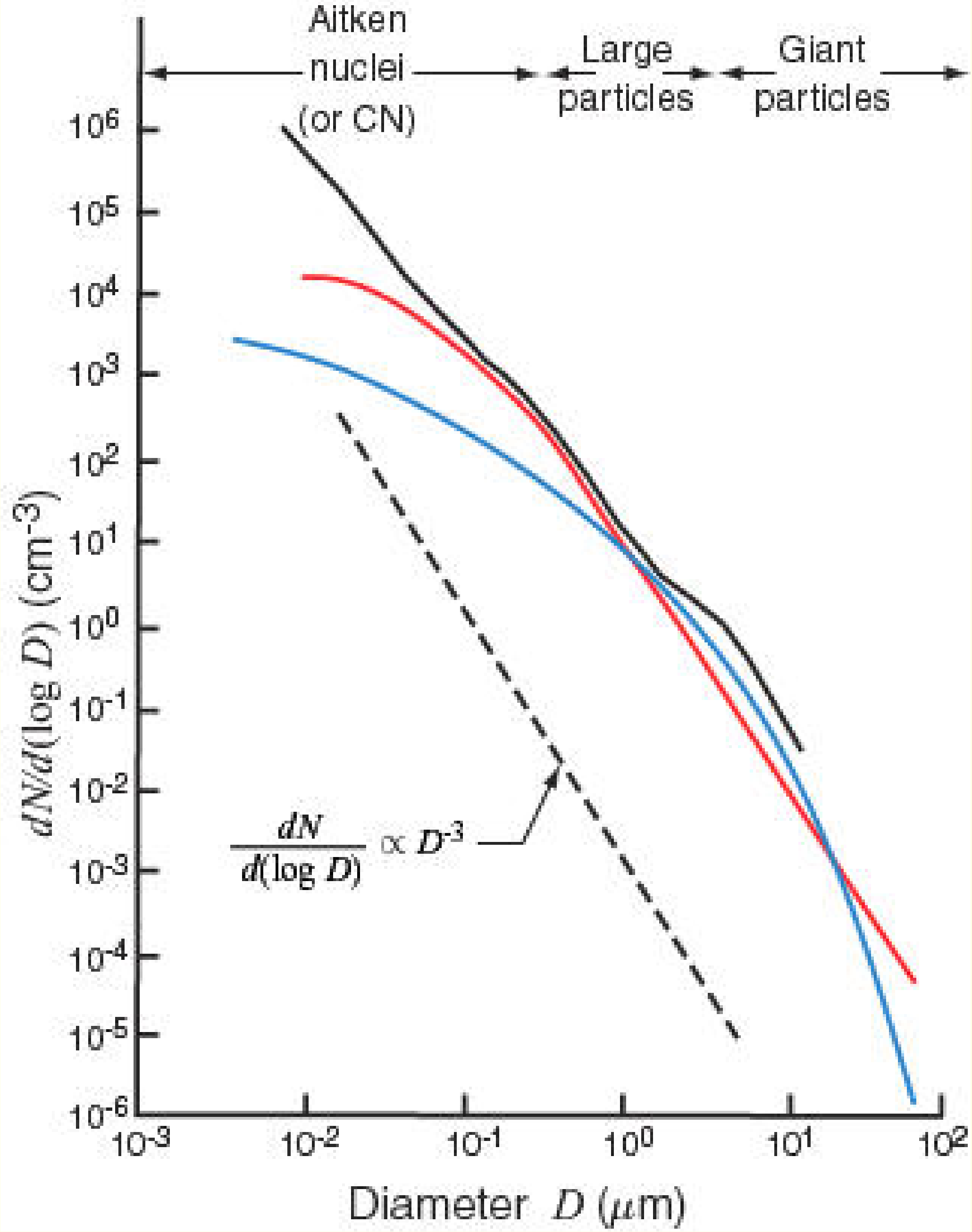
The measurements are plotted in the form of a number distribution in which the ordinate $dN/d(\log N)$ and the abscissa (D) are plotted on logarithmic scales, where dN is the number concentration of particles with diameters between D and $D + dD$.



Number distributions of tropospheric particles in continental (red), marine (blue), and urban polluted (black) air.

Conclusions from results shown in Figure.

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- **Those portions of the number distribution curves that are straight lines in the Figure can be represented by an expression of the form**

$$\log \frac{dN}{d(\log D)} = \textbf{const} - \beta \log D$$

or, taking antilogs,

$$\frac{dN}{d(\log D)} = CD^{-\beta}$$

- **The number distributions of particles shown confirm CN measurements, which indicate that the total concentrations of particles are, on average, greatest in urban polluted air and least in marine air.**

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- **The concentrations of particles with diameters $>2\,\mu$m (giant particles) are, on average, rather similar in continental, marine, and urban polluted air.**

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Dispersion in the vertical is particularly restricted under stable conditions.

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Ideal (or complete) combustion of a hydrocarbon fuel yields only CO_2 and H_2O. However, for a given quantity of fuel, a precise amount of oxygen is required for complete combustion, and this ideal combination of fuel and oxygen is rarely achieved.

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There are also lower temperature sources of air pollutants; for example, leakages of hydrocarbons from natural gas lines, organics from the evaporation of solvents, and nitrogen gases from fertilizers.

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Sulfur dioxide gas absorbs into the fog droplets where it is oxidized to form sulfuric acid.

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In the Great Smog, as it was called, SO_2 reached peak mixing ratios of about 0.7 ppmv (compared to typical annual mean mixing ratios of about 0.1 ppmv in polluted cities with large coal usage), and the peak particle concentrations were 1.7 $\mathrm{mg\,m^{-3}}$.

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In particular, bituminous coal has been banned in Dublin for about twenty years.

Thank you, Mary Harney!

Nevertheless, pollution is still prevalent in significant quantities in many cities in Europe and the United States. Also, many large cities, particularly in developing countries (e.g., China, India), still suffer from London-type smogs due to the burning of coal and wood and to the lack of strict air pollution controls.

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The chemical reactions that lead to photochemical smog are complex, and still not completely understood. For an outline, see ***Wallace & Hobbs***.

Regional and Global Pollution

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The fact that pollutants can be transported over large distances is well illustrated by air pollution episodes in the Arctic, known as arctic haze, which can be as severe as those in cities. The pollutants originate from fossil-fuel combustion, smelting, and other industrial processes in northern Europe and Russia.

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Glacial records show that air pollution in the Arctic has increased markedly since the 1950s, paralleling the increases in SO_2 and NO_x emissions in Europe.

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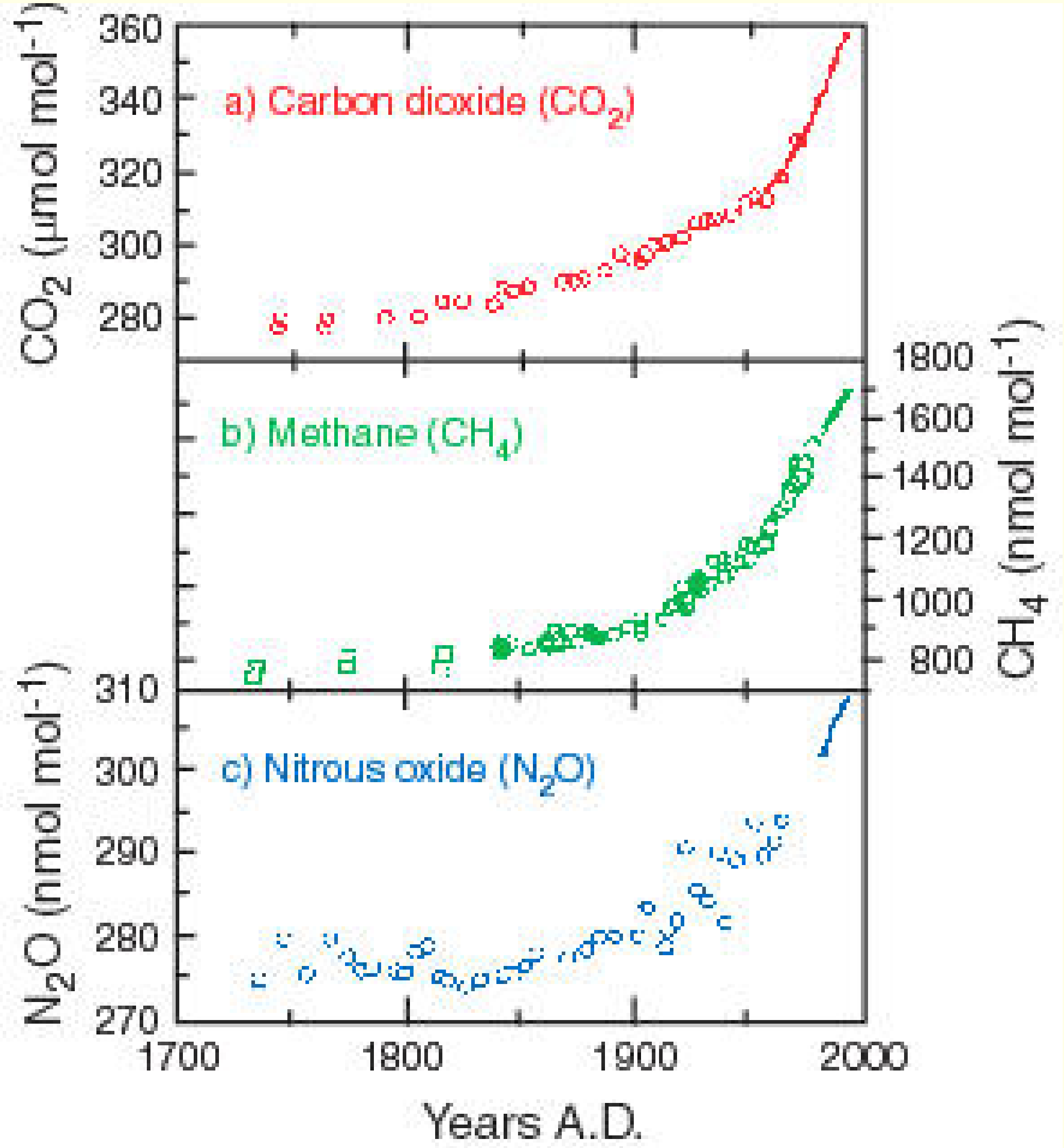
Anthropogenic influences are now apparent on a global scale, as illustrated by the world-wide increase in CO_2 concentrations since the Industrial Revolution (following Figure). Other trace gases (e.g., CH_4 and N_2O) also show increasing concentrations worldwide over the past 150 years or so.



Changes in the concentrations of (a) CO_2, (b) CH_4, and (c) N_2O over 300 years deduced from analyses of ice cores.

6. Tropospheric Chemical Cycles

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Here we will consider the tropospheric portions of the biogeochemical cycles of nitrogen and sulfur. We will be concerned with relatively rapid interchanges involving the atmosphere and other reservoirs (generally the oceans and the biosphere).

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Also, the magnitudes of the various emission fluxes are not necessarily equivalent to the importance of the species, since atmospheric residence times must also be taken into account.

The Nitrogen Cycle

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Nitric oxide and NO_2 play important roles in both tropospheric and stratospheric chemistry.

The principal sources and sinks of nitrogen-containing species in the atmosphere are shown in the following Figure. The main atmospheric sources of nitrogen-containing species are biogenic emissions from the Earth and the oceans (NH_3, N_2O, and NO_x), decomposition of proteins and urea from animals (NH_3), biomass burning and fossil fuel consumption (NO_x, NH_3, and N_2), and lightning (NO_x).

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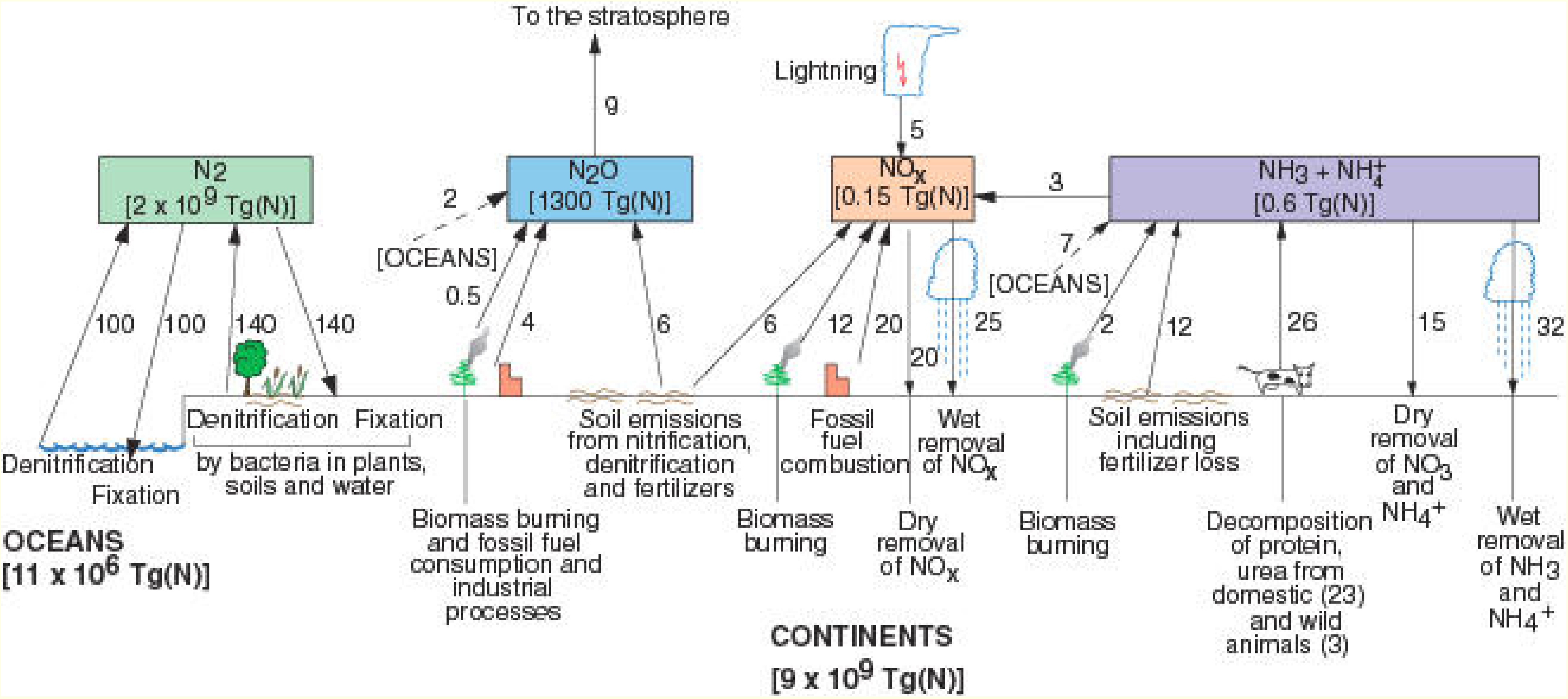
Since anthropogenic sources of NH_3, N_2O, and NO_x (from fossil fuel consumption, biomass burning, and agricultural nitrate fertilization) are appreciable, they may be causing significant perturbations in the budgets of these species in the atmosphere.



Principal sources and sinks of nitrogen-containing gases in the atmosphere.

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The global sulfur budget is significantly affected by anthropogenic emissions. These are almost entirely in the form of SO_2, and 90% are from the Northern Hemisphere. The main sources are the burning of coal and the smelting of sulfide ores.

The main mechanisms for removing sulfur from the atmosphere are wet and dry deposition.

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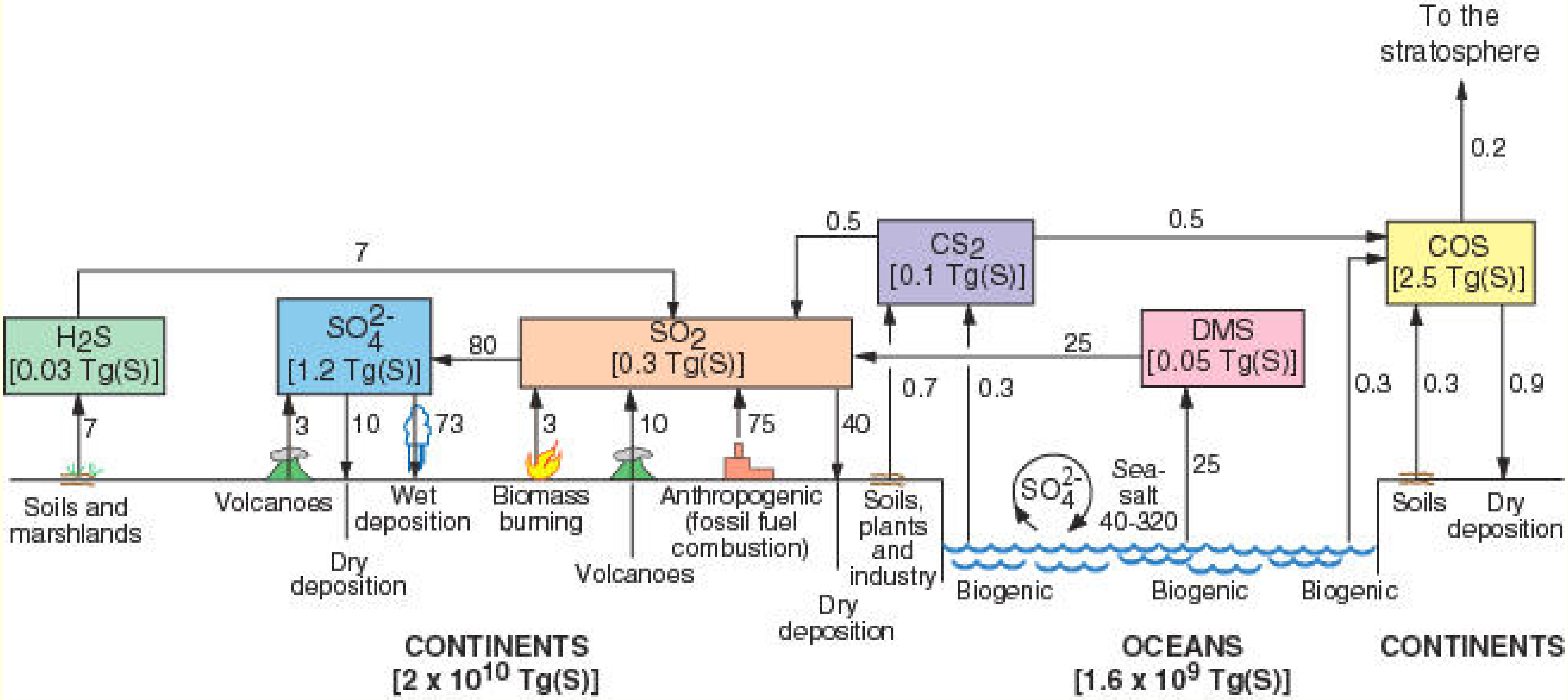
For example, of the 80 Tg(S) per year of SO_2 that are oxidized to SO_4^{2-}, about 70 Tg(S) per year occurs in clouds, which is subsequently wet deposited.



Principal sources and sinks of sulpher-containing gases in the atmosphere.

Residence Time. Spatial Scales

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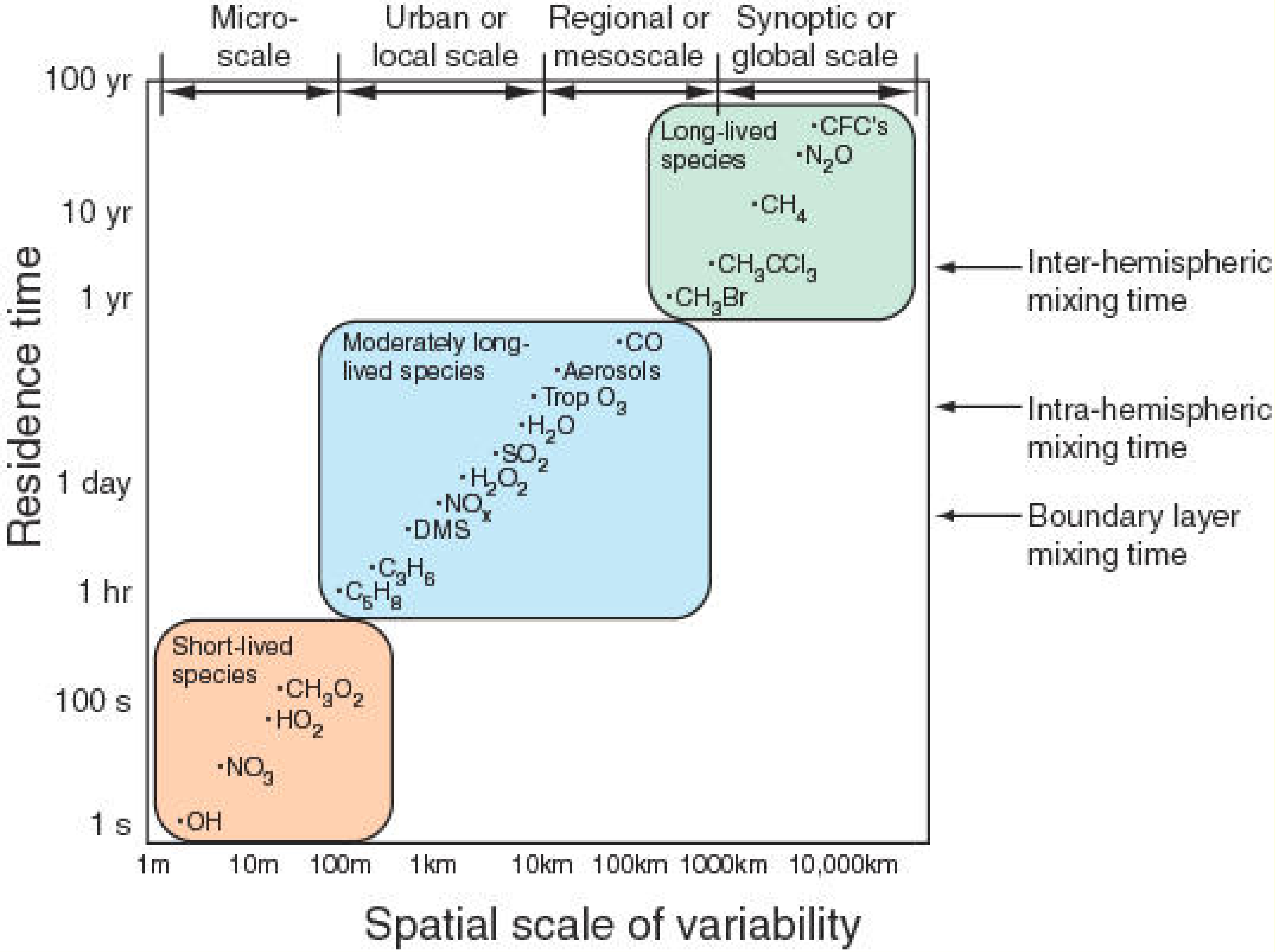
An analogy is a tank of water, which can represent the atmosphere. Assume water is pumped into and removed from the tank at rate F. The mean time spent by each small element of water is M/F, where M is the volume of the tank.



Spatial and temporal scales of variability for some atmospheric constituents. The temporal scale is represented by residence time.

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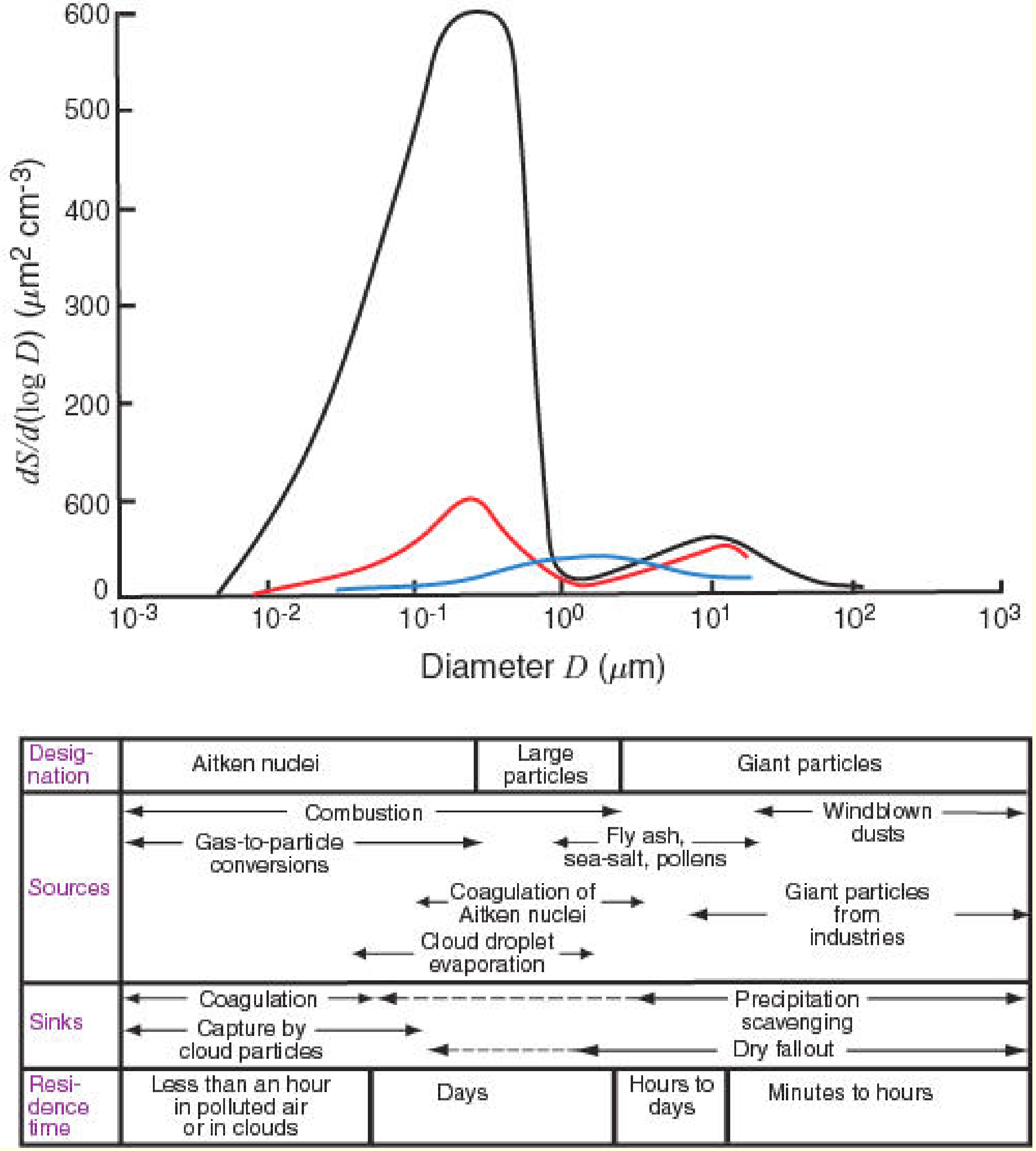
The residence times of particles in the atmosphere as a function of their size are shown below.



Desig-nation	Aitken nuclei Large particles Giant particles
Sources	Combustion Gas-to-particle conversions Fly ash, sea-salt, pollens Windblown dusts Coagulation of Aitken nuclei Cloud droplet evaporation Giant particles from industries
Sinks	Coagulation Capture by cloud particles Precipitation scavenging Dry fallout
Resi-dence time	Less than an hour in polluted air or in clouds Days Hours to days Minutes to hours

Above: Schematic curves of particle surface area distributions for urban polluted air (black line), continental air (red line) and marine air (blue line).

Below: principal sources and sinks of atmospheric particles and estimates of their mean residence times in the troposphere.