Lecture 25. <u>Regional radiative effects due to anthropogenic aerosols.</u>
<u>**Part1:**</u> **Natural and anthropogenic aerosols.**

Objectives:

1. What are atmospheric aerosols? Atmospheric aerosol classification.

2. Particle size distribution of atmospheric aerosols.

Readings: Turco: p. 46-48; Brimblecombe: 55-73;

1. <u>What are atmospheric aerosols?</u>

Atmospheric aerosols (or particulate matter) are solid or liquid particles
or both suspended in air with diameters between about 0.002 µm to about
100 µm.

- Aerosol particles vary greatly in size, source, chemical composition,
  amount and distribution in space and time, and how long they survive in
  the atmosphere.

Primary atmospheric aerosols are particulates that emitted directly into the
atmosphere (for instance, sea-salt, mineral aerosols (or dust), volcanic dust, smoke and
soot, some organics).

Secondary atmospheric aerosols are particulates that formed in the atmosphere by
gas-to-particles conversion processes (for instance, sulfates, nitrates, some organics).

$\Rightarrow$ A significant fraction of the atmospheric aerosols is anthropogenic in origin.
Therefore, atmospheric **natural and anthropogenic aerosols** are defined.

Major physical properties of atmospheric aerosols:

(i) can scatter, absorb and emit electromagnetic radiation

(ii) can serve as cloud nuclei

Major chemical properties of atmospheric aerosols:

(i) serve as media upon which chemical reactions can occur

Importance of atmospheric aerosols:

- heterogeneous chemistry

- air quality and human health

- visibility reduction (will be discussed in Lecture 26)

- acid deposition

- cloud formation

- climate and climate change (will be discussed in Lectures 39-41)

Key atmospheric aerosol characteristics:
size of an aerosol particle and its composition

NOTE: Diameter or radius of a particle are both used to characterized its size. If particle is non-spherical, its equivalent radius is introduced. There are several ways to define particle equivalent radius (for instance, aerodynamic equivalent radius, which is radius of a sphere that experience the same resistance to motion as the nonspherical particle).

NOTE: Particle may consist of a single compound or have complex chemical composition. Often, chemical composition varies with particle size.

Some criteria used in atmospheric aerosol classification:

1) **particle size: fine mode** (d < 2.5 μm) and **coarse mode** (d > 2.5 μm); fine mode is divided on the **nuclei mode** (about 0.005 μm < d < 0.1 μm) and **accumulation mode** (0.1μm < d < 2.5 μm).

NOTE: The distinction between fine and coarse particles is a fundamental because, in general, the fine and coarse particles mode originate separately, are transformed separately, are removed from the atmosphere by different mechanisms, have different chemical composition, have different optical properties, etc.

2) **chemical composition**: **sulfate** (SO_4^{2-}), **nitrate** (NO_3^-), **soot** (elemental carbon), **sea-salt** (NaCl); etc.

3) **geographical location: marine, continental, rural, industrial, polar, desert** aerosols, etc.

4) **location in the atmosphere**: **stratospheric and tropospheric** aerosols.

Once in the atmosphere, atmospheric aerosols evolve in time and space:

1. may be transported in the atmosphere;
2. may be removed from the atmosphere (by dry deposition, wet removal, and gravitational sedimentation);
3. can change their size and composition due to microphysical transformation processes;
4. can undergo chemical transformation.

Aerosol microphysical transformation processes: nucleation, coagulation, and condensation/evaporation.

- **Nucleation** is a process by which gas molecules aggregate together to form a cluster. When the number of molecules in the cluster is large enough (reaching a critical size), the cluster becomes stable and can grow further by condensation of additional molecules. **Heterogeneous nucleation** occurs when the gas forms a critical cluster on an existing surface, such as of an existing particle. **Homogeneous nucleation** occurs when the gas nucleates without the aid of a surface to nucleate upon.

Example: nucleation of sulfuric acid gas.

- **Coagulation** is a process by which particles collide and stick together.

⇒ Particles that can become activated to grow to fog and cloud droplets in the presence of supersaturation of water vapor are termed cloud condensation nuclei (**CCN**).

Figure 25.1 Idealized schematic of the distribution of particle surface area of an atmospheric aerosols (from Whitby and Cantrell, 1976).
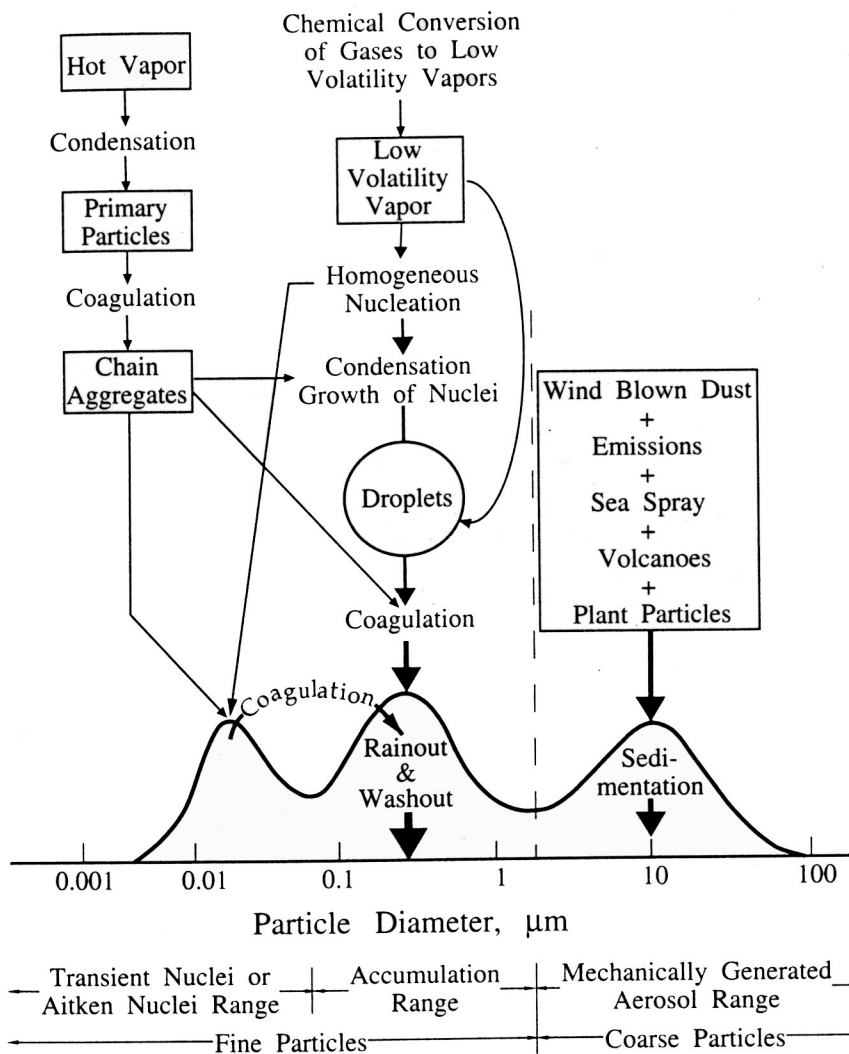
Chemical components of atmospheric aerosols:

Stratospheric aerosol is:

- composed of an aqueous sulfuric acid solution of 60 to 80% sulfuric acid for temperatures -80 to -45°C, respectively;

- formed by oxidation of carbonyl sulfide (OCS) under normal (background) stratospheric conditions;

- formed by oxidation of SO_2 injected into stratosphere by volcanic eruptions.

NOTE: more discussion of stratospheric aerosol, and its connection to PSCs (polar stratospheric clouds) and ozone depletion will be given in Lectures

Troposheric aerosol is composed of various chemical species.

Figure 25.2 Schematic description of the main pathways for production of atmospheric aerosols and aerosol major chemical components. (NOTE: OC means organic carbon, EC means elemental (or black) carbon).
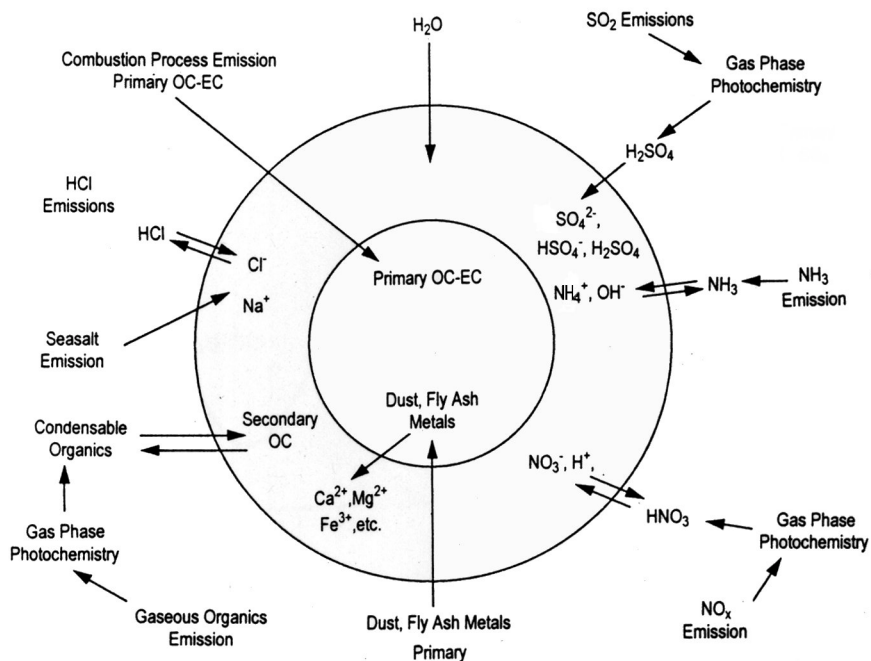
Table 25.1 Global emission estimates for major aerosol types (**estimated flux Tg yr^{-1}**)

Source	Low	High	Best
NATURAL			
Primary:			
soil dust	1000	3000	1500
sea salt	1000	10000	1300
volcanic dust	4	10000	30
biological debris	26	80	50
Secondary:			
sulfates from biogenic gases	80	150	130
sulfates from volcanic SO2	5	60	20
organic matter from biogenic VOC	40	200	60
nitrates	15	50	30
Total natural	*2200*	*23500*	*3100*
ANTHROPOGENIC			
Primary:			
industrial particulates	40	130	100
dust	300	1000	600
soot	5	20	10
Secondary:			
sulfates from SO2	170	250	190
biomass burning	60	150	90
nitrates from NOx	25	65	50
organics from anthropogenic VOC	5	25	10
Total anthropogenic	*600*	*1640*	*1050*
Total	**2800**	**26780**	**4150**

2. **Particle size distribution of atmospheric aerosols.**

- The diameters of atmospheric aerosol particles span over four orders of magnitude, from a few nanometers to around 100 μm. Particle number concentrations may be as high as 10^7 to 10^8 cm^{-3}. Thus, a complete description of the aerosol size distribution may be a challenging problem. Therefore, several mathematical approaches are used to characterize the aerosol size distribution.

Discrete approximation: particle size range is divided into discrete intervals (or size bins) and the number of particles is calculated in each size bin.

Continuos approximation: particle size distribution is represented by analytical function vs. radius.

Let's consider first **discrete approximation** of aerosol size distribution.

Table 25.2. Example of segregated aerosol size information.

Size range (μm)	Concentration (cm^{-3})	Cumulative concentration (cm^{-3})	Normalized concentration (μm^{-1}cm^{-3})
0.001 - 0.01	100	100	11111
0.01-0.02	200	300	20000
0.02-0.03	30	330	3000
0.03-0.04	20	350	2000
0.04-0.08	40	390	1000
0.08-0.16	60	450	750
0.16-0.32	200	650	1250
0.32-0.64	180	830	563
0.64-1.25	60	890	98
1.25-2.5	20	910	16
2.5-5.0	5	915	2
5.0-10.0	1	916	0.2

Cumulative concentration is defined as the concentration of particles that are smaller than or equal to a given size range.

Normalized concentration is defined as the concentration of particles in a size bin divided by the width of this bin.

If the i-bin has N_i particle concentration, thus normalized concentration in the i-bin is

$n_{Ni} = N_i / \Delta D_i$

where ΔD_i is the width of the i-bin.

- Discrete size distribution is typically presented in the form of histogram.

Figure 25.3 Histogram of aerosol particle number concentrations vs. the size range for the distribution of Table 25.2.
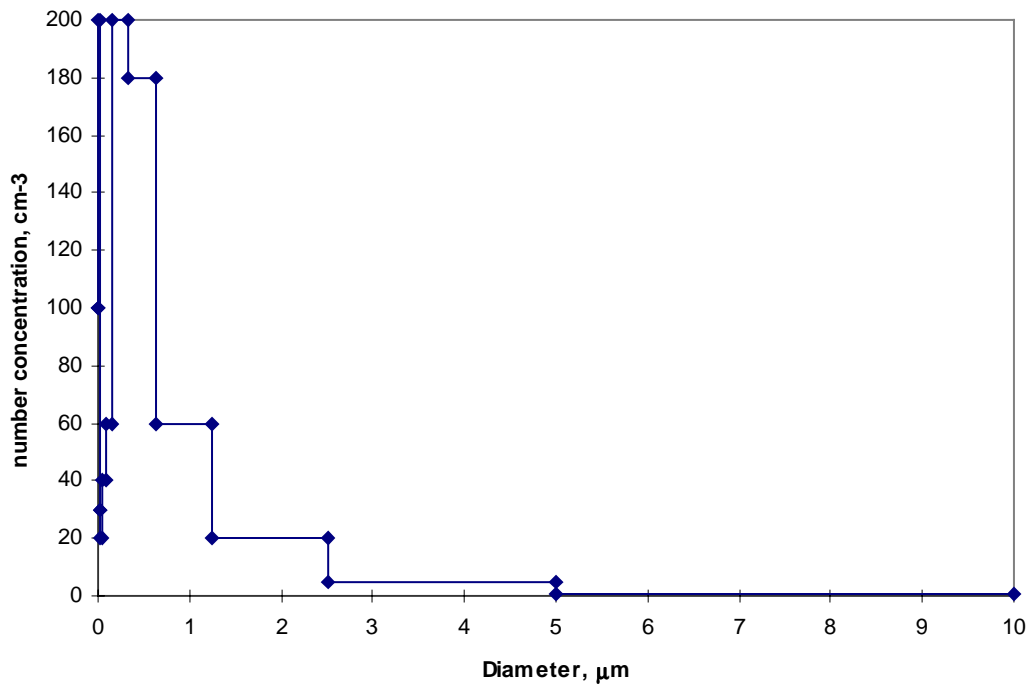
Figure 25.4 Histogram of aerosol particle number concentration normalized by the width of the size range for the distribution of Table 25.2.
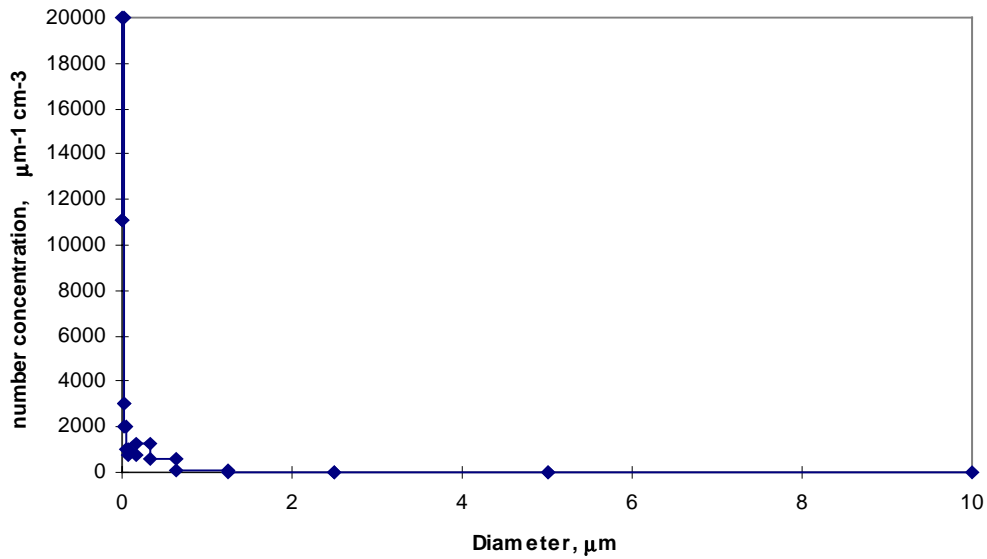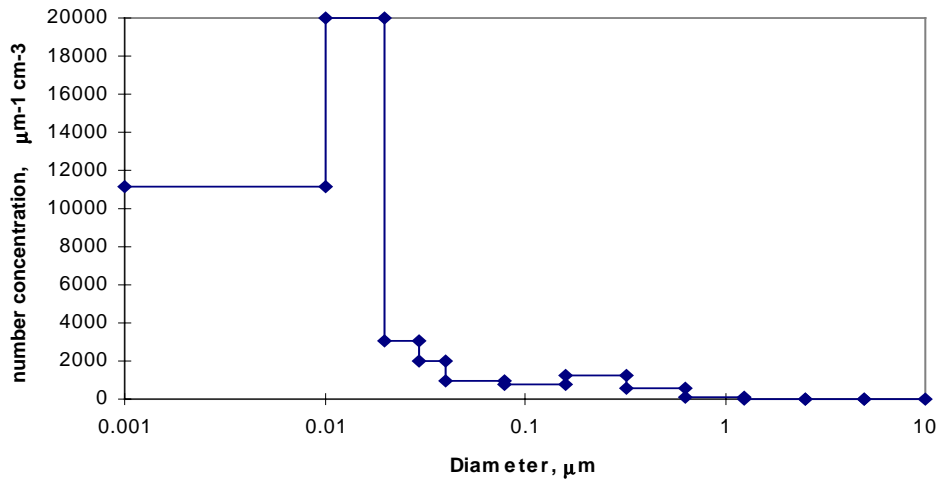

Figure 25.5 Same as Figure 25.4 but plotted vs. the logarithm of the diameter.

NOTE: That in Figures 25.3-25.4 smaller particles are hardly seen, but if a logarithmic scale is used for the diameter (Figure 25.5) both the large- and small-particles regions are depicted.

Major limitation of discrete approximation:

loss of information about the distribution structure inside each bin.

Let's consider **continuos approximation**.

We can define the size distribution function $n_N(D)$ as follows:

$n_N(D)\ dD$ = the number of particles per cm^3 of air having diameters in the range D and

  D+dD (here dD is an infinitesimally small increase in diameter).

If units of $n_N(D)$ are **$\mu m^{-1} cm^{-3}$** and the total number of particles per **cm^{-3}**, N, is then just

$$N = \int\ n_N(D)\ dD$$

On the other hand

$$n_N(D) = dN/dD$$

NOTE: both sides of the equation above represent the same aerosol distribution, and both notations are widely used.

Several aerosol properties depend on the particle surface area and volume distributions with respect to particle size.

Let's define aerosol surface area distribution $n_S(D)$ as

$n_S(D)\ dD$ = the surface area of particles per cm^3 of air having diameters in the range D

  and D+dD (here dD is an infinitesimally small increase in diameter).

If all particles are spherical and have the same diameter D in this infinitesimally narrow size range that each of them has surface area πD^2, we have

$$n_S(D) = \pi D^2\ n_N(D)$$

Here $n_S(D)$ is in **$\mu m\ cm^{-3}$**.

Thus the total surface area **S** of the aerosol particles per cm^3 of air is

$$S = \pi \int\ D^2\ n_N(D)\ dD = \int\ n_S(D)\ dD$$

Here S is in **$\mu m^2\ cm^{-3}$**.

Let's define aerosol volume distribution $n_V(D)$ as

$n_V(D)\ dD$ = the volume of particles per cm³ of air having diameters in the range D

and D+dD (here dD is an infinitesimally small increase in diameter),

and therefore

$$n_V(D) = \pi D^3\ n_N(D)\ /6$$

Here $n_V(D)$ is in $\mu m^2\ cm^{-3}$.

Thus the total aerosol volume **V** per cm³ of air is

$$V = \pi/6 \int D^3\ n_N(D)\ dD = \int n_V(D)\ dD$$

Here V is in $\mu m^3\ cm^{-3}$.

♦ The aerosol distribution is more convenient to express as functions of ln(D) or log(D), because particle sizes span several orders of magnitude.

Let's define the number distribution function $n_N^e(D)$ in **cm⁻³** as

$n_N^e(\ln(D))\ d\ln(D)$ = the number of particles per cm³ of air having diameters in the range ln(D) and ln(D) +d ln(D).

NOTE: We cannot take the logarithm of a dimensional quantity. Thus, when we write ln(D) we really mean ln(D/1), where the "reference" particle diameter is 1 μm is not explicitly indicated.

The total number of particles per **cm⁻³**, N, is then just

$$N = \int n_N^e(\ln(D))\ d\ln(D)$$

The surface area and volume distributions as functions of ln(D) can be defined similarly to those with respect to D, as

$$n_S^e(\ln(D)) = \pi D^2\, n_N^e(\ln(D))$$

$$n_V^e(\ln(D)) = \pi D^3\, n_N^e(\ln(D))\, /6$$

Here $n_S^e(\ln(D))$ is in $\mu m^2\, cm^{-3}$, and $n_V^e(\ln(D))$ is in $\mu m^3\, cm^{-3}$.

Thus for S and V we have

$$S = \pi \int D^2\, n_N^e(\ln(D))\, d\ln(D) = \int n_S^e(\ln(D))\, d\ln(D)$$

$$V = \pi/6 \int D^3\, n_N^e(\ln(D))\, d\ln(D) = \int n_V^e(\ln(D))\, d\ln(D)$$

NOTE: The above aerosol distributions can be also expressed as functions of the base 10 logarithm log (D), defining $n_N^o(\log(D)),\ n_S^o(\log(D)),$ and $n_V^o(\log(D)).$

Thus we have

$$dN = n_N(D)\, dD = n_N^e(\ln(D))\, d\ln(D) = n_N^o(\log(D))\, d\log(D)$$

$$dS = n_S(D)\, dD = n_S^e(\ln(D))\, d\ln(D) = n_S^o(\log(D))\, d\log(D)$$

$$dV = n_V(D)\, dD = n_V^e(\ln(D))\, d\ln(D) = n_V^o(\log(D))\, d\log(D)$$

Since d log(D) = d ln(D) / 2.303 = dD /2.303 D , we can relate the distributions above as:

$$n_N^e(\ln(D)) = D\, n_N(D)$$

$$n_S^e(\ln(D)) = D\, n_S(D)$$

$$n_V^e(\ln(D)) = D\, n_V(D)$$

$$n_N^o(\log(D)) = 2.303\, D\, n_N(D)$$

$$n_S^o(\log(D)) = 2.303\, D\, n_S(D)$$

$$n_V^o(\log(D)) = 2.303\, D\, n_V(D)$$

♦ Several mathematical functions are used to describe the atmospheric aerosol distribution (log-normal function, power-law function, etc.)

Log-normal function:

$$n_N(D) = dN/dD = N \exp\left(-[\ln(D) - \ln(D_g)]^2 / \{2 \ln^2(\sigma_g)\}\right) / \{ (2\pi)^{1/2} D \ln(\sigma_g)\}$$

or

$$n_N(\ln(D)) = dN/d\ln(D) = N \exp\left(-[\ln(D) - \ln(D_g)]^2 / \{2 \ln^2(\sigma_g)\}\right) /$$
$$/ \{(2\pi)^{1/2} \ln(\sigma_g)\}$$

Where N is the total aerosol number concentration, D_g and σ_g are the parameters of a log-normal distribution: D_g is the **median diameter**, that is, the diameter for which exactly one-half of the particles are smaller and one-half are larger; and σ_g is termed **geometric standard deviation**, which is a ratio of the diameter below which 84.1% of the particles lie to the median diameter.

NOTE: A log-normal function is very often used to represent aerosol size distribution because of its properties.

Some properties of the log-normal distribution:

- If the number distribution $n_N(D)$ is log-normal, the surface distribution $n_S(D)$ is also log-normal with the same geometric standard deviation σ_g and with the surface median diameter, D_{gS}, given by

$$\ln(D_{gS}) = \ln(D_g) + 2 \ln^2(\sigma_g)$$

- If the number distribution $n_N(D)$ is log-normal, the volume distribution $n_V(D)$ is also log-normal with the same geometric standard deviation σ_g and with the volume median diameter, D_{gV}, given by $\ln(D_{gV}) = \ln(D_g) + 3 \ln^2(\sigma_g)$

Figure 25.6 Particle number log-normal distribution with $D_g = 0.8$ µm and $\sigma_g = 1.5$, for $N = 1000$ cm^{-3}
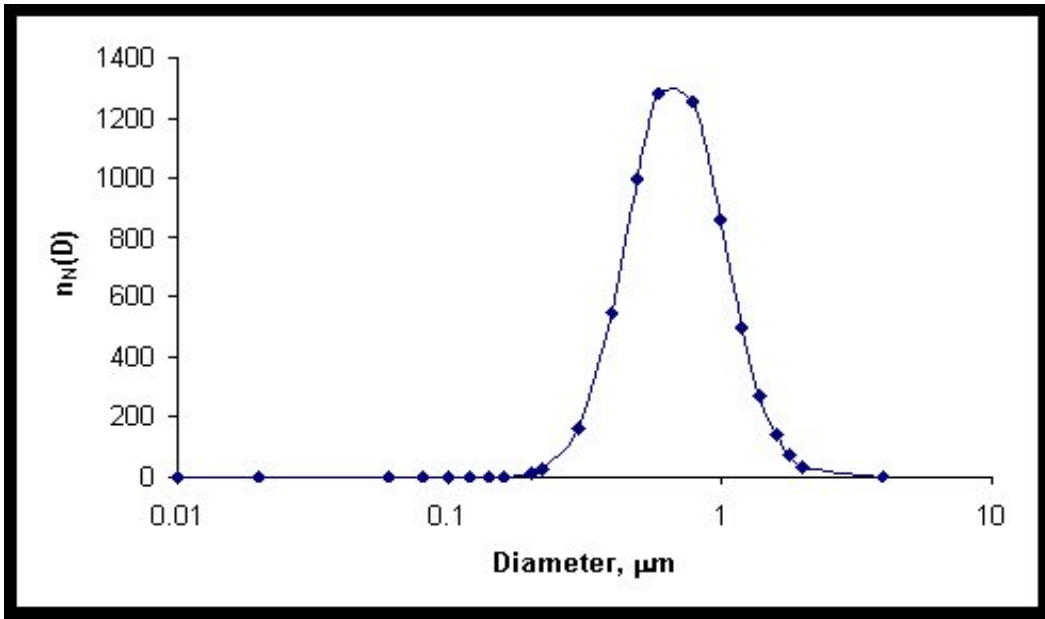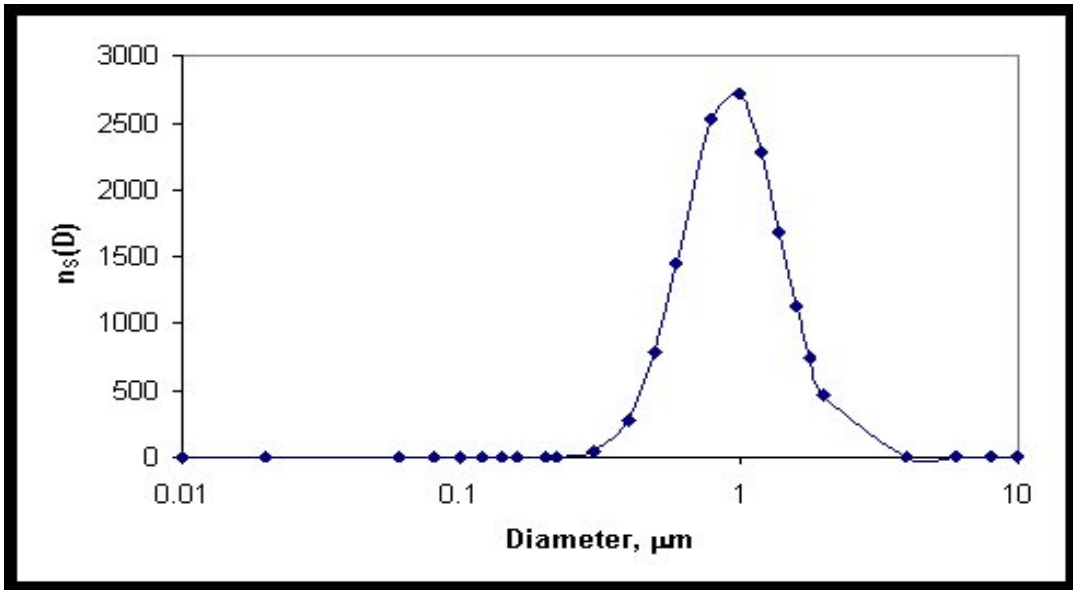

Figure 25.7 Particle surface log-normal distribution for number distribution from Figure 25.6

NOTE: $n_N(D) = dN/dD$ and $n_S(D) = dS/dD$

Power-law function (or Junge distribution):

$$n_N^o(\log(D)) = C / (D)^\alpha$$

where C and α are constants.

Plotting of the power-law distribution on log-log coordinates results in a straight line with slope $-\alpha$ and for $D = 1$ μm, $n_N^o = C$.

- This distribution function assumes that the aerosol number concentration decreases monotonically with increasing particle size. This is not generally true for atmospheric aerosols so the power-law can be used for particles of $D > 0.1$ μm.
- The main advantage of power-law distribution is its simplicity.