Chapter 3
Surface Aerosol Characteristics Using
Low Pressure Impactor

3.1 Introduction

Earth being the important source of atmospheric aerosols, the characteristics of aerosol particles near the surface provide valuable information on the source characteristics. Study of near surface aerosols is important in this context. Physical and chemical properties of aerosols are important in assessing air quality. Mass loading and size distribution of near surface aerosols at Trivandrum obtained using the 14 stage Low Pressure Impactor is presented in this chapter. The system details and principle of operation of the Low Pressure Impactor (LPI) is described in Chapter 2 (section (2.3)). The data obtained for a period of nine years (1990 to 1998) are used for the present study.

3.2 Estimation of Impactor Cut Points

As discussed in Chapter 2, the collection characteristics of the cascade impactor depends on the cut points of different impactor stages which is given by

\[ D_p = \left( \frac{9 \mu \Delta t \cdot D_j}{\rho_p C_n V_j} \right)^{1/2} \quad (3.1) \]
where $\mu$ is the viscosity of air in poise, $S$ is the Stokes Number, $D$ is the diameter of the jet, $\rho$ is the density of the particle, $C_n$ is the Cunningham Slip Correction Factor and $V$ is the velocity of the jet.

The viscosity of air, in poise, at temperature $T_0$ K is given by

$$\mu = (63 + 0.4T) \times 10^{-6}$$

The Cunningham Slip Correction Factor is a measure of how easily a particle can slip in between gas molecules when crossing the bulk flow streams to reach the impaction surface. This factor is expressed as (Gussman, 1969)

$$C_n = 1 + 1.257 \left( \frac{2L}{D_\rho} \right)$$

where $D_\rho$ is the particle diameter and $L$ is the mean free path of the gas molecules.

The mean free path is given by

$$L = \left( \frac{82.057\mu T}{0.499PM} \right) \left( \frac{8R_g T}{\pi M} \right)$$

where $P$ is the atmospheric pressure, $M$ is the mean molecular weight of air (29.9) and $R_g$ is the gas constant.

The impactor cut points are usually referred in terms of aerodynamic diameters which is defined as the diameter of a sphere of unit density that would behave in the impactor in the same way as the particle (i.e., the diameter of a unit density sphere having the same terminal settling velocity in air as that of the particle). Thus in equation (3.1), $D_p$ represents the aerodynamic diameter ($D_p$) of each stage, if the particle density is assumed to be 1 gm cm$^{-3}$. If the actual density of the particle is used for $\rho$ in equation (3.1), the resultant cut point is called Stokes Diameter ($D_s$). The Stokes Diameter of a particle is defined as the diameter of a sphere with the same density as the particle which would behave in the impactor in the same way as the
particle (i.e., the diameter of a sphere with the same density as the particle with the same terminal settling velocity). Thus the Stokes diameter, which is closer to the physical diameter, can be calculated only if the actual density of the particle is known.

The aerodynamic cut points of different impactor stages are calculated using the known values of \( D_i \), \( V_i \), and \( S_j \) and assuming the particle density \( (\rho_p) \) as 1 gm cm\(^{-3}\). But the Cunningham Slip Correction Factor given by equation (3.3) is also a function of \( D_s \). Hence for the calculation of \( D_s \), the two equations (3.1) and (3.3) are solved iteratively starting with \( C_o \) as unity. The value of \( D_s \) thus obtained from equation (3.1) is used to estimate the actual value of \( C_o \), using equation (3.3). This value of \( C_o \) is again substituted back in equation (3.1) to re-estimate the value of \( D_s \). This iterative process of estimating \( D_s \) is continued till the values of \( D_s \) obtained at the end of two successive iterations converge within 0.001%. Because the first eight stages (0 to 7) of the low pressure impactor are operated at the atmospheric pressure condition, the value of \( P \) in equation (3.4) is 1 atmosphere. For the remaining six low pressure stages (L1 to LF), the value of \( P \) is 0.15 atmosphere, corresponding to the standard critical orifice pressure of 114 Torr. The lower and upper aerodynamic size limit of particles collected in different impactor stages is respectively the aerodynamic cut point of the particular stage and that of its previous stage.

In order to describe the aerosol physical and optical properties it is always convenient to use the geometrical size of the particles. In this case it is necessary to know the Stokes cut off diameter for different impactor stages. As stated, the above iterative procedure itself can be used to evaluate this quantity except for the fact that the particle density in equation (3.1) should be replaced by the actual density of the aerosol particles. Since the atmospheric aerosols in general are heterogeneous their densities can be different depending on the chemical composition. In such cases the average density of particles in different size ranges should be used for calculating the cut points in Stokes diameters. In addition to this, the particle density will change with the atmospheric relative humidity if they are hygroscopic in nature. For example, Na and
Mg (found abundantly in oceanic aerosols) salts have very high affinity to water vapor. Water-soluble like sulfate and nitrate aerosols exist in the atmosphere mostly in droplet form. These droplets grow in size with increase in atmospheric relative humidity. Except for carbonaceous and silicate particles atmospheric aerosols are mostly hygroscopic in nature. Once a dry particle embryo absorbs water vapor from the atmosphere, it dissolves in that water and the effective density of the particle now depends on the amount of water absorbed which increases with increase in relative humidity.

3.3 Effect of Relative Humidity (RH) on Aerosol Size and Density

The changes in the physical properties such as particle size, refractive index and composition with RH are important in obtaining the optical and chemical properties of atmospheric aerosols. The behavior of aerosols with changes in RH has been examined based on theoretical modeling (Hanel, 1976; Shettle and Fenn, 1979; Pitisn et al., 1989) as well as through experimental observations (Ho et al., 1974; Fitzgerald et al., 1982; McMurry and Stolzenburg, 1989; Kato et al., 2000). Covert et al. (1972) and Charlson et al. (1974a, 1974b, 1978) used a humidifier in conjunction with an integrating nephelometer to measure the aerosol scattering coefficient as a function of RH. Shettle and Fenn (1979), using different models of aerosols estimated theoretically the effect of RH on aerosol size distribution and refractive index and also the resulting changes in extinction. They found that at high RH values, the extinction increases very significantly. Sloane and Wolff (1985) used impactor, filter extract and particle counter data to describe the light scattering behavior of urban aerosol with a semi empirical model similar to that of Hanel (1976). The effect of changes in aerosol size distribution due to changes in RH on light scattering has been studied in detail by Hegg et al. (1993). Hegg et al. (1996) observed an abrupt increase in light scattering coefficient as RH increases above 70%. Parameswaran (1996) has shown that the effect on optical properties (scattering and extinction) is significant above 70% RH level and also depends strongly on the nature of the size distribution. The scattering cross section of
an ammonium sulphate solution droplet at 50% RH is twice the value than when the same aerosol is dry (Boucher and Anderson, 1995).

In the atmosphere, the changes of aerosol properties with relative humidity is mainly due to condensation of water vapor on the particles with increasing RH and evaporation of water content from particles with decreasing RH. The condensed water changes the mean density, size and refractive index of particles with consequent impact on the radiative properties of atmospheric aerosols (Hegg et al., 1993; Pilinis et al., 1995b). These changes which result from the changes in RH depend on the type of the material with which the particle in its dry state is composed of and on the total mass of dry material in the particle. Two recent studies (Boucher and Anderson, 1995; Nemesure et al., 1995) on sulfate aerosols have shown that the aerosol direct radiative forcing is a strong function of the ambient RH.

The processes of condensation and evaporation are controlled primarily by the equilibrium vapor pressure over the particle surface. The condensation of water vapor on the aerosol particles increases the vapor pressure and evaporation of water from the aerosol particles decreases the vapor pressure over the particle. The particle will be in equilibrium with the atmosphere when the vapor pressure of the atmosphere equals the vapor pressure over it. Thus as RH increases, condensation take place to maintain the particle in equilibrium with the ambient RH. Conversely, as RH decreases evaporation takes place. Thus, the aerosol particles grow as RH increases and shrink as RH decreases. Because of surface tension, the particle assumes spherical shape so that area to volume ratio is minimum. Smaller the particle, more will be the equilibrium vapor pressure over it. This is called the curvature effect. The surface energy associated with a curved surface has an important effect on the equilibrium vapor pressure and on the processes of condensation and evaporation (Hanel, 1976). Hence the effect of curvature of the particle should be taken into account, while applying correction for relative humidity.
The vapor pressure required for equilibrium over a curved surface \((e_c)\) of pure water droplet is greater than that required for saturation over a plane surface \((e_s)\). The ratio of these two vapor pressures are given by \((Pruppacher and Klett, 1978)\)

\[
\frac{e_c}{e_s} = \exp\left(\frac{2\sigma_w V_w}{R_w T r}\right)
\]

where \(R_w\) is the specific gas constant for water, \(V_w\) is the specific volume of water, \(T\) is the absolute temperature, \(r\) is the radius of curvature of the surface and \(\sigma_w\) is the surface tension of water.

According to Hanel's model \((1976)\), the change in particle size is related to the relative humidity through the equation

\[
r_R = r_0 \left(1 + \frac{\rho_0 m(w)}{m_0}\right)^{1/3}
\]

where \(r_R\) is the particle radius at the relative humidity \(R\), \(r_0\) is the dry particle radius, \(\rho_0\) is the dry particle density relative to water, \(m_0\) is the dry particle mass and \(m(w)\) is the mass of condensed water which is a function of relative humidity. The amount of water condensed \(m(w)\) depends on the water activity \((a_w)\) of the aerosol particle. Using equation (3.5) this can be written as

\[
a_w = R \exp\left(-\frac{2\sigma_w V_w}{R_w T r_R}\right)
\]

As \(r_R \to \infty, a_w \to R\). Thus the water activity is the equilibrium relative humidity over the particle corrected for the curvature of the surface or \(a_w\) is the equilibrium relative humidity over the particle when its surface would be plane.

Substituting the known parameters \(\sigma_w, R_w\) and \(V_w\), the value of \(2\sigma_w V_w / R_w T\) at 300°K is 0.001056 μm. Thus water activity can be expressed as \((Pruppacher and Klett, 1978)\)

\[
a_w = R \exp\left(-\frac{0.001056}{r_R}\right)
\]
Hanel (1976) has tabulated $m(w)/m_0$ versus $a_w$ for various types of natural aerosols. To interpolate between Hanel’s data of $m(w)/m_0$ for different water activities $a_w$ and $a_w^{i+1}$, the following equation is used (Shettle and Fenn, 1979)

$$\frac{m(a_w)}{m(a_w^{i+1})} = \left( \frac{1 - a_w}{1 - a_w^{i+1}} \right)^{\nu_i} \tag{3.9}$$

But even with this data on the relative mass of condensed water in equation (3.6) it is not possible to combine equation (3.6) and equation (3.8) into an exact analytical expression giving aerosol radius $r_R$ as an explicit function of relative humidity, because $r_R$ is also a function of $a_w$. For this, equations (3.6) and (3.8) are used alternatively in an iterative manner until they converge, starting with $a_w = R$ on the right side of equation (3.8). The value of $a_w$ thus obtained from equation (3.8) is used to find $r_R$ in equation (3.8) and repeating the iteration until the values of $r_R$ and $a_w$ converge. Thus using equation (3.6) and (3.8) the value of $r_R$ for any relative humidity can be estimated for a given value of the particle size at a given relative humidity condition. Once the wet aerosol particle size is estimated, the effective density $\rho_R$ which is the volume weighted average of the densities of dry aerosol ($\rho_0$) and water ($\rho_w$) can be obtained as (Parameswaran and Vijayakumar, 1994)

$$\rho_R = \rho_w + (\rho_0 - \rho_w) \left( \frac{r_R}{r_0} \right) \tag{3.10}$$

This equation can also be written in terms of the mass ratio of condensed water and dry particle mass as (Hanel, 1976)

$$\rho_R = \rho_0 + \frac{m(w)}{m_0} \left( \frac{\rho_0}{\rho_w} \right) \left( \frac{m_0}{m(w)} \right) \tag{3.11}$$

The mass of aerosol particles, $m_R$, at a relative humidity $R$ can be written in terms of the dry mass $m_0$ and mass of condensed water $m(w)$ as
Thus, knowing the water activity of the aerosol particles, the effective density and mass of the particle at any relative humidity can be estimated from its dry density and dry mass using equations (3.11) and (3.12). Conversely, the dry mass of the particle can be estimated from the humid mass \( m_r \) knowing \( a_w \). Equation (3.12) can also be written in terms of the particle radii and dry density as (Paramneswaran and Vijayakumar, 1994)

\[
m_r = m_0 \left( 1 + \frac{m(w)}{m_0} \right)
\]

(3.12)

The above relationship obtained for a single aerosol particle is true for a group of homogeneous particles having the same mean radius and water activity.

The change of particle property with RH in practice is not as simple as explained above. As RH increases from zero to 100% the dry particle remains in solid form and the growth will not be significant. When RH increases above a critical value (the deliquescence point) the particle turns into a liquid droplet whose size increases drastically. For further increase in RH the particle continues in the same state and grows monotonically (almost exponentially). But when RH decreases, the particle continues in its liquid state even when RH decreases below the deliquescence point, until a very low value (~38%), at which the particle again changes to its solid form. This hysterisis effect which is quite significant for \((\text{NH}_4)_2\text{SO}_4\) (shown in Figure (3.1)) is not the same for all aerosol types. However the semi empirical model for the variation of particle property with RH described above does not account for this hysterisis effect and the particle is assumed to follow a mean pattern in which the particle size and density varies monotonically with variation in RH. This pattern generally lies close to the curve for decreasing RH shown in Figure (3.1).
3.4 Estimation of Stokes Radius and Aerosol Size Distributions and Correction for Relative Humidity

The LPI is operated during the daytime (0900-1630 IST) on 6 to 7 days in a month with rain free fair weather conditions prevailing to collect measurable aerosol samples. The atmospheric RH generally remains steady during this period (within ± 5%). But this will not be true from one sample to the other because of the seasonal variation in atmospheric RH. Figure (3.2a) shows the typical diurnal variation of monthly mean RH observed at the observation site for January and June 1998 (typically dry winter and monsoon months). Figure (3.2b) shows the month-to-month variation of average daytime RH obtained by averaging hourly values of RH during the LPI sampling for the period 1990 to 1998. The vertical bars represent the standard error representing the day to day (in Figure (3.2a) and year to year (in Figure (3.2b)) variabilities. As seen from Figure (3.2a), the diurnal variation of RH shows a maximum during night time (about 85-95%) and decreases gradually after sunrise and reaches a minimum at around noon. The amplitude of the diurnal dip is small during
Figure (3.2) (a) Diurnal variation of mean RH at Trivandrum for January and June 1998.
(b) Month-to-month variation of RH averaged for the period 1990-1998.

the monsoon months. This minimum value of RH in June (typical for monsoon) is about 85% and for January (typical for winter) is about 55%. From Figure (3.2b), it can be seen that the atmospheric RH is higher during the monsoon months than that during the winter months. The RH shows clear seasonal and interannual variations with maximum during the monsoon months and minimum during the winter months as observed from Figure (3.2b).
When the impactor is operated in the open atmosphere the aerosol particles are graded and collected according to their sizes under the prevailing relative humidities. After collection these substrates are unloaded from the impactor and desiccated for ~24 hours, as described earlier. The RH inside the desiccator (R_d) is 45%, which is less than the true atmospheric value. Thus the mass of aerosol particles collected in each LPI stage, obtained from the tare and final masses of the respective stage substrate, corresponds to a RH of R_d prevailing in the desiccator environment, which is same as the room relative humidity in which the weighing are performed. As the particle size decreases with decrease in RH, the upper and lower size limits (as determined by impactor cut points) of the particles collected in each substrate will be less than that during the collection. Thus even though the particles are collected according to their sizes prevailing in the atmosphere, while weighing they change their size and water content according to the prevailing relative humidity conditions. These effects are also to be accounted for obtaining the size distribution of aerosols.

Using the two available informations (viz. mass of aerosols in different size ranges corresponding to a relative humidity of ~45% prevailed at the time of weighing and the aerodynamic cut points of each stage as defined by the impactor design valid for the conditions prevailed during sample collection) assuming the dry particle density and its relative humidity dependence as defined by the above relationships it is possible to obtain the size distribution of aerosols under the real atmospheric relative humidity R (prevailed at the time of samplings). This essentially involves an iterative procedure connecting the aerodynamic diameter, effective density, Stokes diameter and mass of particles collected in each of the LPI stages (Parameswaran and Vijayakumar, 1994).

The average atmospheric relative humidity during the sampling is obtained by averaging the hourly values of RH recorded during the sampling period. To start with, the aerodynamic cut points of each LPI stage is estimated using the appropriate values of D_j, V_j and S_j (given in Table 2.1) employing equation (3.1), keeping \( \rho = 1 \text{ gm cm}^{-3} \). The lower and upper aerodynamic size limits of particles collected in different LPI
stages (at RH=R) are respectively the aerodynamic cut points of the particular stage and that of its previous stage. From these the respective lower and upper size limits of the particles in each substrate corresponding dry size limits (RH=0) and at the desiccated condition (RH=RJ are estimated using equations (3.6) and (3.8). Hanel’s (Hanel, 1976) tables connecting m(w)/m0 and a, applicable for marine aerosols are used for this purpose. A prior knowledge of the density of particle is required for the estimation of the Stokes diameter. This value of dry aerosol density is taken as 2.5 gm cm$^{-3}$, which is generally true for maritime and continental aerosols (Pruppacher and Klett, 1978). The mean diameters corresponding to the three relative humidities (0, R, and R) are estimated by averaging the respective lower and upper size limits of each stage substrate and hence the radii. As a first approximation these aerodynamic radii are taken as the physical radii (Stokes radii) of particles at RH=0, RH=R, and RH=R (say $r_0$, $r_1$ and $r_R$ respectively) and using equation (3.10) the effective particle densities are computed for RH=R, and RH=R (say $\rho_s$ and $\rho_R$) respectively, with $\rho_s=2.5$ gm cm$^{-3}$. The upper and lower Stokes radii limits and hence the mean Stokes radius ($r_R$) of each LPI stage are calculated by substituting $\rho=\rho_R$ in equation (3.1), for RH=R. This is used to re-estimate the mean radius of particles in this LPI stage for the dry condition ($r_0$) and desiccated condition ($r_1$) using equations (3.6) and (3.8) respectively. This is repeated for different LPI stages to give a set of second order values for $r_0$, $r_1$ and $r_R$. These stokes radii are used to re-estimate the effective densities $\rho_s$ and $\rho_R$ using equation (3.10). The resulting new values of $\rho_s$ and $\rho_R$ are again used to estimate a set of third order values of $r_0$, $r_1$ and $r_R$. This process is continued until the corresponding values of $\rho_s$ and $\rho_R$ (and hence $r_1$ and $r_R$) on two successive iterations converge within 0.1%. Usually 5 to 6 iterations are found to be necessary to achieve the desired convergence.

Figure (3.3) shows the variation of $m/m_0$ with RH according to the present semi-empirical model for hygroscopic growth of particles under increasing humidity. The maritime model for water activity is adopted for the present study. The shape of the curve matched fairly well with Figure (3.1), for decreasing RH. The hysterisis
not considered in this model. This is quite reasonable for the present case because atmospheric aerosols are sampled at a higher humidity level during the day, which has already gone through an RH cycling during the night. The nascent aerosols produced from sea surf also come from high RH value (in liquid phase) to the prevailing atmospheric RH condition.

![Graph](https://example.com/graph.png)

Figure (3.3) Variation of $m/m_0$ with RH according to equation (3.13).

The dry aerosol mass ($m_0$) at RH = 0 and the humid aerosol mass at RH = R can be estimated from the measured mass ($m_0$) using equation (3.12), knowing the water activity of the aerosol particles $a_w$ corresponding to sizes $r_s$ and $r_R$ and Hanel's table connecting $m(w)/m_0$ with $a_w$. These quantities can also be estimated using equation (3.12) by substituting the known values of $\rho_0$, $\rho_s$, $\rho_w$, $r_0$, $r_s$, and $r_R$. For the present study, equation (3.13) is employed for the computation of $m_0$ and $m_R$. The mass distributions of aerosols at the three relative humidities RH = 0, RH = R, and RH = R are obtained by dividing the respective masses by the corresponding Stokes radii intervals (the difference between the upper and lower Stokes radii limits of particles in each LPI stage at the respective relative humidities obtained at the end of iteration process) denoted by $r_0$, $r_s$ and $r_R$ respectively.
3.5 Mass and Number Distributions of Near Surface Aerosols

A typical plot of the mass size distribution in different months for the year 1998 for the dry condition is shown in Figure (3.4). Figure (3.5) is similar to Figure (3.4), but for the observed RH conditions (referred hereafter as humid condition) when the correction for RH is incorporated. During the months of July and September, the data in general is scarce due to adverse weather conditions. Very frequent rainfall in these months makes it difficult to operate the sampler almost continuously for 40 hrs. Overall shape of the distribution in figures (3.4) and (3.5) are similar. This is quite expected because the correction for relative humidity generally shifts the mean radius, but will not introduce any undulations. Increase in RH shifts the aerosol size spectrum towards larger size range (Hegg et al., 1993; Parameswran, 1996). The difference between Figure (3.4) and Figure (3.5) is significant only for June to October because of the large values of RH encountered during these months. In general the mass size distribution shows a decrease with increase in radius, except of some undulations. It may be noted in this context that the standard error associated with $\frac{dm}{dr}$ is much smaller than the amplitudes of these undulations. The error bars are too small to be depicted in these figures due to compressed scale of Y-axis. The size distribution of March 1998 shows a steep decrease in the small particle regime ($r<0.5$ $\mu$m). The size distribution of May 1998 is remarkably different from other months. A very broad and prominent peak in the mass distribution is observed at around 0.5 $\mu$m during May 1998. During December 1998 a sharp decrease in submicron particle concentration is observed.

For a simple form, the overall decrease of $\log (\frac{dm}{dr})$ with $\log (r)$ can be approximated to be linear in which the dependence of $\frac{dm}{dr}$ on $r$ becomes a power law with a negative size index (inverse dependence). The power law size index of the aerosol size distribution can be obtained by least square fitting of the power law function to the values of the mass size distribution, considering all points between the stage 1 to L5. The best-fit size index (designated as $v_m$) for each curve is given in the
Figure 3.4 A typical plot of dry mass size distributions in different months for the year 1998.
Figure (3.5) A typical plot of humid mass size distributions in different months for the year 1998.
respective figure. This index lies in the range 0.8 to 1.03 except for March 1998 where size index is 1.42. The size index is greater than unity up to April 1998 and less than unity for the rest of the months. Lower values of size index are indicative of increased abundance of larger size particles. In most of the cases the size index is almost the same (considering the error bars) for both dry and humid cases because increase in RH shifts the aerosol size spectrum as a whole towards the larger size regime and will not cause any significant change in the shape of the spectrum (Parameswaran, 1996) unless non-linear growth (for RH >90%) becomes important (Hanel, 1972) over and above the general decrease of $\frac{dm}{dr}$ with $r$. This effect of nonlinear growth is seen in $v_m$ for the period June to October 1998 ($v_m$ for humid case lower than that for the respective dry case) when the RH values are generally high. In such cases the growth of smaller size particles will be more than that of large particles causing a relative increase of larger size particles. This reduces the slope of the size distribution. The size index in different months does not show any systematic seasonal pattern.

The Low Pressure Impactor, in principle gives the mass of the aerosol particles in different size ranges and hence the mass distribution. This information can be used to derive information on number distribution based on certain assumptions. Firstly, the aerosols are assumed to be spherical. In practice atmospheric aerosols are seldom truly spherical, (as described in Chapter 1) in which case one has to take into account the equivalent diameter. Then the mass of aerosol particles can be expressed as the product of volume and density. The mass of aerosol particles in a particular size range can be converted to the number of spherical particles in the same size range, which has contributed for this observed mass. The number size distribution at the prevailing relative humidity (R) can be expressed in terms of the mass distribution as (Harrison and Van Grieken, 1998)

$$\frac{dn_R(r_R)}{dr_R} = \frac{3}{4\pi r_R^3 \rho_R} \frac{dm_R(r_R)}{dr_R}$$  \hspace{1cm} (3.14)
where \( dn_{\varphi}(r_{\varphi}) \) is the number of aerosol particles in the radius range \( r_{\varphi} \) and \( r_{\varphi} + dr_{R} \) at the prevailing relative humidity \( R \).

Similarly the number size distribution corresponding to dry condition can be obtained from the respective mass size distributions as

\[
\frac{dn_{0}(r_{0})}{dr_{0}} = \frac{3}{4 \pi r_{0}^{2} \rho_{0}} \frac{dm_{0}(r_{0})}{dr_{0}}
\]

(3.15)

where \( dn_{0}(r_{0}) \) represents the number of aerosol particles in the radius range \( r_{0} \) and \( r_{0} + dr_{0} \) for the dry condition.

A typical plot of number size distribution for the year 1998 for dry condition obtained from the mass distribution shown in Figure (3.4) is shown in Figure (3.6). Similarly Figure (3.7) shows the number size distribution for humid conditions obtained from the mass distribution shown in Figure (3.5). From these figures, it can be seen that the gross form of the number size distribution can be approximated to a power law type size distribution (the undulations are less prominent compared to that in mass distribution presented in figures (3.4) and (3.5) due to compressed Y-axis scale). The best fit size indices for these distributions are marked in the respective frames in figures (3.6) and (3.7). The size index generally lies in the range 3.8 to 4.4. A decrease in size index from dry to humid case due to nonlinear growth is observable for the period June to October 1998 in number size distribution also.

3.6 Analytical Model of Aerosol Size Distributions

Several analytical functions have been proposed to represent the atmospheric aerosol size distribution including power laws, modified gamma distributions and lognormal distributions. From impactor measurements (Junge, 1955, 1963) Junge first introduced an inverse power law type distribution for atmospheric aerosols. Other
Figure (3.6) A typical plot of dry number size distributions in different months for the year 1998.
Figure (3.7) A typical plot of humid number size distributions in different months for the year 1998.
workers also observed aerosol size distributions that can be approximated by inverse power law function (Pasceri and Friedlander, 1965; Clarke and Whitby, 1967; Bliford and Ringer, 1969; Yamamoto and Tanaka, 1969; Taylor and Wu, 1992). But this form of size distribution could not account for all the aerosol features especially those of large particles. Later studies, from different locations reported aerosol size distributions deviating from this form of size distribution function (Quenzel, 1970; King et al., 1978; Choularton et al., 1982; Frick and Hoppel, 1993).

The lognormal distribution is a convenient way to describe an aerosol size distribution. This distribution covers the full radius range observed in maritime and continental regions. The shape of the size distribution curves permits estimates on possible origin of the particles. Aerosol size distributions influenced by multiple sources are generally represented as a sum of lognormal distributions with different mode radii (Chapter 1). In practice the size distribution of atmospheric aerosols can be represented by a combination of three lognormal distributions (Whitby, 1978; Shettle and Fenn, 1979; Gathman, 1983). Thus traditionally, atmospheric aerosols are described by a trimodal size distribution (Whitby et al., 1975) consisting of the nucleation (0.01-0.1 μm in diameter), accumulation (0.1-1.0 μm) and coarse (>1μm) modes. Recent observations indicated double-peaked characteristic in aerosol size spectra in 0.01-0.2 μm diameter range (peaks at 0.2 and 0.04-0.08 μm separated by a minimum at 0.12 μm) (Hoppel and Frick, 1990) and also in 0.1-1 μm diameter range. Depending on atmospheric conditions, the aerosol size distribution can generally consist of several modes. Such multimodal spectra can be approximated using the sum of 'N' lognormal distribution functions described by 3N parameters. In several cases, such a detailed description of spectra is not required because modes cannot be separated due to their instability.

Size distributions of atmospheric aerosol particles have been investigated by many authors using various instruments for size segregation for a variety of aerosols. Using an optical particle counter, size distributions and concentrations of the fine and
coarse mode of continental aerosol over United States are given by Kim et al (1988). Recent measurements by Frick and Hoppel (1993), using airborne particle counters have shown that the size distribution in general is multimodal. Examining figures (3.4) and (3.5) in the light of these observations, it can be seen that the undulations observed in these size distribution indicates the presence of modes. For example the size distribution for January 1998 clearly shows the presence of three modes whereas the size distribution for May 1998 shows only two modes.

3.7 Characteristics of Aerosol Size Distributions

The monthly mean aerosol size distributions in different years show small undulations. With a view to examine the general features of aerosol size distributions, all the data in the same month for different years during the period 1990-1998 are grouped and averaged to obtain the respective monthly mean mass size and number size distributions. Figure (3.8) shows the monthly mean mass size distributions for the dry condition and Figure (3.9) shows the same for humid condition. The best-fit power law size indices are also given in the respective frames of the figures. For mass size distributions, it generally lies in the range 0.93 to 1.23. The corresponding number size distributions are given in Figure (3.10) and Figure (3.11) respectively. For number size distributions, the size index of the power law type size distribution is in the range 3.92 to 4.22. The values of aerosol size index obtained in the present investigation are nearly the same as those reported earlier (Pasceri and Friedlander, 1965; Blifford and Ringer, 1969; Goel et al., 1985: Parameswaran and Vijayakumar, 1993) for continental and tropospheric aerosols at lower altitudes by direct sampling technique.

Even though the general form of the size distribution can be represented by a power law function, an examination of the nature of size distributions revealed that the small undulations present in the mass size distributions clearly indicate the presence of modes. Hence to characterize the size distributions, it is necessary to represent the size distributions as a combination of one or more lognormal distributions or a combination
Figure (3.8) Monthly mean dry mass size distributions for the period 1990-1998.
Figure (3.9) Observed mean mass size (humid) distributions in different months for the period 1990-1998.
Figure (3.10) Mean dry number size distributions in different months for the period 1990-1998.
Figure (3.11) Observed mean number size distributions in different months for the period 1990-1998.
of power law with lognormal distributions. In Figure (3.9), the mass size distribution of January shows a maximum around 0.03 μm and decreases slowly up to 0.1 μm where it falls by one order in magnitude. Thereafter it shows a secondary maximum around 0.56 μm and then falls off showing a third maximum around 4.18 μm. Thus the size distribution of January clearly shows three modes; the small particle mode at ~0.05 μm, large particle mode at ~0.56 μm and a giant mode at ~4.18 μm. The dry size distribution for January also shows a similar feature. The size distribution spectrum spreads over a wider size range from 0.03 μm to 10 μm. The size distribution for February falls initially with increase in radius and then increases depicting a prominent peak ~0.1 μm. The size distribution shows a shift in the peak of the small particle mode towards a larger radius compared to the size distribution curve for January. Thereafter it decreases showing a secondary maximum ~0.54 μm and a broad peak ~4.31 μm. The months of January and February are characterized by weak surface winds and insignificant rainfall. Also the surface temperatures are low and convective activities weak. Hence the aerosols produced in these months corresponds to the prevailing condition at Trivandrum.

The size distribution for March indicates a small particle mode ~0.11 μm which is followed by a secondary broad maximum in the large particle regime. This large particle mode is not sharp in March as in the case of previous size distributions. The mean of this broad maximum is ~0.87 μm. Thereafter the mass concentration decreases showing a giant particle mode ~6.12 μm. The size distribution of April also shows a similar feature with small particle mode ~0.18 μm, large particle mode ~0.49 μm and giant mode ~5.93 μm. The aerosol size distributions show a trimodal structure when the total aerosol mass concentration is low (will be seen in later section). Owing to the low concentrations of particles, the coagulation and condensation processes work slowly and cannot fill the gaps in aerosol size distribution. Subsequently, the spectra with separate modes can form. From May onwards, the small particle mode is not seen explicitly because it is getting shifted below the lower cut off diameter of the LPI. Thus the size
distribution shows a transition from trimodal form to bimodal form exhibiting two explicit modes. For May, large particle mode radius is obtained as 0.39 μm and the giant mode radius as 3.08 μm. The size distribution of the monsoon months of June, July and August is bimodal though the giant mode of July is not seen explicitly. During the period August to October, the large particle mode gets split into two. The size distribution of November shows a monotonic decrease with increase in particle radius up to ~0.3 μm and then shows a maximum ~0.36 μm. Thereafter the concentration decreases with increase in radius. The basic nature of the size distribution of December is same as that of January and February, except that in this case the small particle mode is not seen explicitly. Whitby (1978) termed the large particle mode ~0.5 μm as the accumulation mode and stated that its main source of mass is from the coagulation of the smaller size particles. The mode appearing ~6 μm indicates the presence of a coarse particle mode which according to Whitby (1978) generally results from mechanical processes such as those that create wind blown dust or sea-spray.

Table 3.1 gives a summary of the mean characteristics of the aerosol mass size distributions. In general the observed size distributions are trimodal in nature showing three modes; one each in the submicron, large and giant particle regime. Three modes are well discernable in the month of January, February, March and April. During the months of May, June and July the second mode is rather broad which gets split into two sub modes in August, September and October. Particles in this size range are mostly contributed by sea-spray whose life times are of the order of few days. The mode appearing in the coarse size range (r>1 μm) are also contributed by oceanic aerosols whose residence times are rather less. The mode radii are shown in the table for humid as well as for dry distributions. The present study on the aerosol size distributions which are deduced from the mass concentration measurements made by an Andersen Low Pressure Impactor at Trivandrum essentially reveals the modal nature of the aerosol size distributions.
### Table (3.1) Mean Characteristics of surface ASD using LPI for the period 1990-1998 based on mass size distribution.

<table>
<thead>
<tr>
<th>Month</th>
<th>Mode 1 (µm)</th>
<th>Mode 2 (µm)</th>
<th>Mode 3 (µm)</th>
<th>Mode 1 (µm)</th>
<th>Mode 2 (µm)</th>
<th>Mode 3 (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>January</td>
<td>0.05</td>
<td>0.56</td>
<td>4.18</td>
<td>0.05</td>
<td>0.53</td>
<td>3.95</td>
</tr>
<tr>
<td>February</td>
<td>0.10</td>
<td>0.54</td>
<td>4.31</td>
<td>0.09</td>
<td>0.51</td>
<td>4.10</td>
</tr>
<tr>
<td>March</td>
<td>0.11</td>
<td>0.87</td>
<td>6.12</td>
<td>0.09</td>
<td>0.82</td>
<td>5.66</td>
</tr>
<tr>
<td>April</td>
<td>0.18</td>
<td>0.49</td>
<td>5.93</td>
<td>0.49</td>
<td>3.98</td>
<td></td>
</tr>
<tr>
<td>May</td>
<td>0.39</td>
<td>3.08</td>
<td></td>
<td>0.33</td>
<td>2.62</td>
<td></td>
</tr>
<tr>
<td>June</td>
<td>0.50</td>
<td>5.7</td>
<td></td>
<td>0.31</td>
<td>3.63</td>
<td></td>
</tr>
<tr>
<td>July</td>
<td>0.50</td>
<td>not clear</td>
<td></td>
<td>0.29</td>
<td>not clear</td>
<td></td>
</tr>
<tr>
<td>August</td>
<td>0.49, 1.17</td>
<td></td>
<td>5.74</td>
<td>0.29</td>
<td>3.32</td>
<td></td>
</tr>
<tr>
<td>September</td>
<td>0.29, 0.72</td>
<td></td>
<td>6.22</td>
<td>0.31</td>
<td>5.29</td>
<td></td>
</tr>
<tr>
<td>October</td>
<td>0.28, 0.69</td>
<td></td>
<td>5.38</td>
<td>0.31</td>
<td>3.89</td>
<td></td>
</tr>
<tr>
<td>November</td>
<td>0.36</td>
<td></td>
<td>not clear</td>
<td>0.29</td>
<td>5.26</td>
<td></td>
</tr>
<tr>
<td>December</td>
<td>0.57</td>
<td>4.44</td>
<td></td>
<td>0.52</td>
<td>4.07</td>
<td></td>
</tr>
</tbody>
</table>

In this context it is worthwhile to discuss the results on the nature of aerosol size distributions at Trivandrum in the light of the studies carried out at other locations. Most of the recent results on the nature of the aerosol size distributions suggest multimodal form. Blifford and Ringer (1969) made a series of airborne measurements in the Central United States at altitudes from 0.3 to 9 km above the ground. The size distributions show a decrease in particle counts for all sizes relative to the boundary layer size distribution, with a relatively larger decrease for the largest and smallest particles. Tropospheric size distribution of aerosols with significant soil derived component are actually composed of three modes, each characterized by a lognormal
size distribution, with size ranges of about 20 to 200, 2 to 20, and 0.04 to 1 µm in diameter (Patterson and Gillette, 1977). The aerosol number size distributions measured in continental air over southwestern United States during the 1977 Gametag flights (Patterson et al., 1980) indicated that the size distributions are bimodal. Similar bimodal continental boundary layer aerosol distributions have been reported by a number of investigators (Whitby et al., 1972; Sverdrup et al., 1975).

The surface measurements of Khemani et al. (1982), from Pune (18.5°N, 73.1°E) indicated the presence of two modes in the size distributions which are nearly lognormal and the modes were around 0.4 to 0.6 µm and 5 to 6 µm respectively. Their study also showed that the first mode is predominant during winter and the second mode during the monsoon season. They attributed that the small particle mode is due to particles of continental origin and the large particle mode is due to particles of marine origin. Aircraft measurements at Western Europe by Fitch and Cress (1983) indicated the presence of three modes in aerosol size distributions. These modes are represented by lognormal distribution functions and are attributed to different types of aerosols namely anthropogenic, ambient and maritime. Based on the studies of aerosol characteristics at a desert location M’bour (16.9°W, 14.3°N), Tanre et al. (1988) found that the size distribution is bimodal with primary mode ~0.03 µm and another mode varying between 0.3 and 2 µm whose magnitude depends on the amount of dustiness. Measurements of Hoppel et al. (1990) on boundary layer aerosols in marine environments exhibit distinct modes, which are explained on the basis of different aerosol formation mechanisms and meteorological conditions. Prodi et al. (1983) also obtained similar results on their study on marine aerosols.

Zhang et al. (1993) found that the mass size distributions of dust-derived elements and non-dust elements over the Loess Plateau were approximately lognormal. Zhang et al. (1994) also demonstrated the existence of three modes over the Loess Plateau with size ranges of about 20 µm (the heavy mode), 2 to 20 µm (normal or central mode), and less than 1 µm (background mode). Concentration and size
distribution of the continental remote atmospheric aerosols at different locations in Siberia are obtained using a screen diffusion battery and impactor technique (Koutsenogii and Jaenicke, 1994). The size distributions are bimodal for particles with radius less than 0.1 μm. For larger particles the size distributions show a power decrease with a mean exponent of about 3. Artaxo and Hansson (1995) measured the size distribution and elemental composition of natural background aerosol particles from the tropical rain forest of the Amazon basin. The size distribution of the elements associated with the wind blown dust shows a coarse mode, with an average aerodynamic diameter of 4 μm. A fine mode component (~0.5 μm) and the mode biogenic component (~3 μm) also were observed. Horvath et al. (1996) based on the studies conducted at Vienna reported two modes, one between 0.2 and 0.8 μm and a coarse mode above 3 μm of particle diameter. Occasionally they observed an indication of a mode below 0.5 μm, which compares favorably with the submicron mode observed in the present analysis.

All these studies on aerosol size distributions clearly brings out that the aerosol size distributions are generally characterized by one or more modes each of which representing a particular aerosol type depending on their origin. The aerosol size distributions at Trivandrum retrieved for different months show consistent trimodal characteristics except in a few cases. The three modes can be attributed to different production mechanisms, with the submicron mode attributed to particles of continental origin and the large particle mode can be attributed to aged sea-spray aerosols related to the average sea breeze condition prevailing during the day. The third mode appearing in the giant size range is contributed by nascent sea-spray aerosols.

3.8 Seasonal Mean Size Distributions

As seen from the above discussions, the meteorological parameters change from one season to other. Hence most of the times it would be worth presenting a seasonal mean size distribution. The seasonal mean aerosol size distributions are obtained by
grouping the aerosol size distributions in different months in seasons and then averaged. Three distinct seasons can be attributed for Trivandrum; summer (S), monsoon (M) and winter (W). The monsoon season can again be subdivided into two; M1 and M2 each consisting of three months. Thus the year is classified into four seasons viz., summer (March-May), M1 (June-August), M2 (September-November) and winter (December-February). Thus, henceforth for all discussions this criteria is followed to distinguish the seasons in a year. Figure (3.12) shows this seasonal mean aerosol mass distributions obtained using the database of the mass size distributions during 1990-1998 for dry and humid conditions. Figure (3.13) shows the respective number size distributions. From Figure (3.12), it can be seen that the aerosol size distribution is bimodal in summer and monsoon (M1 and M2) months. The lower end of the submicron mode is below lower size limit of LPI and hence is not clearly observable. In these seasons the accumulation mode is around 0.35 μm and rather broad. In winter the three modes are seen clearly (with a submicron mode appearing around 0.04 μm).

3.9 Seasonal Variation of Aerosol Mass Concentration

The LPI is operated 8 to 10 days in a month covering a time period of 40 hrs (confined to day time), depending on the weather conditions. The mass of particles collected in all the 12 (1-1.5) impactor stages are added to get the total mass of aerosol particles. The mass concentration is estimated by dividing the total mass of the collected aerosol particles by the volume of the air sampled, which is estimated as the product of flow rate and sampling period.

A significant component of aerosol particles especially near the surface at this coastal station is contributed by oceanic aerosols (Parameswaran et al., 1995). These particles are generally hygroscopic in nature. In the LPI sampling, the size distribution and mass concentration are estimated for the average relative humidity prevailed during the sampling period. From this mass concentration of aerosol particles (μg/m³), the dry aerosol mass concentration representing the mass of the solid component present in
Dry Condition

![Graphs for dry condition showing mass size distribution for different seasons and years.]

Humid Condition

![Graphs for humid condition showing mass size distribution for different seasons and years.]

Figure (3.12) Seasonal mean mass size distribution for 1990-1998.
Dry Condition

Humid Condition

Figure (3.13) Seasonal mean number size distribution for 1990-1998.
these aerosols is estimated by normalizing to RH→0. The monthly average values of dry and humid (\(\bar{m}_d\) and \(\bar{m}_h\)) mass concentrations are presented in Figure (3.14a) and Figure (3.14b). \(\bar{m}_h\) representing the mass concentration actually present in the atmosphere and \(\bar{m}_d\) the mass concentration of their embryos. The vertical bars in these figures represent the associated standard errors. The humid mass concentration shows a prominent maximum during the southwest monsoon period. A small secondary peak observed in the winter months builds up, when the correction for relative humidity is applied (as is in Figure (3.14b)).

![Figure 3.14a](image-url)

![Figure 3.14b](image-url)

**Figure (3.14)** Mean month to month variation of humid and dry aerosol mass concentration for the period 1991-1997.
It is true that the atmospheric relative humidity increases significantly in southwest monsoon season (Figure (3.2)) which lead to increase in total suspended particulate mass concentration due to hygroscopic growth. As seen from Figure (3.14b) this is not the only reason for the observed increase in \( m_h \) as \( m_d \) (the dry mass concentration obtained after eliminating the hygroscopic growth effect) also shows a peak during this period. This can be attributed to increased contribution from sea-spray aerosols. The strong monsoon winds blowing over the sea surface can generate a lot of sea-surf and results in the generation of aerosol particles. They will be abundant in particle sizes above 0.1 \( \mu \text{m} \) significantly contributing for aerosol mass. \textit{O' Dowd and Smith} (1993) observed the presence of sub-micron sea-salt in accumulation mode aerosol down to sizes of 0.05 \( \mu \text{m} \) radius and showed that, under moderately high wind speeds, it could dominate the number concentration in this size range. It is interesting to see the build up of \( m_e \) in winter. This peak is mainly contributed by particles of continental origin (dominant in sub-micron and accumulation mode).

### 3.10 Principal Components

Aerosols in the coastal atmosphere are formed by complex processes. The sea spray aerosols produced by bubble bursting mechanism gets modified when the marine air mixes with the anthropogenically formed aerosols of continental origin. These secondary aerosols may contain large fractions of sulfate, nitrate and ammonium. Studies on the modification of sea salt particles in the coastal atmosphere have been carried out by many workers (Roth and Okada, 1997; von Salzen \textit{et al.}, 1997; von Salzen and Schlunzen, 1999). The physical and optical properties of atmospheric aerosols depend on their chemical composition also. For example the soot particles are not generally hygroscopic and as such they have little affinity to water vapor. They significantly absorb visible radiation and thereby reducing the single scatter albedo. Sodium and Magnesium have strong affinity to water vapor and they grow in size with
increase in humidity. They are good scatterers for optical radiation. This is true for sulfates and nitrates also.

In order to have a general understanding on the chemical composition of atmospheric aerosols at Trivandrum few aerosol samples were collected using a High Volume Sampler (Handivol 2000) in the year 1999. Three samples collected during the sea breeze period and three samples collected during the land breeze period have been used for this purpose. Ion chromatography and atomic spectroscopy analysis were used to quantify the presence of cations like Na, K, Mg, Fe, Cu and Zn and anions like Cl, NO₃, and SO₄.

Average relative abundance of these analysed constituents from these six samples is presented in Figure (3.15). No systematic difference in the relative concentration during sea breeze and land breeze conditions was observable. Sodium is the significant cation present in these samples (8-12%), with an average of 11%. Relative abundance of iron is

![Figure (3.15) Relative abundances of different chemical components in near surface aerosols observed at Trivandrum.](image-url)
found to be in the range 2-4% (average 2.3%) and that of potassium in the range 1-2% (average 1.3%). Significant abundance of sulphates is observed in all the samples and is highly variable in the range 4-15% (average 11%). Relative abundances of nitrate and chlorine are found to be in the range 2-8% (on an average of 4% and 6% respectively). It may be noted in this context that only ~40% of the aerosol mass could be accounted by these constitutes. The remaining part is expected to be composed of organic materials, silicates and black carbon, which remains unanalysed at present.

This study on the chemical nature of aerosols at Trivandrum is only an initiation of the work on aerosol chemistry. This work only identifies the principal components in surface aerosols at Trivandrum. More detailed studies on this is warranted. The chemical composition change with season and prevailing meteorological conditions. For example increase in sea breeze is reported to cause an increased concentration of Na and Cl. The present chemical analysis though not exhaustive brings out the fact that sulphates and nitrates are the important cations observed in atmospheric aerosols at Trivandrum (~5 μg/m³ and 2.2 μg/m³ respectively). Iron and potassium content are ~1-2 μg/m³. Being a coastal station significant amount NaCl particles are expected in the atmosphere, which is also revealed by this analysis.

3.11 Summary

The size distribution of surface aerosols at the coastal station, Trivandrum coast has been studied using an Andersen Low Pressure Impactor. The gross form of the number size distribution can be approximated to a power law type with size index in the range 3.7 to 4.4. The aerosol mass size distributions at Trivandrum retrieved for different months show consistent trimodal characteristics except in a few cases. The average aerosol size distribution is generally trimodal, with one mode each in the submicron, large (accumulation) and giant particle size regimes. Significance of these modes and the mode radii shows variation with season. These modes can be attributed to different production mechanisms, with the submicron mode attributed to particles of
continental origin and the large particle mode attributed to aged sea-spray aerosols related to the average sea breeze condition prevailing during the day. The third mode appearing in the giant size range is contributed by nascent sea-spray aerosols. The average mass loading of aerosols near the surface varies in the range 100 to 250 μg/m³. It is maximum during the monsoon and winter season. The monsoon peak is attributed to increased contribution from sea-spray aerosols and the winter peak to increased contribution from particles of continental origin. Chemical analysis of aerosol samples collected from this coast indicates the presence of cations like Na, K, Mg, Fe and Zn and anions like Cl, NO₃ and SO₄. These constituents, however, could account for only ~40% of total aerosol mass, the rest of which could be made up of organic materials and black carbon.