

Atmospheric aerosol formation and its growth during the cold season in India

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The effects of molecular diffusivity of H₂SO₄ and NH₃ vapours on nucleated particles of SO₄²⁻ and NO₃⁻ species are reported. Condensation sink and source rate of H₂SO₄ and NH₃ vapours, growth rates and ratios of real to apparent nucleation rates are calculated for SO₄²⁻ and NO₃⁻ aerosols using fractional contributions of them in total aerosol size-distribution during the measurement period at Pune, reported in Chate and Pranasha (2004). The percentage of nucleated SO₄²⁻ and NO₃⁻ aerosols of mid-point diameter 13 nm are 2% and 3% respectively of the total particles (13 nm ≤ D_p ≤ 750 nm) for both H₂SO₄ and NH₃ diffusion. In the diameter range 75 nm ≤ D_p ≤ 133 nm, it is 48% and 45% of SO₄²⁻ and NO₃⁻ aerosols, respectively for NH₃ diffusion and 43% and 36% of SO₄²⁻ and NO₃⁻ for H₂SO₄ diffusion. Increase in percentage of nucleated particles of these species corresponding to mid-point diameter 133 nm around 0900 h IST is significantly higher than that of mid-point diameter 13 nm and it is due to photo-chemical nucleation, coagulation and coalescence among nucleated clusters. The ratios of real to apparent formation rates for SO₄²⁻ and NO₃⁻ aerosols are 12% and 11% respectively, corresponding to mid-point diameter 13 nm, 17% and 13%, for mid-point diameter 133 nm and 12% and 9.5%, for mid-point diameter 750 nm. The results indicate that nucleation involving H₂SO₄ and acidic NH₃ diffusion on SO₄²⁻ and NO₃⁻ particles is the most relevant mechanism in this region.

1. Introduction

Atmospheric new particle formation processes contribute significantly to the global aerosol distributions (Spracklen *et al* 2006). A review of literature compiled about 100 papers reports observations of ‘aerosol nucleation’ throughout the troposphere (Kulmala *et al* 2004). Nucleation from the gaseous precursors leads to the formation of nucleated particles in the diameter range 3 nm ≤ D_p ≤ 20 nm. Precursors such as SO₂, NO₂ and organic compounds are emitted mostly from combustion sources. Increased concentrations of O₃, SO₂, NO₂ and organic compounds can influence the conversion of Volatile Organic Compounds (VOC) into condensable vapours to form nucleated clusters and these clusters grow to particles

through condensation of organic and inorganic vapours. Freshly nucleated particles typically grow to 10 to 100 nm at rates of 1 to 20 nm h⁻¹ during the course of a day (Kulmala *et al* 2004). Further growth of nucleated particles takes place by diffusion of vapour molecules (Seinfeld and Pandis 1998). Various nucleation mechanisms are found in the literature involving water and sulphuric acid (Vehkamäki *et al* 2002), water-sulphuric acid-ammonia (Merikanto *et al* 2007), ion-induced nucleation (Modgil *et al* 2005), ion induced and sulfate aerosols (Kazil and Lovejoy 2007), and sulphuric-acid vapour (Riipinen *et al* 2007; Kuang *et al* 2008). However, specifying the most relevant nucleation mechanism for new particle formations in various environments is a challenging task.

Keywords. Nucleation; coagulation; condensation; photo-chemistry; gaseous precursors.

In India, formation and growth rates of particles were estimated from the measured aerosol size distributions at Delhi (Mönkkönen *et al* 2005). But it is difficult to classify the newly formed and the pre-existing particles when background aerosol concentrations are higher (Alam *et al* 2003). Chate and Devara (2005) have estimated nucleation and growth rates of aerosols using measured aerosol size distributions reported in Chate and Pranesha (2004) at a relatively less polluted environmental site, Pune. Particle size distributions were measured with an Electrical Aerosol Analyzer (EAA Model 3030, TSI Inc.) which covers 10 size ranges of 3.2–5.6, 5.6–10, 10–17.8, 17.8–31.6, 31.6–56.2, 56.2–100, 100–178, 178–316, 316–562 and 562–1000 nm and gives the number concentration against mid-point diameters which are the logarithmic centre of these size ranges. Recently, Murugavel and Chate (2009) have reported the formation and growth rates of particles from the size distributions of aerosols in the diameter range $20 \text{ nm} \leq D_p \leq 600 \text{ nm}$ measured at this site using Scanning Mobility Particle Sizer (Model 3936, TSI, USA). To the authors' knowledge no attempt has been made to study the chemistry of the associated particles and condensing vapours involved in photo-chemically driven nucleation and growth of nucleated particles over Indian region.

Nucleation bursts start producing molecular clusters which are of very small diameter below 1 nm and then they grow to diameter which can be detected by the measurement systems. Nucleated particles start to be observed only if the clusters grow to the detectable equivalent diameter of the aerosol analyzers (aerodynamic and stokes diameter, optical equivalent, electrical mobility equivalent and diffusion equivalent diameters), which means that they have already grown for some time starting from their initial diameter. Aerosol nucleation strongly depends on concentrations of sulphuric acid and other condensable vapours (H_2O and acidic NH_3) of low volatility. Solar radiation, atmospheric mixing processes, levels of precursors and chemistry of aerosols affect the nucleation processes. The elapsed-time evolutions of poly-dispersed aerosols of individual chemical compounds during nucleation bursts are difficult to measure using aerosol analyzers.

The diffusion of molecules of condensable vapours to the surface of nucleated clusters results in the growth of nucleated particles of various compounds. Determination of the formation and growth rates when molecules of various condensable vapours diffuse on freshly produced particles of major species is important to understand the nucleation processes. The concentration of vapours (H_2O , acidic NH_3 , H_2SO_4 , etc.) and its source

rate for particles of major species and diameters are likely to be of interest to modellers who deal with the physico-chemical properties of aerosols. Apparent nucleation rates and real formation rates calculated from the measured aerosol size-distribution are also important for extractions of the number concentrations of nucleated particles of major species before they grow to detectable diameters. Nucleated clusters are initially of 1 nm in diameter and as they are too small to be detected by aerosol analyzers, one actually measures the apparent formation rates at which aerosols appear at detectable diameters instead of real ones. For estimations of real nucleation rates and number of nucleated aerosols of major species, an alternative is to rely on the assumption of number concentrations of particles of major species distributed in total aerosols. We report the effects of molecular diffusivity of H_2SO_4 and NH_3 vapours on nucleated SO_4^{2-} and NO_3^- particles. We present the concentrations of freshly produced nucleated particles of sulfates and nitrates, their nucleation rates and growth properties from the analysis of aerosol size distributions measured in the field experiments of Chate and Pranesha (2004). The details of instruments used for the measurement of chemical compounds are found in Momin *et al* (1999).

2. Methodology

The Knudsen numbers (K_n), transitional correction factors (β_m) for the condensational mass flux of vapour concentrations (C) and factors γ as a function of particle size distributions are taken from Chate and Devara (2005). Condensation sink (CS) depends on the diameter of the particles and is a measure of the rate by which the vapour condenses onto the whole particle population and also it determines how rapidly vapour molecules will condense onto pre-existing aerosols. The growth rate (GR), CS and source rates (Q) of condensing vapours are derived as below.

Diffusion coefficient for condensing vapours in air for temperatures between -40 and 40°C (Pruppacher and Klett 2000) as a function of temperature and pressure is expressed as:

$$D_v(T, P) = D_v(0, 1) \left(\frac{T}{T_0} \right)^{1.94} \left(\frac{P_0}{P} \right), \quad (1)$$

where $D_v(0, 1)$ is the diffusion coefficient of gaseous species at STP with $T_0 = 273.15 \text{ K}$, $P_0 = 1023.25 \text{ mb}$, $T = 293.15 \text{ K}$, $P = 950 \text{ mb}$ and D_v in cm^2s^{-1} . Molecular diffusivities or diffusion coefficients are adopted from Massman (1998).

Assuming growth of particles at constant rate by condensation, the GR is expressed as (Kulmala *et al* 1998a, 2004):

$$\frac{dD_p}{dt} = \frac{4m_v\beta_m D_v C}{D_p \rho_p}, \quad (2)$$

where m_v is the molecular mass of condensable vapour, C is responsible for the growth of newly formed particles, and ρ_p is the density of aerosol particle. Equation (2) can be integrated from D_{p0} to D_p for C (Kulmala *et al* 2001a, 2004) as:

$$C = \frac{\rho_p}{\Delta t D_v m_v} \left\{ \left(\frac{D_p^2 - D_{p0}^2}{8} \right) + \frac{\lambda(D_p - D_{p0})}{2} \right. \\ \left. \times \left(\frac{4}{3\alpha} - 0.623 \right) + 0.623\lambda^2 \ln \frac{(2\lambda + D_p)}{(2\lambda + D_{p0})} \right\}. \quad (3)$$

Here α is assumed to be unity and Δt is the time difference between formation of new particles and their growth from initial diameter D_{p0} to larger D_p .

CS depends on molecular diffusivities, aerosol size and distribution functions of different species (Pirjola *et al* 1999, 2002; Kulmala *et al* 2001b, 2004),

$$CS = 2\pi D_v \int_0^\infty D_p \beta_m N(D_p) dD_p, \quad (4)$$

where $N(D_p)$ is fractional size distribution of particles of various species in total aerosols.

Assuming vapour molecules of H_2O , H_2SO_4 and acidic NH_3 diffuses to the surface of the nucleated particles, the time dependence of the vapour concentration can be expressed as (Kulmala *et al* 1998b; Kerminen *et al* 2004):

$$\frac{dC}{dt} = Q - CS \cdot C. \quad (5)$$

Assuming a steady state vapour concentration, the source rate Q can be estimated from:

$$Q = CS \cdot C. \quad (6)$$

Parameter η is a measure of the number concentrations of nucleated particles and function of CS at $\alpha = 1$ and GR (Kerminen and Kulmala 2002)

$$\eta = \frac{\gamma CS'_{\alpha=1}}{GR}, \quad (7)$$

where

$$CS'_{\alpha=1} = \sum_i 0.5 D_{p,j} \beta_m N(D_p). \quad (8)$$

Chate and Pranesha (2004) measured the distributions of particles of mid-point diameter ≥ 13 nm. Number concentrations of newly formed particles corresponding to already grown sizes,

$$N(D_{\text{nuc,ini}}) = \frac{N(D_p)}{\exp(\eta/D_p - \eta/D_{\text{nuc,ini}})}, \quad (9)$$

where $N(D_p)$ is the measured aerosol number concentrations, $D_{\text{nuc,ini}}$ is the initial size of nucleated clusters. Real formation rate (Kerminen and Kulmala 2002) prior to the growth of newly formed nucleated particles is written as:

$$J(t)_{\text{real}} = \frac{N(D_{\text{nuc,ini}})}{\Delta t}. \quad (10)$$

Apparent formation rate is related to the real formation rate corresponding to the number of new particles as (Kerminen and Kulmala 2002):

$$J(t)_{\text{apparent}} = J(t)_{\text{real}} \exp[\eta/D_p - \eta/D_{\text{nuc,ini}}]. \quad (11)$$

3. Results

It has been observed by Momin *et al* (1999) at IITM, Pune site that total fine size particles were fractionally distributed in the form of:

- water soluble particles including those produced from gas-to-particle conversions (30%),
- conversions of VOCs (40%), and
- particles emitted from the combustion sources (30%) as shown in figure 1.

We have assumed these fractional distributions for water soluble (SO_4 and NO_3) fine mode particles ($D_p \leq 1000$ nm) (figure 1) and used with the aerosol size-distribution data reported in Chate and Pranesha (2004) to investigate the effects of H_2SO_4 and acidic NH_3 vapours on formation and growth of nucleated aerosols in this study, because to date, no data are available on size-distributions of aerosols of various species at this site.

From the diurnal variation of aerosol size distributions reported in Chate and Pranesha (2004), the baseline distributions at 0300 h IST (corresponding to 82.5°E longitude), depleted number distributions owing to fog formation at 0600 h IST and enhanced number distributions of total

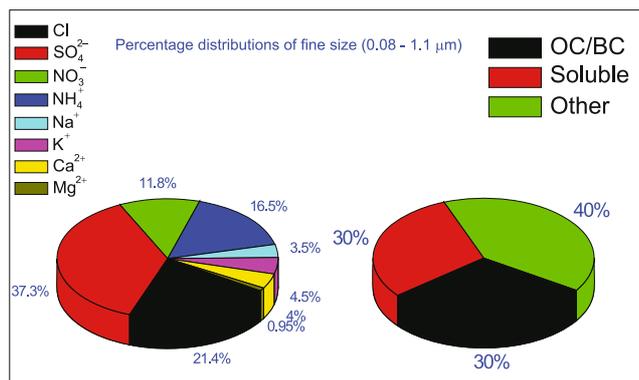


Figure 1. Percentage distributions of aerosols of various species in fine size particles in total distributions at Pune, India (Momin *et al* 1999).

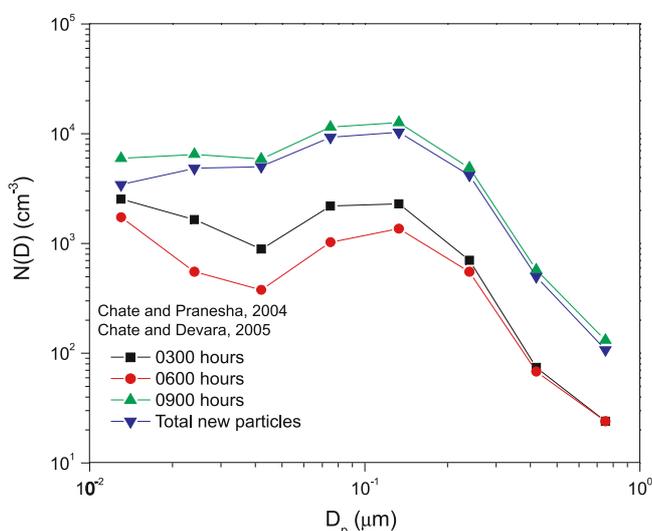


Figure 2. Particle size distributions at 0300, 0600 and 0900 h IST and the total new particles during cold season at Pune (estimated from measurements of Chate and Pranesha 2004).

nucleated particles around 0900 h IST are estimated and plotted in figure 2. The Earth's surface layer starts cooling at about 0300 h IST and continues to cool till morning 0600 h IST. Due to moisture contents in the cold air, fraction of hygroscopic particles present in the measured distributions at 0300 h IST start serving as nuclei for fog droplets. As a result, number-size distributions of total particles around 0600–0700 h IST are less than those observed at 0300–0600 h IST. Photo-chemically driven nucleation could occur only after the sunrise and produces many folds of fresh particles around 0800–0900 h IST. The growth of freshly produced particles takes place mainly through condensation of vapours (H_2SO_4 , acidic NH_3 , etc.), coagulation and coalescence among nucleated clusters. Particles released through evaporation of fog droplets after sunrise

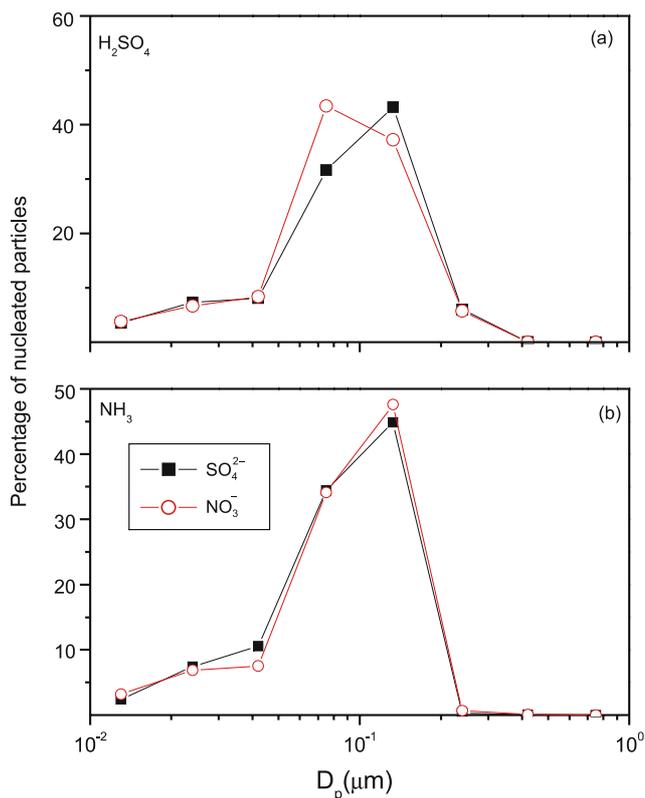


Figure 3. Percentage of SO_4 and NO_3 particles with size for H_2SO_4 and acidic NH_3 diffusions.

superimpose on photo-chemically formed particles which have already grown to detectable size of measuring system. Therefore, measured particle number-size distributions around 0900 h IST (starting point of atmospheric mixing processes) shows a sharp increase in number concentration. The difference between size-distributions at 0900 h IST and distributions at 0300 h IST is corresponding to freshly formed particles as shown in figure 2. This excess concentration of particles in the size range $13 \text{ nm} \leq D_p \leq 750 \text{ nm}$ suggests that nucleation is photo-chemically driven and condensation, coagulation and coalescence processes are responsible for the growth of these particles.

It is desirable to quantify the influence of molecular mass and diffusivity of vapours of different species on formation rate and growth properties of nucleated aerosols. Percentages of number concentration of SO_4^{2-} and NO_3^- aerosols formed through condensation of H_2SO_4 and acidic NH_3 are illustrated in figure 3. At the mid-point diameter 13 nm, the percentages of freshly produced and already grown SO_4^{2-} and NO_3^- aerosols are 2 and 3% respectively of the total particles ($13 \text{ nm} \leq D_p \leq 750 \text{ nm}$) for both H_2SO_4 and acidic NH_3 diffusions. Whereas in the mid-point diameter range $75 \text{ nm} \leq D_p \leq 133 \text{ nm}$, it is 48% of SO_4^{2-} and 45% of NO_3^- aerosols for acidic NH_3

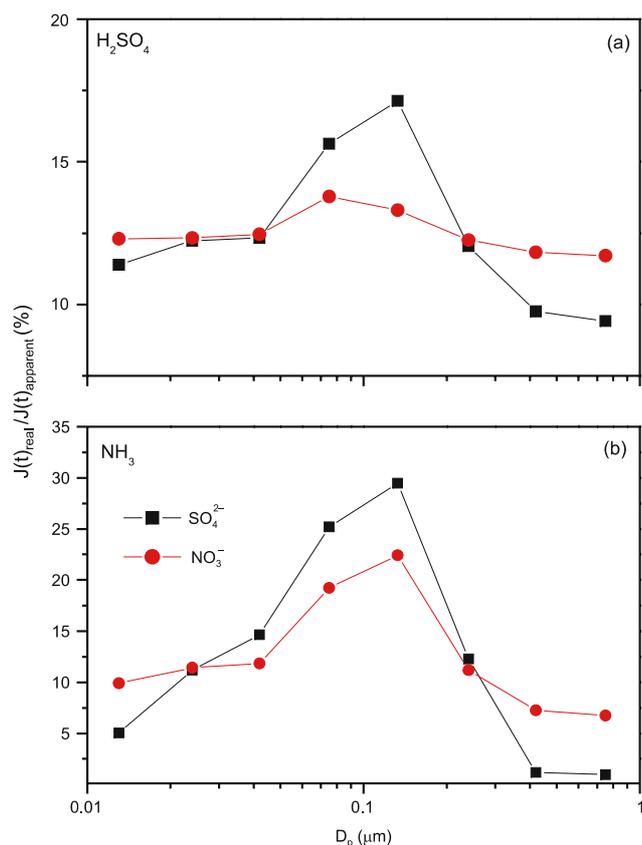


Figure 4. Percentage ratios of real to apparent nucleation rate for SO_4 and NO_3 particles with size for H_2SO_4 and acidic NH_3 diffusions.

diffusion and 43% of SO_4^{2-} and 36% of NO_3^- for H_2SO_4 diffusion (figure 3). The particles in this diameter range are found in the atmosphere generally due to vehicular emissions in urban environments (Zhu *et al* 2002). However, wind speed was almost zero during early morning to 0900 h IST and hence advection of ultrafine particles emitted from the vehicular emission in this diameter range to the point of measurement is a remote possibility. This feature for particles of mid-point diameter 133 nm is in agreement with our previous results (Chate and Devara 2005). The strong interplay between the nuclei growth and their loss by coagulation may be responsible for the higher percentage of $75 \text{ nm} \leq D_p \leq 133 \text{ nm}$ particles. Photo-chemically driven nucleation by solar radiation, coagulation of nuclei onto pre-existing particles and also coalescence among freshly produced nucleated clusters resulted into major share of $75 \text{ nm} \leq D_p \leq 133 \text{ nm}$ particles. Further observations including solar radiation would provide the insight into quantitative strengths of photo-chemical nucleation relative to coagulation.

The apparent nucleation rates, real number concentrations of newly formed SO_4^{2-} and NO_3^- particles are computed based on the percentages of

chemical species given in figure 1, for the measured particle size distributions from the equation (2) to equation (11). In figure 4, the variation in percentage ratios of real to apparent formation rates for SO_4^{2-} and NO_3^- particles are shown as a function of diameter. The ratios of real to apparent formation rates ($J(t)_{\text{real}}/J(t)_{\text{apparent}}(\%)$) for SO_4^{2-} and NO_3^- aerosols for H_2SO_4 diffusion are 12% and 11% corresponding to mid-point diameter 13 nm, 17% and 13% corresponding to mid-point diameter 133 nm, and 12% and 9.5% corresponding to mid-point diameter 750 nm. Similar trends are followed for percentage ratios as a function of SO_4^{2-} and NO_3^- particle diameters for NH_3 diffusion as shown in figure 4(b). Thus percentage of $J(t)_{\text{real}}/J(t)_{\text{apparent}}$ depends on the fractional number concentrations of particles of various chemical species in total nucleated particles and it is a measure of number concentration of freshly produced particles by photo-chemical nucleation. The results indicate that aerosol nucleation mechanism is coupled strongly with chemistry, particularly involving H_2SO_4 and acidic NH_3 diffusion on freshly nucleated particles of SO_4^{2-} and NO_3^- at semi-urban environment (Pune, India).

Despite the importance of photo-chemical nucleation and growth properties of nucleated aerosols of various compositions over this location, some comparison with the published results is desirable. Real formation rates derived in this study are 17 and 79 particles $\text{cm}^{-3}\text{s}^{-1}$ for SO_4^{2-} and NO_3^- nucleated particles respectively corresponding to mid-point diameter 13 nm. The formation rate worked out by Kulmala *et al* (2004) vary between 0.5 and 16 $\text{cm}^{-3}\text{s}^{-1}$ for 15 nm particles over subtropic rural desert site, between 1 and 1.5 $\text{cm}^{-3}\text{s}^{-1}$ for 10 nm particles over mid-latitude coastal land and between 5 and 40 $\text{cm}^{-3}\text{s}^{-1}$ over mid-latitude rural land. Nucleation rates as high as 10^4 to 10^5 particles $\text{cm}^{-3}\text{s}^{-1}$ have been reported for 3 nm particles in coastal environments and industrial plumes (Kulmala 2003). Growth rates of diameter 3 nm varied between 11.6 and 16 nm h^{-1} at New Delhi, India (Mönkkönen *et al* 2005) as against 0.07 to 0.7 nm h^{-1} at Pune for both NO_3^- and SO_4^{2-} particles corresponding to mid-point diameter 13 nm. Large concentrations of pre-existing/background aerosols with higher levels of condensing vapours at a mega-city (New Delhi) relative to Pune (semi-urban) may be responsible for the discrepancy in the formation rate. Other factors responsible for the discrepancy may be large vehicular traffic density, entirely different atmospheric conditions including solar radiation and observational period at New Delhi as compared to clear, calm conditions during measurements at Pune. Measurements of real-time chemical compositions of particle

size-spectra may be possible in future during nucleation events in tropical region (Douglas *et al* 2003). One can derive the nucleation coefficients for freshly produced nucleated particles of various species in terms of real and apparent nucleation rates, provided appreciable data of real-time chemical compositions of particle size distributions, levels of various condensing vapours and magnitude of solar radiation are made available.

4. Conclusions

The formation rates and growth properties of atmospheric particles by nucleation mechanisms have received much attention of research community in the recent years. The condensation sink and source rates of H₂SO₄ and acidic NH₃ vapours, growth rate and the ratios of real to apparent formation rates are calculated for SO₄²⁻ and NO₃⁻ particles. The nucleated SO₄²⁻ and NO₃⁻ aerosols of mid-point diameter 13 nm are found 2% and 3% of the total particles for H₂SO₄ and NH₃ diffusions. In the diameter range 75 nm ≤ D_p ≤ 133 nm, photo-chemically driven nucleation, coagulation and coalescence of nucleated clusters causes 48% of SO₄²⁻ and 45% of NO₃⁻ aerosols for NH₃ diffusion and 43% of SO₄²⁻ and 36% of NO₃⁻ for H₂SO₄ diffusion. The percentage of J(t)_{real}/J(t)_{apparent} depends on the fractional concentrations of particles of various species in total nucleated particles and it is a measure of number concentration of freshly produced particles during photo-chemical nucleation. The results presented indicate that nucleation involving H₂SO₄ and acidic NH₃ diffusion on SO₄²⁻ and NO₃⁻ particles is the most important mechanism at Pune, India. The results need support with the real-time measurements of chemical compositions of aerosol size spectra and H₂SO₄ and acidic NH₃ vapours during nucleation events. Further efforts are warranted to identify the nucleation events in different environments over Indian region to collect appreciable data of chemical compositions of particle size-spectra with meteorological parameters including magnitude of solar radiation, temperatures and humidity. Relative humidity (RH) affects primarily in moisture uptake of hygroscopic nucleated clusters and particles. Pre-existing hygroscopic particles absorb more moisture as RH increases and newly formed particles become a major sink for condensing vapours. However, there are number of practical problems in dealing with the aerosols of various chemical compositions associated to the atmospheric nucleation events. For example, yet the actual nucleation mechanism and the role of chemical constituents remain to be identified.

Future work should include observations of chemical composition of aerosol size distributions in different environments, measurements of gaseous compounds participating in nucleation and growth properties of nucleated particles.

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