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A review of particle formation events and growth in the atmosphere in the various environments and discussion of mechanistic implications

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Abstract

This review highlights recent observations from a large number of studies investigating formation and growth within different environments and discusses the importance of various mechanisms of particle formation and growth between the different environments. Whilst, several mechanisms for new particle formation have been proposed the importance of each mechanism is still the centre of much debate. Proposed nucleation mechanisms include condensation of a binary mixture of sulfuric acid and water; ternary nucleation of sulfuric acid, water and a third molecule, most likely ammonia; ion induced nucleation; secondary organic aerosol formation involving condensation of low or non volatile organic compounds and homogeneous nucleation of iodine oxides. Laboratory and modelling studies have shown these mechanisms can occur in the atmosphere although the contribution depends on the concentrations of precursor compounds present. In addition, atmospheric particle formation events are significantly affected by environmental factors, such as temperature, humidity and the surface area of pre-existing particles, which is also discussed here. One major problem hampering our current understanding is that these new particles are smaller than the lower size detection limit of most instruments and are only observed after some particle growth has occurred.

Particles growth occurs through condensation of supersaturated vapours on the surface of the nucleated particles. This requires a lower degree of supersaturation than nucleation and thus condensation of the nucleating species reduces the rate of particle formation. Therefore, it is believed that particle growth often occurs through the condensation of other gases, including organic and inorganic compounds, than those responsible for nucleation. This decoupling of nucleation and growth means that the individual gases responsible for nucleation and growth can be unclear.

Since observations of particle formation only occur following growth to observable sizes it is possible that a pool of undetectable particles exist at all times but are only observed following significant condensational growth.

1. Introduction

Over recent years there has been increased research into the effects of particles in the atmosphere. Whilst PM_{10} (mass of particles with an aerodynamic diameter less than $10\ \mu\text{m}$) emissions are regulated and there are plans to include regulation of $PM_{2.5}$ (mass of particles with an aerodynamic diameter less than $2.5\ \mu\text{m}$) in several countries, no regulations exist with respect to submicrometre particles ($d < 1\ \mu\text{m}$) or ultrafine ($d < 100\text{nm}$) in terms of particle number. Recent health studies (Donaldson et al. 1998; Oberdorster 2000; Oberdorster 2001; Donaldson et al. 2002; Pope et al. 2002; Nemmar et al. 2003) have shown that ultrafine particles can have a greater adverse effect on our health than larger particles of the same composition. Furthermore, the smaller particles are capable of penetrating deeper into the respiratory tract. Studies have shown that whilst ultrafine particles have been measured to account for over 65% of the submicrometre particles they accounted for less than 5% of the submicrometre mass (Morawska et al. 1998; Rodriguez et al. 2005).

Furthermore, particles have been shown to influence visibility (Jung and Kim 2006) and the radiative balance of the atmosphere through the absorption and scattering of the incoming radiation (Sokolik and Toon 1996), with the extent and direction of the climatic forcing dependant on the size distribution and nature of the aerosols.

These problems show that not only is total particle concentration important but also the size distribution of the particles. Therefore, there has been considerable interest in

the size distribution of atmospheric particles and mechanism of formation and growth of the particles.

Kulmala et al. (2004)(Kulmala et al. 2004) published a review detailing over 100 campaigns in which the formation and growth of particles were observed. However, in this review there was only limited discussion as to the source or mechanism of the observations. This review discusses more fully the observations from a number of measurement campaigns, conducted in different environments, aimed at investigating particle number concentration and based on modelling and laboratory studies examines the mechanistic implications of rates and aerosol composition in the various environments.

Aerosol dynamics describes the processes governing aerosol formation, growth and loss. New particles, about 1 nm in diameter, are formed by nucleation through a number of different mechanisms. These particles grow as a result of coagulation with other particles or condensation of gas phase constituents at a rate dependent on factors including particle size, chemical composition, concentration and temperature. Particle loss occurs through deposition.

2. Nucleation

New particles are formed by nucleation of non- or low- volatile gas phase compounds, emitted from either biogenic or anthropogenic sources, followed by growth into small particles. New particle generation has been observed in a variety of environments, including the pristine atmosphere of the Arctic(Birmili et al. 2000; Komppula et al. 2003), above forests, around coastal areas and within urban centres(Wählén et al. 2001; Wehner et al. 2002; Charron and Harrison 2003; Fine et al. 2004; Stanier et al. 2004; Stanier et al. 2004). Our current understanding is restricted by the lack of

measurement methods capable of detecting and characterising nucleation particles. Until recently it was not possible to detect particles smaller than 10 nm, which represents a particle containing approximately 10000 molecules. However, current instruments are able to detect particles as small as 3 nm. Despite this advance in technology there can still be a considerable lag time of upto 4 hours between nucleation and detection as a result of the time required for the particles to grow to a detectable size. Differences in the observations show that new particle formation is highly sensitive and depends on several factors including, surface area of existing aerosols and age of the aerosols as well as ambient gas phase concentrations.

Most new particle formation within the atmosphere is assumed to occur by several possible mechanisms: i) binary nucleation of sulfuric acid and water or ii) ternary nucleation involving a third molecule. The most likely third species is ammonia, which is abundant in the troposphere and has been shown to enhance nucleation rates of sulfuric acid(Weber et al. 1998).

Other mechanisms of new particle formation include condensation of semi volatile organic aerosols (SVOAs) (O'Dowd et al. 2000; Jang and Kamens 2001; Kavouras and Stephanou 2002; O'Dowd et al. 2002) and ion-induced nucleation (IIN). In order to successfully model the formation of SVOAs a comprehensive description of the atmospheric chemistry is required. A discussion of the chemistry within the troposphere is outside the scope of this review, but the reader is directed to Jenkin and Clemitshaw (2000)(Jenkin and Clemitshaw 2000). The contribution of SVOAs to total organic content of aerosols has been modelled through various chemical mechanisms(Pandis et al. 1992), such as Master Chemical Mechanism (MCM)((MCM) Master Chemical Mechanism) and Regional Atmospheric Chemistry Mechanism (RACM)(Stockwell et al. 2000). The MCM is a near explicit mechanism

describing the pathways of 135 volatile organic compounds (VOCs) within the troposphere, whilst the RACM works by lumping compounds into classes, depending on functional groups within the molecule, and assigning the classes a relevant reaction rate. For full review of the mechanisms the reader is referred to Gross and Stockwell (2003)(Gross and Stockwell 2003) and references within, Carter et al. (2000)(Carter 2000) and Jimenez et al. (2003)(Jimenez et al. 2003).

Due to computational demands involved with calculation of the rates from classical theory parameterisation of the nucleation rates is generally preferred and results in considerable reductions in the computing time required.

2.1.1 Binary Nucleation

Spontaneous nucleation can occur when the vapour pressure of sulfuric acid exceeds the saturation vapour pressure of the sulfuric acid-water mixture. However, the rates of nucleation are often much smaller than the observed production, therefore in the majority of cases new particle formation is dominated by processes other than binary nucleation. However, under certain conditions binary nucleation rates of sulfuric acid and water mixtures can still be significant.

Several parameterisations currently exist for binary nucleation; however their results differ significantly.

In general, all schemes are based on the classical theory with the sulfate aerosols generated treated as liquid droplets. Vehkamäki et al. (2002)(Vehkamäki et al. 2002) recently developed parameterised equations for the sulfuric acid-water nucleation under atmospheric conditions, in which nucleation was a function of the surface tension, density of the solution and equilibrium vapour pressures of both sulfuric acid and water above the solution. This parameterisation was a revision to one previously

developed by Kulmala et al. (1998)(Kulmala et al. 1998) and corrected the activity coefficients and errors made in the kinetic assumptions in the previous parameterisation. However, the theoretical basis of the parameterisation was still based on classical theory developed by Wilemski et al. (1984)(Wilemski 1984). Kulmala et al. (1998)(Kulmala et al. 1998) examined previous treatment of nucleation and concluded that previous parameterisations based on theory developed by Doyle (1961)(Doyle 1961) were thermodynamically incorrect.

The new parameterisation of the nucleation rate was shown to be in good agreement with theoretical rates for the temperatures between 230 and 300 K, relative humidities between 0.01 and 100% and for total sulfuric acid concentrations between 10^4 and 10^{11} cm^{-3} . However, when the number of molecules in the critical cluster exceeded 25 the fit between the parameterised rates and theoretical calculations was not so good.

A recent extension of the parameterisation of Vehkamäki et al. (2002)(Vehkamäki et al. 2002) was proposed by Herzog et al. (2004)(Herzog et al. 2004) down to 190K. Surface tension was calculated using the parameterisations of Vehkamäki et al (2002)(Vehkamäki et al. 2002), saturation vapour pressure for water according to Preining et al. (1981)(Preining et al. 1981), and saturation vapour pressure of sulfuric acid from Ayers et al. (1980)(Ayers et al. 1980) using the low temperature correction from Kulmala and Laaksonen (1990)(Kulmala and Laaksonen 1990). The composition of the particle generated is given by the parameterisation developed by Tabazadeh et al. (1997)(Tabazadeh et al. 1997), valid for temperatures between 185K and 260K.

2.1.2 Ternary Nucleation

As discussed in Section 2.2 particle formation rates often vastly exceed binary nucleation rates indicating that an additional formation mechanism must exist. Because of its high concentration in the troposphere and ability to decrease the vapour pressure of sulfuric acid above a solution it has been proposed that the enhanced nucleation rate is a result of a ternary reaction between $\text{H}_2\text{O}/\text{H}_2\text{SO}_4$ and NH_3 .

Parameterisation of ternary nucleation is consistent with observations and showed that nucleation rate increased in general with increased ammonia and sulfuric acid concentrations, although under limiting conditions this is not always the case, and decreased relative humidity and temperature. Model results were all within one order of magnitude with the largest errors observed at 298.15K where the low nucleation rates mean that the error is acceptable. Sensitivity analysis of the parameters showed that a NH_3 mixing ratio above 100 ppt had no significant effect on the nucleation rate except at very low sulfuric acid concentrations so the authors recommended that a mixing ratio of ammonia is 100 ppt for concentrations above 100 ppt. Comparison between the parameterised model and the full classical treatment of ternary dynamics showed that the parameterised predictions fitted in between the full model calculations. However, the parameterised version reduced the computing time by a factor of 10^5 . Due to limitations of the classical theory there are certain restrictions to the use of the model. Under low ammonia mixing ratios the mole fraction of the critical cluster changes rapidly which causes the classical theory to fail. In addition, the diffusion coefficient used in the model is not valid for highly surface active systems for example at very high concentrations of sulfuric acid and ammonia, where the surface concentration is vastly different from that of the bulk. Recent model predictions using measurements from the QUEST measurement campaign have highlighted a few more serious problems with the full ternary model. The results

showed that under certain conditions the nucleation rate calculated by the model exceeded the kinetic limit. Anttila et al. (2005)(Anttila et al. 2005) conclude that the reason for this discrepancy is that the model ignores the formation of ammonium bisulfate, which has a smaller nucleation potential than free sulfuric acid thus reducing the nucleation rate. Classical theory suggests that sulfuric acid cannot exist in free form and is either bound in ammonium bisulfate or ammonium sulfate cluster or hydrates. The authors compared the results of the new ternary model with particle formation observations and conclude that the new model cannot explain every event thus there must be other so far unknown mechanisms operating.

2.1.3 Ion induced nucleation

Ionic charge in particles can increase the formation of larger particle as a result of enhanced stability of the charge clusters and higher growth rates due to the electrostatic forces. Several models exist that can predict the rates of ion induced nucleation to varying degrees of accuracy. The mechanism of IIN is still not clear and model simulations are generally based on the assumption that the core consists of negative bisulfate ions and the critical cluster is stabilised by ammonia.

They all predict that IIN increased as ion production rate increased, temperature decreased and within the non limiting range with increasing sulfuric acid concentration. However, Kazil et al (2004)(Kazil and Lovejoy 2004) and Modgil et al. (2005)(Modgil et al. 2005) found that IIN could be responsible for the particle formation observations above the middle troposphere they were not consistent with observations of particle formation in the lower troposphere. Kazil et al. (2004) (Kazil and Lovejoy 2004)suggested that this was due to enhanced evaporation of the charged particles.

These results were in contrast to Laakso et al. (2002)(Laakso et al. 2002), who showed that IIN was capable of producing high concentrations of nucleation mode particles when existing particle surface area was low. Under certain conditions their model could reproduce the nucleation rates between 10 and 100 $\text{cm}^{-3} \text{s}^{-1}$ as observed above forests.

2.2 Observations of nucleation events and implications to the mechanisms

2.2.1 Remote environment

Recent measurements in a remote environment showed particle formation following an increase in the atmospheric concentration of sulfuric acid. Weber et al. (1996)(Weber et al. 1996) observed that the increase in particle number occurred about 1-2 hrs after an increase in sulfuric acid was measured at the ground based station at Mauna Loa Observatory. They concluded that part of the lag time was due to the time required for the particles to grow to measurable sizes and based on particle formation through homogeneous nucleation estimated a rate of 1 $\text{cm}^{-3} \text{s}^{-1}$.

Marti et al. (1997)(Marti et al. 1997) observed several events in which new particle generation occurred shortly after sunrise on days in which the measurement area received clean, near background air. These events showed a linear relationship between ultrafine particle number and production rate of sulfuric acid consistent with observations of Weber et al. (1996)(Weber et al. 1996). The increases in ultrafine particle number correlated more highly with increased sulfuric acid concentrations than increased concentrations of either anthropogenic or biogenic organic compounds. An increase in sulfuric acid concentration was observed about two hours prior to the ultrafine particle peak on all but one of the nucleation events. This time delay was similar to that observed by Weber and McMurry (1996)(Weber and McMurry

1996) and was presumably a result of the time required for the particles to grow to the minimum observable size (3 nm). In order to determine the source of this burst of nucleation particles the authors calculated the rates of sulfuric acid production, terpene generation and anthropogenic organic compounds. They found that particle formation correlated with sulfuric acid concentration and on one occasion ultrafine particles formed as a result of terpene oxidation. However, in this event the particle number concentration was much smaller than for the other events and occurred when the sulfuric acid concentration and the total aerosol surface area were much less than the average values. Therefore, although new particle production more closely correlated with sulfuric acid concentrations, biogenic organics have been linked to new particle formation in clean environments. This influence of terpenes has been more clearly demonstrated in studies over boreal areas, which will be discussed later.

Modelling studies on the effect of relative humidity, temperature and sulfuric acid concentration showed that the nucleation rate was not significantly affected when either the sulfuric acid concentration was increased to 1 pptv, or the surface area reduced, as a result of precipitation. However, when these were changed in conjunction with a decrease in temperature of 10 °C an increased nucleation rate of $0.1 \text{ cm}^{-3} \text{ s}^{-1}$ was predicted, similar to observations of Hoppel and Frick (1990)(Hoppel and Frick 1990), but significantly less than calculated by Weber et al. (1996)(Weber et al. 1996). The observations of new particle formation in Mauna Loa and Colorado(Weber et al. 1996) showed significant differences from classical binary theory of nucleation. Particles between 3 and 4 nm were observed at much lower concentrations than predicted by binary nucleation. In addition, plots of the flux of ultrafine particles as a function of sulphuric acid concentration showed a much different gradient than that expected based upon binary nucleation theory. As a

result the authors concluded that a third molecule, such as ammonia, might stabilise the subcritical clusters and thus enhance the nucleation rate.

These conclusions were consistent with simultaneous measurements of gas phase concentrations and submicrometre particle concentrations at a remote mountain site in Germany (Birmili et al. 2000). Estimated nucleation rates, on the order of $3 \text{ cm}^{-3} \text{ s}^{-1}$, required a sulfuric acid gas phase concentration of $3 \times 10^9 \text{ cm}^{-3}$, which is over two orders of magnitude higher than observed. However, using parameterisation of the ternary nucleation rate (Napari et al. 2002) and an estimated atmospheric ammonia concentration of 20 pptv the authors predicted that a sulfuric acid concentration of between 1 and $2 \times 10^7 \text{ cm}^{-3}$, consistent with their study, showed good agreement with the observed values.

A recent simulation of the different nucleation rates (Korhonen et al. 2003), based on atmospheric sulfuric acid concentrations of the order of 10^5 - 10^7 molecules cm^{-3} , showed that within the lower troposphere, at temperatures above 240K, ternary nucleation involving NH_3 - H_2SO_4 - H_2O could be over 10 orders of magnitude faster than binary nucleation.

The above studies indicate that elevated sulfuric acid concentrations and low surface area are required for nucleation to occur and are indeed favoured in the free troposphere, where temperatures are lower. Such rate enhancements could be achieved by the involvement of a third species, such as ammonia, or in the outflow of clouds, in which increased concentration of the sulfuric acid were observed as a result of increased photochemical production and decreased loss by condensation onto existing particles, as a result of the decreased particle surface area. The studies generally concluded that the nucleation rates exceeded those predicted by binary nucleation. Therefore, it appears only ternary nucleation is important when

investigating particle dispersion in a remote atmosphere. However, binary nucleation was observed to be significant in the upper troposphere(Weber et al. 1999), since temperature in the troposphere decreases with height and ammonia concentrations are generally too low for ternary nucleation to be important.

Kulmala et al. (2000)(Kulmala et al. 2000) showed that ternary nucleation could explain the particle formation observations of Weber et al. (1999)(Weber et al. 1999). They predicted that whilst under normal atmospheric conditions ternary nucleation could generate particles around 1 nm in diameter additional compounds were required for the particles to grow to 3 nm.

Recent increased measurements of positive and negative clusters in the upper troposphere–low stratosphere (UT-LS) suggest that ions could play an important role in particle formation and growth. Lee et al. (2003)(Lee et al. 2003) measured high concentrations of particles smaller than 9 nm between 7 and 13 km that had formed when clean air rose to 5 km, at which height a temperature less than 240K is expected. Lovejoy et al. (2004)(Lovejoy et al. 2004) showed that nucleation from negative sulfuric acid-water clusters is thermodynamically favoured at temperatures below 240K. Their measurements showed that new particle formation was favoured by increased sunlight and decreased surface area and the measured particle concentrations agreed with an ion-induced model simulation. Whilst ion-induced nucleation can explain some of the observed nucleation events in the UT-LS it is unlikely that it is responsible for particle formation in the boundary layer.

2.2.2 *Above forests*

A thorough study into the formation and growth of aerosols resulting from biogenic emissions was conducted above a coniferous forest in Southern Finland, as part of

the BIOFOR study, and the reader is directed to an overview of the results (Kulmala et al. 2001). The major findings of the study are outlined below. Nucleation events were predominantly observed in the spring and autumn with concentrations increasing during this time from about 2000 cm^{-3} to 10000 cm^{-3} . During all studies particle production was not detected when particle surface area exceeded $100 \mu\text{m}^2 \text{ cm}^{-3}$ (Aalto et al. 2001).

Due to the small size of the particles individual characterisation was impossible. However, Hameri et al. (2001) (Hameri et al. 2001) investigated the chemical composition of the particles through measurement of the hygroscopic growth rates of the particles and chromatographical analysis of particles collected on a micro orifice impactor. Growth rates of the nucleation particles, measured using two Tandem Differential Mobility Analysers, showed identical growth factors consistent with the particles being internally mixed with the growth factor remaining constant for particles formed during the morning and increasing in the particles generated in the early afternoon, indicating a change in particle composition with growth. The investigation of the growth as a function of relative humidity (RH), showed that either the particles were composed of a single soluble compound, such as ammonium bisulfate or sulfuric acid but not ammonium sulfate, or the soluble fraction is a mixture of several compounds with combined deliquescence below 70% RH. The growth of the nucleation particles indicated that, whilst the gas phase sulfuric acid concentrations were consistent with the formation of new particles by ternary nucleation they were not high enough to explain the observed growth rates. Therefore, the authors concluded that the soluble mass fraction of the nucleation particles must include a significant amount of soluble organic compounds. The analysis of the particles collected on the impactor showed very small differences between event

and non event periods. However, particles from event days always contained both methanesulfonic acid (MSA) and dimethylamine (DiMA). MSA is indicative of marine air and suggested that the nucleation events occurred on days when the air was blown from the Arctic and polar regions. This air is relatively clean and would be expected to have reduced surface area, a condition favourable for nucleation. DiMA is a basic end product of the microbial degradation of organic matter and expected to enhance the rate of nucleation in an identical manner to ammonia. A similar conclusion was reached by Bigg et al. (2004)(Bigg 2004), who observed an increase in nucleation particle concentration when microbial activity was at its highest, providing that sufficient moisture was present.

Secondary organic aerosols (SOAs) are another possible source of new particles in a forest environment. SOAs are low or semi volatile organic compounds with vapour pressures lower than 1.3×10^{-4} atm(Turpin et al. 2000) formed by atmospheric oxidation of reactive organic gases emitted by a large variety of anthropogenic and natural sources, including combustion of fossil fuels and wood, biomass burning, solvent use, emission by vegetation and the oceans(Duce et al. 1983; Seinfeld and Pandis 1998; Jacobson et al. 2000). Once the vapour pressure of the SOA exceeds the saturation vapour pressure the compound condenses to form a particle. Whilst most reaction rates increase with increasing temperature, adsorption and condensation rates decrease with increasing temperature.

The Intergovernmental Panel on Climate Change estimate that between 8 to 40 Tg/yr of SOAs come from biogenic sources(Houghton et al. 2001), whilst Kanakidou (2000)(Kanakidou et al. 2000) estimated that anthropogenic sources could increase SOA production by upto 50 Tg/yr. However, no method currently exists capable of distinguishing between primary organic and secondary organic aerosols.

Rogge et al. (1993)(Rogge et al. 1993) observed a seasonal variation in the formation of organic aerosols, with a maximum concentration of organic acids in the early summer consistent with increased formation by photooxidation as a result of increased incident uv radiation. In addition, Schauer et al. (1996)(Schauer et al. 1996) studied the ratio of atmospheric concentrations of organics to their emission rate. Whilst inert aerosol species had ratios much smaller than 1, other species had ratios much greater than 1 suggesting that they were being formed in the atmosphere.

Originally terpenes were suspected to be the major contributor of SOAs due to their low vapour pressure and ubiquitous presence over forests. Limbeck et al. (2003)(Limbeck et al. 2003) showed that secondary aerosol formation of atmospheric polymers could occur by heterogeneous reaction of isoprenoids or terpenoids in the presence of a sulfuric acid aerosol catalyst and could be an additional source of secondary aerosols in the continental aerosol. However, Janson et al. (2001)(Janson et al. 2001) observed that monoterpene production was greatest during periods in which nucleation was not observed and a minimum during maximum nucleation activity. They concluded that whilst terpenes could enhance growth rates they were not responsible for the new particle formation. Furthermore, Odum et al. (1996)(Odum et al. 1996) observed a dependence of aerosol yield on aerosol mass, indicating that the absorption and adsorption of SVOCs onto pre-existing molecules was more important than homogeneous nucleation.

Observations of particle formation rates upto $100 \text{ cm}^{-3} \text{ s}^{-1}$ within a forest suggest that the majority of particles are formed by ternary nucleation. Although at various times of the year the SOA formation could significantly increase and indeed dominate the particle concentrations. In addition, the increased soluble organic fraction observed by Hameri et al. (2001)(Hameri et al. 2001) and rate enhancements resulting from

either complex formation between organic acids and sulfuric acid or reaction with basic compounds produced by decaying vegetation suggest that organics could have a significant role in aerosol production above forests and indicate that more research is required to ascertain their role in new particle formation.

Joutsensaari et al. (2005)(Joutsensaari et al. 2005) recently showed that VOC emissions from plants increased dramatically when they are subjected to stress. The authors concluded that concentrations of non volatile organics originating from plants that were required for nucleation were an order of magnitude greater than that observed in particle formation events and so homogeneous or ion induced nucleation was responsible for the particle nucleation.

In spite of the debate into the nature of the compounds responsible for SOA formation the importance of SOAs in certain environments is not in doubt.

2.2.3 *Marine Boundary layer (MBL)*

A review of aerosols over remote oceans (Fitzgerald 1991) concluded that the majority of the aerosols are of marine origin with relatively uniform concentration in trade wind regions upto $300 \text{ particles cm}^{-3}$. Submicrometer particle, which showed a distinct bimodal appearance, contributed upto 95 % of the total particle number consisted mainly of non sea salt sulfate formed principally from DMS oxidation. However, sea salt particle concentrations were found to be much larger with a strong dependence on wind speeds.

More recent ocean studies, including (Clarke et al. 2006) have shown that sea salt aerosols produced by breaking waves are a significant constituent of marine aerosols with sizes as small as 10 nm observed and upto 60 % of the particles smaller than 100 nm in diameter. Hygroscopic growth rates have shown that the majority of these

particles are sea salt consistent with earlier studies. (Clarke et al. 2006) estimated that in marine regions between 5 and 90% of the particles originated from the sea salt flux with the remainder entrained from the free troposphere, consistent with observations. Similarly during the INDOEX campaign large concentrations of aerosols between 400 and 10000 particles cm^{-3} were observed in the monsoon season with higher concentrations observed towards the northern Intertropical Convergence Zone(Kamra et al. 2003). The nucleation mode showed large variability with a bimodal distribution occurring further away from the coastline and Kamra et al (2003) concluded that homogeneous or heterogeneous growth was responsible for the shift in particle distribution with the maximum in the accumulation mode observed at 133nm. The nucleation mode particles resulted from the homogeneous nucleation in the outflow flow of clouds followed by entrainment of these air masses from the free troposphere. The sulfur dioxide concentration observed over the open ocean was observed to be 2 orders of magnitude smaller than required for new particle production (Cainey and Harvey 2002) and they concluded that a significant proportion of the sub micron sulfate aerosol originated in the free troposphere. This is consistent with other studies that showed that only under clean air conditions could DMS contribute to new particle formation in the open ocean(Yoon and Brimblecombe 2002).

Similarly Weber et al (2001) ³(Weber et al. 2001) observed no nucleation events over the ocean between Hawaii and Tahiti despite sulfuric acid concentrations between 10^7 and 10^8 molecules cm^{-3} . This however was in contrast to a previous study (Clarke et al. 1998; Clarke et al. 1998) where strong nucleation events were observed under similar conditions. The difference in the two studies was speculated to be the result of ternary nucleation and that differences in ammonia concentrations, which were not measured could be responsible.

However the oxidation of dimethyl sulfide, emitted from phytoplankton, has also been shown to positively correlate with cloud condensation nuclei. Arsene et al (2005) (Arsene et al. 2005) concluded that DMS contributed significantly to non sea salt sulfate with the MBL.

Thus three sources of particle have been shown to exist in the remote MBL with sea salt emissions, resulting from the ocean to be the dominant source, whilst entrainment of particles from the free troposphere formed in clean air in the outflow of clouds could also contribute significantly to particle number. The local formation of particles from DMS oxidation was generally observed to account for less than 5% of the total submicrometer particle number.

Using a model that calculated particle number concentration based on the combined contributions of sea salt emissions and homogeneous nucleation Capaldo et al. (1999)(Capaldo et al. 1999) showed that observations of particle number concentrations typically agreed with the model predictions in the MBL. However, occasionally significant differences between the model predictions and observations occurred that could not be fitted using the existing model. Whilst binary nucleation can be an important source of new particles in order to predict the large oscillations observed in the ultrafine particle number in the MBL a rate enhancement in the H_2O - H_2SO_4 reaction of between 10^7 - 10^{10} was required. They suggested that the new particles may have originated due to entrainment of clean air from the free troposphere or achieved by an ammonia concentration of 1pptv.

Clarke et al. (1999)(Clarke et al. 1999) observed no evidence of new particle generation in the MBL but observed new particle concentrations between three or four orders of magnitude larger in the free troposphere. These high nucleation events occurred in the outflow of clouds and resulted from increased H_2SO_4 concentrations,

which were generally associated with increased photochemical production, combined with a reduced surface area in this region. The peaks were observed in the ultrafine particle number when the particle surface area was between 5 and 10 $\mu\text{m}^2 \text{cm}^{-3}$. However when the surface area was either greater than 20 $\mu\text{m}^2 \text{cm}^{-3}$ the ultrafine particle number varied about zero or when the surface area was below 5 $\mu\text{m}^2 \text{cm}^{-3}$ particle number was low. They concluded that this behaviour was due to the lower water content of the air as this air was not influenced by clouds. The distinct diurnal variation in ultrafine particle concentrations observed in the afternoon was consistent with the increased photochemical production of H_2SO_4 in the outflow of the clouds. These observations inferred that homogeneous nucleation played a significant role in nucleation in the free troposphere in the downwind region of clouds and the entrainment of this free tropospheric air could result in the increased ultrafine particle numbers observed by Capaldo et al. (1999)(Capaldo et al. 1999).

Although particle numbers in the open ocean are generally low and dominated by sea salt particles massive particle formation events have been observed in coastal areas, where the tidal variations expose considerable quantities of phytoplankton and seaweed to the atmosphere. As a result large bursts of particles have been observed. O'Dowd et al. (2002) (O'Dowd et al. 2002) observed bursts of new particles have been observed in coastal areas with peak particle concentrations exceeding 10^6cm^{-3} . However, Kulmala et al. (2002)(Kulmala et al. 2002) were unable to reproduce the observed particle formation events during the PARFORCE campaign using a ternary nucleation model. Whilst ternary nucleation is still likely to occur in coastal regions, the correlation of particle formation with low tide conditions and solar radiation (O'Dowd et al. 1998; O'Dowd et al. 1999) suggested that another source of particle formation exists in coastal regions.

De Leeuw et al. (2002)(de Leeuw et al. 2002) observed that bursts of new particles over a coastal region were strongly affected by tidal flows. They found that the particle production events showed no clear correlation with wind speeds or temperature but were significantly affected by enhanced heat fluxes. These corresponded to times when the shore biota were exposed and thus suffered increased stress due to lack of water and exposure to uv radiation.

Gas phase measurements showed that although sulfuric acid and MSA did not correlate with the low tide occurrences(Berresheim et al. 2002) diiodomethane concentrations did(Carpenter et al. 1999). In addition, Carpenter et al. (1999, 2000)(Carpenter et al. 1999; Carpenter et al. 2000) have shown that under conditions of stress biota produce increased biogenic vapours. Analysis of the nucleation particles showed that all the particles contained detectable amounts of iodine with most of them also containing sulfate(Makela et al. 2002). A recent chamber study(Jimenez et al. 2003) showed that the photolysis of atmospherically relevant concentrations of diiodomethane, of about 15 ppt, in the presence of ozone resulted in significant new particle formation followed by rapid condensational growth. They observed no change in the nucleation rate with increased relative humidity, which contrasts with modelling predictions for either binary or ternary nucleation and further suggests that binary or ternary nucleation are not responsible for the particle formation events in coastal areas. Particle composition of aerosols greater than 20 nm showed no change in relative intensity of the peaks in the mass spectrum, indicating that the compounds responsible for the particle growth were the same as those responsible for nucleation and concluded that although OIO is most likely responsible for the observations the chemical analysis was not conclusive. Whilst the absence of particles in the absence of ozone implies that solid iodine particles are not

responsible for nucleation the non constant concentrations of the iodide species at the onset of nucleation suggests that the exact mechanism is incomplete. These observations are consistent with the low hygroscopic growth rates of the particles formed during low sulfuric acid concentrations measured by Väkevä et al. (2002)(Väkevä et al. 2002) and O'Dowd et al. (2002)(O'Dowd et al. 2002), which contained considerable amounts of iodine. The hygroscopic low growth rates observed for particles smaller than 20 nm was inconsistent with the presence of ammonium sulfate or sulfuric acid, and suggests that the particles were mainly composed of insoluble inorganic or organic compounds. These observations agree with laboratory findings and together with the absence of high concentrations of VOCs suggest that new particle formation in coastal areas is linked to iodine oxide. Particles larger than 20nm were more probably composed of common salts based on the higher hygroscopic growth factors of these aerosols. Similar to growth rates observed for aged marine aerosols(Zhou et al. 2001).

The particle nucleation rates were predicted to be comparable to those measured in the PARFORCE study, approximately $1 \times 10^5 \text{ cm}^3 \text{ s}^{-1}$. However growth rates were considerably lower than the upper limit predicted by O'Dowd et al (2002)(O'Dowd et al. 2002). The authors consider this could be a result of the large uncertainties in the measurements of the ultrafine particles and precursor concentrations at PARFORCE.

Whilst new particle occurrences have been observed as a result of increased sulfuric acid concentrations in the MBL the extremely high particle concentrations and rates of formation in coastal regions were strongly influenced by tidal and ultraviolet factors. This suggests that dimethylsulfide oxidation does not lead to appreciable aerosol formation within coastal regions in the MBL(Berresheim et al. 2002; Yoon and Brimblecombe 2002; Lucas and Prinn 2003) and the particle events are a result

of photolysis of iodocompounds produced by marine organisms or entrainment of particle rich air.

2.2.4 Urban Environments

Within urban areas two mechanisms for ultrafine particles formation exist. The first involves emission of particles formed either inside or with the first metre of exiting the exhaust pipe, which appears to be a result of the condensation of lubricating oil vapour. This is the dominant process and largely determines the number concentration of particles in urban air (Morawska et al. 1998; Morawska 2003). The second process appears to be associated with nucleation probably arising from sulfur dioxide oxidation with subsequent condensational growth of particles, probably from VOC oxidation products. This occurs on a much larger spatial scale than the first process.

A review of particle emission is outside the scope of this section and the reader is directed to a comprehensive review of vehicles as sources of ultrafine particles within urban areas by Morawska (2003) (Morawska 2003).

Studies investigating new particle formation eliminated particles directly emitted from the exhaust based on the correlation of the ultrafine particle (UFP) concentration with CO and NO_x. Since UFPs, CO and NO_x are emitted by vehicles, UFPs emitted from vehicles correlate strongly with CO and NO_x, whereas the UFP formed in the atmosphere by nucleation and growth should not correlate with CO but would correlate well with SO₂. Based on the above correlations significant nucleation events have been observed in urban studies (Jeong et al. 2004; Zhang et al. 2004). In a number of studies higher particle numbers were observed in the morning rush hour compared to the afternoon rush hour. Whilst direct emissions were responsible for the majority of particles smaller than 30 nm (Wählén et al. 2001; Wehner et al. 2002)

(Molnar et al. 2002), based on correlations with CO, NO_x and vehicle numbers, Charron and Harrison (2003) (Charron and Harrison 2003) postulated that the variation in particle surface area present could be responsible for the diurnal variation observed. The low particle number concentration prior to the morning rush hour did not provide sufficient surface area for low volatile gases, namely sulfuric acid, to condense and thus allowed the gases to nucleate and grow, whereas in the afternoon the high particle concentration promoted the condensation of these nucleating gases and so reduced particle formation. Charron and Harrison (2003)(Charron and Harrison 2003) observed no correlation between particles smaller than 30 nm and traffic counts and found that the highest concentrations of particles smaller than 30 nm were measured at the start of the rush hour, during the nights between Friday and Saturday and Saturday and Sunday and increased particle numbers occurred immediately after rain events. They concluded the particle events the particles were being formed via nucleation processes as opposed to emitted directly from the tailpipe as a result of the cleaner air prior to the increase in traffic numbers. Furthermore, they observed a reasonable correlation ($R^2=0.73$) between the decrease in nucleation events and increasing temperature. These observations were consistent with Alam et al. (2003)(Alam et al. 2003), who observed a link between particles with diameters between 30 and 60 nm and light vehicles, but no correlation between vehicle numbers and particles ($11 \text{ nm} < d < 30 \text{ nm}$). They concluded that the smaller particles were not emitted by the vehicles but formed in the atmosphere. The correlation between the larger particles and vehicles was consistent with the size distribution emitted from spark injection and diesel vehicles, where the majority of the particles were measured to be in the size range 20 to 60 nm and 20 to 130 nm respectively(Guenther et al. 1996; Maricq et al. 1998; Morawska et al. 1998; Ristovski et al. 1998)

Zhang et al. (2004)(Zhang et al. 2004) observed new particle formation at the same time as an increase of SO₂, a decrease of CO and modelled rise of the boundary layer height. The changes in gas phase concentration and boundary layer height indicated the break up of the morning inversion layer and rapid mixing of SO₂ enriched air from the mid troposphere with the more polluted city air.

Stanier et al. (2004)(Stanier et al. 2004) compared nucleation events during summer and winter in Pittsburgh with predicted particle formation curves based on the binary nucleation mechanism. During the study they observed nucleation occurred on between 30 to 50% of the days at much higher surface areas and lower sulfuric acid concentrations than predicted by the models, suggesting that additional factors were involved. These observations contradicted aerosol dynamics simulations(Pohjola et al. 2003) of the emission of pollutants from exhausts, that showed high concentration of particles in the plume acted as a highly effective condensational sink for sulfuric acid, and was sufficient to prevent new particle formation through either binary or ternary nucleation. The reasons for the nucleation events during days with higher surface areas and lower sulfuric acid than predicted were not clear.

The charge fraction of particles emitted from diesel vehicles using an SMPS coupled to an Electro Static Filter (ESF) was measured and comparison on the SMPS signal with the ESF on and off showed that the nuclei particles contained only a small amount of charge compared to the accumulation mode particles (Jung and Kittelson 2005). Therefore, Jung and Kittelson concluded that ion-induced nucleation was not the dominant mechanism in urban particle formation

Shi and Harrison (1999)(Shi and Harrison 1999) calculated that during the dilution of the exhaust binary nucleation can occur, with higher nucleation rates predicted at lower temperatures and higher humidities. This is supported by Hee-Kim et al.

(2002)(Kim et al. 2002) and Vehkamäki et al. (2002)(Vehkamäki et al. 2002) who predicted that the critical nucleation cluster size decreased with increasing relative humidity. However, these predicted rates were still about two orders of magnitude lower than the measured rates. In addition, Napari et al. (2002)(Napari et al. 2002), predicted that ternary nucleation rates decreased with increasing relative humidity.

Friedlander et al. (1977)(Friedlander 1977) commented that the saturation reached a maximum with a dilution ratio of between 5:1 and 50:1 due to the combined effects of a decreased vapour pressure with increased dilution and the non-linear decrease in saturation vapour pressure with dilution due to a decrease in the exhaust temperature. However, the supersaturation necessary for spontaneous nucleation is not generally achieved.

Recent simulations(Zhang et al. 2004) showed that the barrier to nucleation could be lowered through the formation of an irreversible complex between organic acids and sulfuric acid. Chamber studies confirmed the rate enhancement, as a marked increase in the particle concentration was observed within the chamber upon addition of benzoic, p-toluic or m-toluic acids to a fixed concentration of H₂SO₄, with a shift in the particle size distribution to larger diameters, indicating that the organic acids were capable of enhancing the particle formation by up to a factor of 13 compared to binary nucleation. They concluded that the magnitude was comparable to the magnitude of the ternary rate enhancement observed with 0.1ppb of ammonia, and could be responsible for the enhanced particle formation observed in plumes over Asia, in which elevated concentrations of SO₂ and CO were also measured(Weber et al. 2003). The authors suggested that whilst the major mechanism for particle formation was ternary nucleation involving ammonia, the nucleation was limited by the sulfuric acid concentration and thus other mechanisms were also involved. Zhang et al

(2004)(Zhang et al. 2004) showed that organic acids could enhance particle formation even in the absence of water possibly through the formation of a highly stable complex, which would explain the organic weight fraction observed in nucleation particles.

The above studies showed there significant numbers of UFPs exist in an urban environment emitted as primary particles from exhaust and formed in the atmosphere Whilst primary emissions are in general higher than particle formation events in the urban atmosphere, elevated particle number concentrations were observed shortly after clean air periods when nucleation was favoured by low surface area periods concurrent with increased sulfuric acid concentration. It is important to note that most of the studies did not directly measure the sulfuric acid concentration but estimated it from the product of the solar radiation and SO₂ concentration. Elevated particle concentrations were most frequently observed between spring and autumn, since sulfuric acid is generated from the photooxidation of SO₂ and so dependant on solar irradiance.

3. Particle growth

Particle growth occurs through coagulation and condensation both of which are dependant on particle size. Coagulation involves the collision of particles with one another due to the motion between them. In polydisperse particle size distributions coagulation is more effective between particles of different sizes, since it is a function of the particle size, diffusion coefficient of the particle (also size dependent) and particle number. Whilst large particles provide a large surface area for absorption smaller particles have a greater diffusion rate. Condensation is a function of saturation vapour pressure and available particle surface area, both of which are related to

particle diameter. Within the different environments the varying concentrations of sulfuric acid and low volatile organic compounds between clean and polluted areas resulted in significantly different growth rates.

3.1.1 Coagulation

Coagulation results in a decrease in particle number concentration but conserves particle mass through the formation of a single particle following a collision between two aerosols. Algorithms describing coagulation have been developed based on Brownian activity of the particles. In the so called free molecular regime, involving molecules with a diameter less than 200 nm, corresponding to the situation when the mean free path of the diffusing particle is similar to the radius of the particle a correction to the coagulation rate must be made. Other factors influence coagulation rates between atmospheric particles including Coulombic forces between charged particles that can either increase or decrease the rate depending on the relative charges, and hydrodynamic forces that reduce the rate of coagulation due to the incompressibility of the fluid at close distances.

3.1.2 Condensation

Condensation is typically the partitioning of species between the gas and particle phases is the result of concentration differences between the ambient and equilibrium concentrations. However, due to similarity between the size of the nanometre sized particles and the gas molecules condensation onto the new particles is best determined by the rate of collisions between the gas molecules and the particles (Lehtinen and Kulmala 2003). Most condensation models neglect the diffusional effects of the particles molecules through the air. However, for the condensation on to nano

particles, since the gas dimensions are similar to those of the particles, ignoring the diffusion of the particles through the air can lead to an over estimation of the condensation rate.

Depending on the nature of the species the characteristics of the partitioning differs. Absorption of SVOCs can be divided into water soluble and water insoluble compounds, where the water insoluble compounds are partitioned into the organic phase of the particle, whilst the water soluble compounds are absorbed into the water phase. The partitioning of the non water soluble organics is dependent on the composition of the particle and vapour pressure of the compound above the surface, whilst the uptake of water soluble compounds is determined by the Henry's law constant of the species and its ability to dissociate in solution. Thus, the dissociation of solutes into ions can increase the uptake potential of a species.

Within the aqueous phase are inorganic compounds such as nitrate, sulfate, ammonium and sodium ions that can interact with the water soluble organic compounds present and through changes in the pH within the solution can affect the dissociation of the organic acids and bases present.

Condensation of organic compounds depends on their vapour pressure above the particle as well as the particle size, since the equilibrium vapour pressure above a curved surface is increased for small particles by the Kelvin effect. Tang and Munkelwitz (1993)(Tang and Munkelwitz 1993) and Gysel et al. (2002)(Gysel et al. 2002) demonstrated the dependence of growth curves and deliquescence points on temperature and relative humidity.

3.2 Observations of particle growth within the atmosphere

Typical particle growth rates range between 1-20 nm h⁻¹ with lowest growth rates (0.1 nm h⁻¹) observed in clean polar environments. One of the clearest indications of the difference in growth rates between clean and polluted environments is the difference in the lag time between changes in sulfuric acid concentrations and observation of nucleation particles. In remote environments considerable lag times of between 1-2 hours were observed between increases in the SO₂ concentration and detection of particles by the SMPS; however, in urban environments increases in nucleation particle concentrations occurred simultaneously with increased SO₂ concentrations.

A serious problem is that growth rates are often implied based on the distance from the source and size distribution of the nucleation particles. This can result in large errors of upto 100% in the rate due to the size of the critical cluster assumed. For example model calculations using parameterisations of Napari et al. (2002)(Napari et al. 2002) and Vekhamaki et al. (1999) predicted that under identical conditions the critical cluster sizes from ternary and binary nucleation were 1.2 and 2.4 nm respectively. These diameters were calculated using a RH of 20%, however, as the RH increased the difference in critical cluster diameter between the nucleation mechanisms decreased with a particle diameter of 1.6 nm predicted at RHs above 80% for both mechanisms.

Based on observations of particle growth, over rural and agricultural environment 40 km from an urban centre, coupled to thermodesorption patterns of the aerosols (Wehner et al. 2005) predicted that whilst the majority of the core growth of particles resulted from sulfuric acid, upto 40% could be accounted for by non volatile condensation. However, once the particle had reached 10 nm they concluded that growth was dominated by condensation of non volatile compounds. Laasko et al. (2005) predicted that preferential condensation of molecules could occur on

charged particles but gave a maximum growth rate enhancement of less than 2. Thus they calculated a particle growth rate of 2 nm h^{-1} based on a concentration of condensable gases of $1 \times 10^7 \text{ cm}^{-3}$.

3.2.1 Remote environments

A particle growth rate of 2.1 nm h^{-1} was observed at a remote continental site (Birmili et al. 2000). They concluded that the growth was caused by condensation of sulfuric acid and is consistent with the growth rate calculated by Weber et al. (1997)(Weber et al. 1997) based on lag times and changes to UFP concentration through the effects of cluster scavenging by preexisting surface area. Particles smaller than 3 nm grew at a rate of 1.6 nm h^{-1} , with higher growth rates for particles larger than 3 nm. Using estimations of growth rates from Friedlander et al (1977)(Friedlander 1977) based on SO_2 and OH concentrations Weber et al. (1997)(Weber et al. 1997) calculated that these rates were up to 10 times higher than possible through condensation of sulfuric acid and correlations between terpenes and aerosol surface area and volume showed that of terpene condensation was responsible for the particle growth.

Pirjola et al. (1998)(Pirjola et al. 1998) observed particle growth over a remote Arctic environment consistent with condensation of sulfuric acid. The growth rate was higher in the summer consistent with increased sulfuric acid formation from the reaction of SO_2 with OH radicals, although the concentration of sulfuric acid was sufficient for particle growth. Thus all studies show similar growth rates approximately 2 nm hr^{-1} occurring through condensation of either sulfuric acid or terpenes.

3.2.2 Above forests

Dal Maso et al. (2002)(Dal Maso et al. 2002) observed growth rates over forests of between 2-4 nm h⁻¹, consistent with an estimated condensable vapour concentration of 2 to 5 x10⁷ cm⁻³. Modelling simulations(Kulmala et al. 1998) showed that condensation of organics from the gas phase could account for the growth rates observed. Indeed recent simulations(Antilla et al. 2004), showed that reductions in the concentrations of either sulfuric acid or condensable organic compounds decreased or even totally suppressed particle formation altogether, since self coagulation was only effective in promoting cluster growth when the nucleation rate exceeded 10³ cm s⁻¹. Observed nucleation rates, discussed in section 3.1 suggest that this is unlikely and particle growth occurs through condensation of low volatile organics or sulfuric acid. Spontaneous condensation of water soluble organic vapour onto nanometre sized clusters agreed with a modelling simulations of the flux of soluble and insoluble vapour towards the particle surface study performed during the BIOFOR study(Pirjola and Kulmala 2001). The authors showed that the observed sulfuric acid concentration was too low to explain the observed hygroscopic growth and suggested that a significant fraction of the soluble mass of the particle could only be explained by the condensation of a soluble organic compound. Similarly Laakso et al (2002) (Laakso et al. 2002) predicted that without organics growth rates were so small that no particles larger than 3 nm were formed. Thus concluded sulfuric acid alone cannot explain the growth rates in forests.

Joutsensaari et al. (2005)(Joutsensaari et al. 2005) observed growth rates upto 70 nm h⁻¹ during periods when plants were subjected to high stress. However, during these periods the concentration of condensable vapour was approximately an order of magnitude higher than generally measured. When the growth rates were scaled to the observed concentrations of organics the growth rates were consistent with those

observed in forests and thus the authors concluded that non volatile organics originating from plants were responsible for the high growth rates observed over forests.

Antilla et al. (2005)(Anttila et al. 2005) measured higher concentrations of long chain alkanes and C-18 alkanolic acids on the particle formation days compared to non formation days, which suggests that they could be either responsible for new particle formation or condensational growth onto the nucleation particles.

Size effects on the growth rate have been demonstrated by Kulmala et al. (1998)(Kulmala et al. 1998) with the growth rate of nucleation particles of approximately 1 nm h^{-1} . However, then particles grew more rapidly to 70 nm in about 10 hours during the summer and slightly slower in the spring and autumn. A similar trend was found by Hirsikko et al. (2005)(Hirsikko et al. 2005), who observed that the concentrations of cluster ions and intermediate ions over a forest showed a clear seasonal cycle with summer growth rates the highest for particles larger than 3 nm but lowest for particles smaller than 3 nm. This is consistent with observations of increased growth rates for larger particles in remote environments(Weber et al. 1997). UFPs at a rural site(Alfarra et al. 2004; Zhang et al. 2004) contained a significant fraction of organics which correlated with gas phase CO, and unsaturated organics characteristic of vehicle traffic. These observations suggest that particle growth was heavily influenced by condensation of the SVOCs on the nucleation particles. Furthermore, O'Dowd et al. (2000)(O'Dowd et al. 2000) observed that following nucleation the mass fraction of the accumulation mode of fine particles increased to upto 75% indicating that the condensation of organic compounds onto particles over forest could be responsible for much of the particle growth.

3.2.3 *Marine Boundary Layer*

Similar to the increased nucleation rates over coastal areas discussed earlier very high particle growth rates have been observed over coastal areas as a result of the exposure of marine organisms to the sun. From the time required for growth of particles from 1 nm to at least 3 nm O'Dowd et al. (2002)(O'Dowd et al. 2002) inferred a minimum growth rate of 360 nm h^{-1} with rates upto 1300 nm h^{-1} observed during the strongest particle events, resulting from intense biogenic sources close to the shoreline. These growth rates compared to slower rates around 4 nm h^{-1} as the aerosol plume advected upto 180 km offshore(O'Dowd 2002). These figures were slightly higher than those estimated by Dal Maso et al. (2002)(Dal Maso et al. 2002) during coastal particle events. The coastal growth rates could not be fully explained by condensation of sulfuric acid as the sulfuric acid concentrations were at least two orders of magnitude lower than required. A chamber study investigating growth rates around coastal areas observed growth rates between 18 and 300 nm h^{-1} , with analysis of the particles indicating the presence of organics originating from the photo oxidation of diiodomethane(Jimenez et al. 2003). Furthermore hygroscopic growth (Väkevä et al. 2002) showed that the larger particles contained considerable amounts of insoluble material.

Dal Maso et al. (2002)(Dal Maso et al. 2002) observed growth rates between 120 and 180 nm h^{-1} during a clean event day, where the particle source was assumed to be coastal compared to between 15 and 20 nm h^{-1} on a day where the source of the particles were carried in polluted air from upto 3 km from the measurement station.

Therefore, the growth over coastal regions appears to be significantly enhanced by the

condensation of low volatile iodocompounds that are formed from compounds emitted by marine biota due to exposure to uv radiation following low tides.

3.2.4 *Urban environment*

Based on several urban studies typical growth rates in urban centres ranged from 2 to 10 nm h⁻¹ with growth rates upto 18 nm h⁻¹ observed in a highly polluted urban city (Monkkonen et al. 2005), similar to rates from Atlanta (Stolzenburg et al. 2005). Shi et al. (2001)(Shi et al. 2001) observed that the percentage of nanoparticles in the total particle number concentration as distance from the vehicle source increased to 350 m and estimated that growth rates were approximately 4nm h⁻¹, consistent with the lowest rates observed by Stanier et al. (2004)(Stanier et al. 2004). Jung and Kim (2006)(Jung and Kim 2006) showed that growth rates due to coagulation and condensation were of the order of 2 nm h⁻¹ under typical urban conditions.

In a recent dispersion study within a street canyon Gidhagen et al. (2004)(Gidhagen et al. 2004) observed that coagulation contributed significantly to the reduction in particle number concentration under low wind speeds. However, they noted that the changes in particle size distribution could not be fully explained by coagulation and deposition and suggested that the condensation of SVOCs might account for the difference. This agreed with predictions by Kittelson 1998(Kittelson 1998) and Shi et al 1999(Shi and Harrison 1999) who showed that semi-volatile substances could account for the growth of particles in the vehicle exhaust during the first few seconds of dilution.

This agreed with simulations that showed within urban environments under low wind speed conditions coagulation was the major removal process for particles. (Pohjola et al. 2003; Pohjola et al. 2006) predicted an increase in particle number predicted for

the model runs excluding coagulation. Only when the concentration of condensable organic vapour exceeded 10^{13} cm^{-3} did condensation have an effect on particle number concentration. Additionally, when dilution of the exhaust was excluded coagulation reduced the particle concentration an order of magnitude after 25 s. Therefore, rapid dilution of the plume means that coagulation of the particles is only important very close to the emission source or under highly polluted circumstances. Seigneur (1986)(Seigneur et al. 1986) observed that coagulation was only significant in urban conditions.

In contrast, Wehner et al (2002)(Wehner et al. 2002) showed that with a constant concentration of condensable gases of $1 \times 10^9 \text{ cm}^{-3}$ the sectional aerosol dynamics model of Birmili et al. (2000)(Birmili et al. 2000) could reproduce the observed particle size distribution in an urban street canyon. When they included the effects of dilution and entrainment from other streets, by assuming a continuous rates of dilution and entrainment with a ratio of entrainment to dilution of around 0.13 the model, reproduced observations of growth rates (Birmili and Wiedensohler 2000) between 3 and 11 nm h^{-1} after around 30 minutes. Their simulations suggested that both condensation and coagulation are relevant to urban dispersion. Zhang and Wexler (1999) calculated that condensation is the major growth process for particles larger than 50 nm and coagulation dominated for particles smaller than 50 nm in the urban atmosphere.

Ketzel et al. (2005)(Ketzel and Berkowicz 2005) used the multi-plume aerosol and transport model to estimate the individual contributions of coagulation, condensation and deposition to a particle size distribution in an urban environment. The model predictions showed that coagulation and condensation have a considerable effect on the number concentration and caused a small shift to larger diameters. When a

growth rate of 1 nm h^{-1} was used the simulation of all processes showed good agreement with the roof top concentrations and particle size distribution. However, when a growth rate of 6 nm h^{-1} was used the shift in the size distribution and the decrease in particle number concentration below 30 nm was overestimated. A growth rate of 1 nm h^{-1} is considerably smaller than the majority of observations in urban environment and suggests that other factors may be important. For instance, Kim et al. (2002) observed that high concentrations of NO_2 suppressed particle formation through competition between SO_2 and NO_2 for OH radicals. This coupled to the higher growth rates could be responsible for the observations of particle formation from Ketznel et al. (2005) (Ketznel and Berkowicz 2005).

Hee-Kim et al (2002) predicted an increased growth rate when the percentage of sulfur in the fuel was increased from 13 to 125 ppm, suggesting that condensation of sulfuric acid was important in the particle growth close to the exhaust outlet. Their model results excluded the condensation of organics but agreed well with observed concentrations and particle size distributions at different points in the plume.

Väkevä et al. (2000, 2002)(Vakeva et al. 2000; Väkevä et al. 2002) observed an increase in the soluble fraction of the aerosol coincident with particle growth events, indicating that whilst nucleation particles consisted of non or weakly soluble species, the larger particles had hygroscopic properties similar to common salts.

The contrasting contribution of coagulation and condensation as well as the differing opinions of the species responsible for condensational growth with urban environments means that urban growth mechanisms is still the centre of much debate.

4. Conclusion

Significant differences have been observed in the nucleation rates in the various environments, with the highest rates observed in coastal areas, where during low tides uv exposure causes seaweed to emit high quantities of iodocompounds. These are highly photolytic and result in high concentrations of new particle precursors and low volatile compounds that can result in large bursts of new particles together with growth rates of upto 1300 nm h^{-1} . These coastal particle events cannot be explained solely in terms of ternary nucleation, especially under low sulfuric acid conditions where strong particle formation has still been observed. The correlation of these events with tidal and uv cycles strongly suggests that marine organisms are responsible for the nucleation bursts. Furthermore, chamber studies have shown that under periods of stress increased emissions of iodocompounds from seaweed can lead to high concentrations of particles in the laboratory.

However, in remote, forest and urban environments modelling and laboratory studies suggest that particle formation is dominated by ternary nucleation. However, under very high sulfuric acid concentrations the reaction rate is limited by the formation of ammonium bisulfate and so ternary nucleation cannot explain every particle formation event. In addition, several forest studies have concluded that the strong correlation of particle formation events with low volatile organic compounds suggest that secondary organic aerosol formation could be important. Unfortunately in most cases the observations could also be explained by ternary nucleation followed by strong condensational growth of the VOCs on the particles. This would be consistent with observations of increasing organic fraction of the aerosols with increased particle diameter.

However all studies indicate that formation events are favoured by low temperatures and low surface area, thus a further possible source of boundary layer particles has

been suggested to occur through entrainment of air from the outflow of clouds, where lower temperatures coupled to clean air provide an excellent environment for particle production.

Growth rates have been shown to be highly dependent upon the concentration of sulfuric acid and condensable organics with rates generally varying between 1 nm hr^{-1} and 18 nm hr^{-1} for remote and polluted environments respectively. However, since the condensation of sulfuric acid upon particles removes it from the atmosphere and thus reduces the rate of nucleation it is believed that sulfuric acid cannot be solely responsible for condensational growth. Therefore SVOCs are critical to the growth of particles. The rapid growth of particles in coastal environments further indicates the importance of condensable organic compounds since hygroscopic growth rates and mass spectra of the particles support the belief that these particles are composed of insoluble iodo compounds, although the exact nature of the particles is still unclear.

Despite the improvement in technology our understanding of particle formation and growth is sadly lacking. The inability to detect particles smaller than 3 nm means that it is impossible to determine the precise time that particle formation occurs. Therefore, it is possible that a reservoir of undetectable particles exists at all times in the atmosphere and the observations of particle formation are only linked to the growth of these particles to detectable sizes. Furthermore an interesting recent observation from the QUEST study showed that particles smaller than 2 nm had an enhanced concentration of negative ions and suggested this to be a result of either ion induced nucleation or a preferential condensation on negatively charged particles.

In addition, current techniques are unable to provide real time in situ composition of single particles smaller than 200 nm. So chemical characterisation of the particles,

by collection onto media and subsequent analysis, integrated sampling of the particles or hygroscopic growth, is unable to determine the nature of the particle core and can only give general information about the content of the aerosols.

Thus observations of particle formation events are unable to provide a complete description of the nucleation process due to the small size of the particles and current limitations of the instrumentation. However, coupled to aerosol dynamics modelling, which has been used to predict particle formation mechanisms through calculation of the nucleation rates and critical cluster sizes under various conditions, our understanding of particle behaviour over the past 10 years has advanced immensely.

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