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**The Spatial Distribution and Size Evolution of Particles in Asian
Outflow: The Significance of Primary and Secondary Aerosols
during ACE-Asia and TRACE-P**

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Sincerely,

A handwritten signature in black ink, appearing to read 'C. McNaughton', followed by a long horizontal line.

Cameron S. McNaughton
Earthstronaut – April 11th, 2003

1/7

Abstract

During the ACE-Asia and TRACE-P field campaigns aircraft measurements over the Yellow Sea, East China Sea and Sea of Japan revealed widespread secondary aerosol formation in the marine boundary layer. Similar observations were made throughout the day at the Gosan surface site on Jeju Island South Korea and aboard the American research vessel the R/V Ron Brown. Intercomparisons between the surface aerosol platforms and the airborne platforms show excellent agreement. Two post-frontal airmasses were characterized by concentrations of 3 – 12 nm particles as high as $40,000 \text{ cm}^{-3}$, and SO_2 concentrations of 2 – 12 ppbv. Aerosol surface area in the marine boundary layer associated with regional air pollution and in one case, mineral dust, was in excess of $300 \mu\text{m}^2 \text{ cm}^{-3}$ and as high as $1200 \mu\text{m}^2 \text{ cm}^{-3}$. Thermodynamic profiles of the regional airmass suggest that steep gradients of aerosol surface area, relative humidity and temperature associated with elevated levels of SO_2 created microphysical environments where new particle production is favoured.

Although nucleation events were not observed directly, evidence for recently formed secondary aerosols were detected up to 48 hours after leaving the Asian landmass and were associated with SO_2 concentrations in excess of 1 ppbv. Molar ratios of $[\text{NH}_4^+]:(2[\text{SO}_4^{2-}] + [\text{NO}_3^-])$ in excess of 0.68 and volatility analysis showing partial neutralization of the nucleation and accumulation mode aerosols suggest a ternary nucleation mechanism involving H_2SO_4 , H_2O , and NH_3 . Growth rates of nucleation mode aerosols of 2.4 and 1.7 nm hr^{-1} were observed over a broad spatial extent during two consecutive flights. Based on the nucleation mode growth rates, the flux rate of vapour to the full size distribution suggests condensation rates of $2.4 \pm 1.2 \times 10^6 \text{ molecules cm}^{-3} \text{ s}^{-1}$. Calculations of the coagulation rate for the nucleation mode particles suggest that most may be scavenged by the primary aerosol in less than 72 hours over the coastal waters of Asia before being transport out toward the Pacific Ocean.

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1.0 Introduction

The International Panel on Climate Change has recently indicated that our understanding of the origin and evolution of aerosols as well as their impact on global climate is incomplete [IPCC, 2001]. Natural and anthropogenic aerosols from primary emissions and those formed in situ (secondary aerosols) have the ability to directly affect the Earth's radiative balance by scattering and/or absorbing incoming solar radiation. Additionally, aerosols have the potential to affect the number and size of cloud condensation nuclei (CCN) altering cloud albedo in what is referred to as the aerosol indirect effect [Albrecht, 1989; Twomey, 1974].

Aerosols can be divided into two categories based on their sources. Primary aerosols are particles formed by physical or mechanical means that then become suspended in the atmosphere. Examples of primary aerosols are mineral dusts from the Sahara or Gobi deserts, sea salt, pollen and spores, volcanic ash, materials from break parts wear, road dust, and fly ash. Secondary aerosols are formed by gas-to-particle conversion. This process requires gas phase precursors that typically undergo a series of chemical transformations in the Earth's atmosphere. Examples of gas phase precursors for the formation of secondary aerosols are SO_2 (from volcanoes, industrial processes and coal), NH_3 (from agricultural and biological activities), monoterpenes (from forests), halogenated hydrocarbons (from the ocean), H_2SO_4 (volcanoes), NO_x , and volatile organic compounds (VOC's) from vehicle exhaust. Black carbon (BC) particles defy strict classification as primary or secondary aerosols because they are formed from gas phase precursors in high temperature combustion. These aerosols typically condense as particles near their sources (industrial smoke-stacks or engine tail-pipes). Examples of sources for this aerosol type are incomplete combustion in diesel and 2-stroke engines as well as in many industrial processes. In this work BC will be classed as a primary aerosol because they have formed particulate matter well before they were observed.

When the concentration of gas phase precursors become saturated with respect to the ambient atmosphere the gases have the potential to form new secondary aerosols. When a single gas species is involved in the formation of new particles the process is referred to as homogeneous-homomolecular nucleation. Nucleation of this type is rare in the atmosphere

[Seinfeld and Pandis, 1998]. When two or more vapour species exist in the atmosphere nucleation can occur when the gases are saturated with respect to a liquid solution of the components. This can occur even if the gases are not individually saturated with respect to the atmosphere [*Ibid.*]. Nucleation of this type is termed homogeneous-heteromolecular nucleation. Secondary aerosols formed by this mechanism are particularly important for the species being considered in this work.

Sulfuric acid (H_2SO_4), formed from the photo-oxidation of sulfur dioxide (SO_2) precursor exists as a hydrated monomer throughout the earth's atmosphere ($\text{H}_2\text{SO}_4 \cdot n\text{H}_2\text{O}$). The degree of hydration of the monomer is a function of relative humidity and temperature. It has been theorized that equilibrium concentrations of stable sulfuric acid clusters (1-3 nm in diameter) exist throughout the Earth's atmosphere [Kulmala *et al.*, 2000]. When suitable conditions occur, i.e. those that favour cluster stability and growth, a nucleation event is triggered that results in the rapid formation and growth of these clusters. When this process involves only sulfuric acid and its associated waters of hydration this process is termed binary-homogeneous nucleation.

The atmospheric environment considered in this work is classified as "polluted marine" due to the large urban-industrial regions located in Mainland China, North and South Korea, Taiwan and Japan. As a result, tertiary gas phase precursors exist that are available to participate in the homogeneous-heteromolecular nucleation process. Examples of ternary species that might participate in the gas-to particle conversion process for this environment are ammonia and low vapour pressure organics. In this study we focus on the H_2SO_4 - H_2O - NH_3 system. Ternary nucleation involving H_2SO_4 - H_2O and low vapour pressure organics is a poorly understood process. Given the magnitude of the anthropogenic impacts on regional airmasses there is the possibility that ternary nucleation involving organic compounds is also an important pathway for the formation of secondary aerosols.

1.1 The Influence of Primary Aerosols on Secondary Aerosols

The relative significance of secondary aerosols compared to primary aerosols is related to whether their growth and removal rates result in conditions where they contribute new particle number to the background atmosphere. Under conditions that favour their formation and growth secondary aerosols may dominate the number distribution and could

influence the Earth's radiative balance by growing to optically significant sizes or indirectly by affecting the number and size distribution of the cloud condensation nuclei [Albrecht, 1989; Twomey, 1974].

Table 1.1 – Nomenclature and size classes of the aerosol size distribution.

Size Class	Particle Diameters (μm)
Nucleation mode	0.001 – 0.010
Aitken mode	0.010 – 0.100
Accumulation mode	0.100 – 1.0
Coarse mode	1.0 – 20.0

The aerosol size distribution can be divided into four size classes based on particle diameter (Table 1.1). Nucleation mode particles are those that have recently formed from gas-to-particle conversion. These particles are typically on the order of minutes to hours old. The Aitken mode particles represent those aerosols that have recently formed but have experienced condensational growth shifting them to larger size classes. The nucleation and Aitken mode particles typically dominate the aerosol number distribution. For the purpose of this work we will refer to nucleation mode particles as those that exist in both the nucleation mode and the lower half of the Aitken mode. We adopt this convention because of the rapid condensational growth of nucleation mode particles to Aitken mode sizes in this polluted marine environment. Accumulation mode particles are so named because of the tendency of physical and chemical transformations within the atmosphere (particularly cloud processing) to aggregate particles into these size classes [Hoppel *et al.*, 1987; Hoppel *et al.*, 1986]. They are removed through precipitation processes because coagulation and growth of particles out of the accumulation mode size range is relatively slow. Accumulation mode aerosols typically dominate the aerosol surface area distribution. Since accumulation mode aerosols have diameters the same order of magnitude as the wavelengths of visible light this makes them efficient at scattering and absorbing incoming solar radiation.

Coarse mode aerosols within the MBL typically dominate the aerosol volume distribution despite their low number concentration. The diameters of these particles are orders of magnitude larger than the nucleation mode particles making them efficient at collecting smaller particles by coagulation. Condensational processes have little effect on

coarse mode aerosol size. In this environment coarse mode aerosols are typically either sea salt derived from the coastal Pacific or mineral dusts derived from arid regions in Northern and Western China. Mineral dusts represent an alkaline surface while condensing species are typically acidic (sulfuric and nitric acids). Therefore, there is the potential for heterogeneous chemical reactions to occur on the surface of the mineral dusts due to condensation of sulfuric acid.

Once a nucleation event has been triggered, and while gas phase concentrations remain supersaturated (with respect to the liquid solution), material will continue to condense on both the primary and secondary aerosols. The condensation process adds mass to the aerosol size distribution but does not affect total particle number. Because condensation adds similar surface layers to all sizes the nucleation mode particles experience larger relative rate of growth compared to accumulation or coarse mode particles. As a result, condensation can rapidly move nucleation mode particles into the Aitken mode size classes (within hours). The slow relative growth of accumulation and coarse mode aerosols prevents appreciable numbers of accumulation mode aerosols from growing into the coarse mode aerosol population.

Coagulation, in contrast to condensation, does not add mass to the aerosol size distribution. Instead the coagulation process transfers aerosol mass from smaller size classes to larger classes reducing particle number. Smaller, mostly secondary aerosols, are collected by the larger, mostly primary aerosols. Self coagulation¹ is relatively inefficient and peaks at particle diameters near 0.020 – 0.030 μm [Seinfeld and Pandis, 1998]. Coagulation rates for a given particle size are a function of the total aerosol size distribution but are most efficient between nucleation mode particles and coarse mode particles. Rapid Brownian motion of the smallest particles increases the probability of encountering the much larger (1-3 orders of magnitude in diameter) accumulation and coarse mode aerosols.

Coagulation rates under the polluted marine conditions discussed here are on the order of minutes to hours for the nucleation mode particles. Aitken mode particles have coagulation rates from hours to several days (see Section 7.0). Since condensation can move nucleation mode particles into the Aitken mode over several hours, high rates of condensational growth increase the probability that nucleation mode particles will survive as

¹ Coagulation between particles of the same diameter.

new particle number in the background atmosphere. At the same time, coagulation reduces nucleation mode particle number transferring mass to larger size classes. Where coagulation rates are high and growth rates low then nucleation mode particles are likely to contribute few new particles to the background atmosphere.

1.2 Recent Work Related to Secondary Aerosol Formation

Interest in issues related to secondary aerosol formation has stimulated a variety of experiments designed to investigate these processes. In the near-shore environment the PARTicle FORMation and fate in the Coastal Environment (PARFORCE) experiment illustrated that binary homogenous nucleation was insufficient to explain observations related to the formation of secondary aerosols. However, concentrations of sulfuric acid and ammonia were higher than required to cause homogeneous ternary nucleation of H_2SO_4 , H_2O and NH_3 [Kulmala *et al.*, 2002]. Also during PARFORCE, Kunz *et al.* [2002] predicted that H_2SO_4 concentrations were insufficient to produce the observed particle growth. However, co-incident chemical data showed that photo-oxidation of organic CH_2I_2 compounds (from exposed tidal flats) contributed the mass necessary to explain the growth rate of the nucleation mode aerosol. At a clean continental site on the eastern slope of the Rocky Mountains in Colorado Weber *et al.* [1997] found concentrations of H_2SO_4 and H_2O that were well below predicted values for binary nucleation during a nucleation event. In addition, the observed growth rates were approximately 5 – 10 times higher than the rate predicted from sulfuric acid and water alone. This observation implies that NH_3 , organics or some other condensing species is involved in the growth of these particles.

Regardless of the microphysical nature of the newly formed secondary aerosols, Raes *et al.* [2000] suggest that too often we have not examined these secondary aerosols with regard to large-scale atmospheric circulation. Atmospheric processes involving temperature and humidity changes within a single air parcel (atmospheric waves, turbulence, large convective eddies) or mixing of two air parcels with different relative humidity and temperature (gradients and/or entrainment) can enhance binary nucleation for the H_2SO_4 and H_2O system [Easter and Peters, 1994; Kerminen and Wexler, 1994a; Nilsson and Kulmala, 1998]. These same phenomena should enhance any ternary nucleation mechanism involving H_2SO_4 , H_2O and NH_3 . This appears to be the case during the European BIOgenic aerosol

FORMATION in the boreal forest (BIOFOR) experiment where synoptic scale new particle formation was observed in the continental boundary layer [Nilsson *et al.*, 2001].

With regard to gas phase organics as nucleation precursors Buzorius *et al.* [2001] show no support for biogenic gases from the boreal forest as precursors for nucleation during BIOFOR. Leaitch *et al.* [1999] could not distinguish whether H₂SO₄ or forest derived organics initiated a nucleation event at a clean continental site in Eastern Canada. However, they did show that subsequent growth of the aerosol could be attributed to organic oxidation products. More recently Janson *et al.* [2001] observed nucleation over a forest ecosystem at a clean continental site in Finland. They found monoterpene oxidation products were not nucleation precursors but that low vapour pressure organics were needed to explain the observed growth rates because of insufficient concentrations of H₂SO₄ and NH₃. In the TRACE-P and ACE-Asia environments organic vapours could certainly contribute to condensation growth, however due to the magnitude of the regional SO₂ emissions it seems unlikely that gas to particle conversion of organic vapours is the dominant mechanism for forming secondary aerosols. Organic compounds may be important for the subsequent growth of particles to Aitken mode sizes.

Airborne measurements of the transport of natural and anthropogenic aerosols throughout the Pacific have been documented [Clarke *et al.*, 2001; Clarke and Kapustin, 2002; Husar *et al.*, 2001]. Secondary aerosols are of particular interest because of their potential to contribute new particle number to the background atmosphere. However, depending upon environmental conditions condensable material and newly formed particles may be collected by the existing aerosol surface area and therefore contribute new mass but not new number to the atmosphere. In polluted regions with high aerosol surface area we expect that many of these particles will coagulate on the order of 1-2 days with the primary aerosol [Raes *et al.*, 2000]. This work is concerned with answering the following questions with regard to the importance of primary and secondary aerosols.

- Where and when during the TRACE-P and ACE-Asia campaigns were recently formed secondary aerosols found?
- Is the binary homogeneous nucleation mechanism able to explain their formation or is it more likely a ternary mechanism involving species other than H₂SO₄ and H₂O?
- How do the observed growth rates for these nuclei compare with published values?

- Can we use a coagulation/condensation model to evaluate the fate of these newly formed secondary aerosols?

1.3 Regional Climatology and Long Range Transport of Asian Aerosols

Springtime in Asia is a transitional period between the winter and summer monsoon. In winter an intense atmospheric high exists over Asia while the Aleutian low persists over the North Pacific. In summer the situation is reversed with a stable low positioned over Northwestern India and Pakistan with a corresponding high existing over the North Pacific [Tomczak and Godfrey, 1994]. The frequency of wave cyclones is highest during Spring resulting in transient cyclones moving through Mainland China across the Korean peninsula and Japan toward the North Pacific [Hannan *et al.*, submitted 2002]. In the upper free troposphere the Japan jet is strongest at $\sim 30^\circ\text{N}$ along 140°E between the 300 – 200 hPa level (10 – 14 km). Wind speeds are typically $50 - 60 \text{ m s}^{-1}$ at this altitude but may reach speeds of up to 100 m s^{-1} . In the lower free troposphere zonal winds of $10 - 30 \text{ m s}^{-1}$ exist between the 800 – 550 hPa levels (3 – 6 km) [Fuelberg *et al.*, submitted 2002; Merrill *et al.*, 1997].

Three dominant weather phenomena are responsible for transporting mineral dusts and anthropogenic pollution from the planetary boundary layer (PBL) and the marine boundary layer (MBL) into the free troposphere (FT). Wind speeds at the surface over the desert plateaus of Asia (1000 – 2000 m above mean sea level, AMSL) can exceed 20 m s^{-1} transporting dust into the PBL [Husar *et al.*, 2001]. Convection in the warm front associated with the moving cyclone can lift mineral dusts from the PBL into the FT between 3 and 6 kilometers over the Gobi and Taklamakan deserts. Also, upslope flow along mountain ranges such as the Tian Shan (4500 – 5500 m AMSL) to the North of the Taklamakan and along the Tibetan plateau South of the Taklamakan ($\sim 4000 \text{ m AMSL}$) can loft mineral dust into the lower FT through orographic lifting.

Behind the advancing cold front mineral dusts are also transported within the planetary boundary layer toward the coastal regions of China [Uno *et al.*, 2001]. As the weather system moves over the coastal lowlands (0 – 1000 m AMSL) the boundary layer air picks up anthropogenic pollution from the regional urban and industrial complexes. Orographic lifting over the Korean peninsula and along the Japanese archipelago is responsible for some transport of dust and pollution from the boundary layer into the free

troposphere [*Liu et al.*, submitted 2002]. However, most pollution is transported within the MBL fanning out over the coastal bodies of water. Pollution from Mainland China often lingers offshore when the first low dissipates or weakens. As the next low approaches the anthropogenically impacted warm sector is undercut by the advancing cold front and lofted into the FT. This mechanism is the so-called warm conveyor belt (WCB) theory [*Hannan et al.*, submitted 2002; *Liu et al.*, submitted 2002; *Mari et al.*, submitted 2002].

Instead of lingering over the coastal waters, pollution in the MBL fanning out from China can also parallel the coast to be entrained into the Philippine high. Moving around the anti-cyclone the polluted airmass can then be transported toward Southeast Asia. This region experiences deep convection that directly pumps boundary layer air into the FT where it is entrained into the fast upper level Japan jet. This phenomenon is also important for transporting combustion derived pollution because Southeast Asia is an area which experiences poor air quality due to widespread biomass burning [*Liu et al.*, submitted 2002]. Regardless of whether transport from the boundary layer to the FT is due to orographic lifting, warm conveyor belt transport or convection, once the aerosols associated with these airmasses are brought into the FT they are available for long range transport out over the North Pacific toward North America by the zonal upper level winds. Due to the enhanced frequency of cold fronts and their associated wave cyclones during spring it is this time of year that dust and pollution from Asia has the highest potential for reaching North America.

1.4 Transport and Chemical Evolution over the Pacific Experiment (TRACE-P)

The National Aeronautics and Space Administration (NASA) conducted the Transport and Chemical Evolution over the Pacific experiment (TRACE-P) from February 26th to April 9th of 2001. This mission was part of a larger, ongoing research program called the Global Tropospheric Experiment (GTE) [*McNeal et al.*, 1998]. The goals of TRACE-P, as outlined in the white paper (<http://www-gte.larc.nasa.gov/trace/tracep.html>) are:

- ◆ to determine the pathways for outflow of chemically and radiatively important gases and aerosols, and their precursors, from eastern Asia to the western Pacific;
- ◆ to determine the chemical evolution of the Asian outflow over the western Pacific, and understand the ensemble of processes that control this evolution.

TRACE-P was designed as a multi-national, multi-agency experiment involving ship-based, ground-based, aircraft, and satellite data collection together with real-time forecasting by a number of meteorology and atmospheric chemistry transport models (CTM's). An overview of the TRACE-P experiment can be found in *Jacob et al.* [submitted 2002]. The Hawai'i Group for Environmental Aerosol Research (HiGEAR) participated in TRACE-P by supplying a suite of aerosol instrumentation designed to assess the physical and optical properties of aerosols. This instrumentation was installed aboard the NASA P3-B aircraft which completed 20 research flights during the field campaign. Figure 1.1 shows the flight tracks of the NASA P3-B during TRACE-P.

Figure 1.1 – Flight paths for the NASA P3-B and NSF/NCAR C-130 during TRACE-P and ACE-Asia.

Flights 4 through 14 were based out of Hong Kong and were designed to intercept biomass burning and urban emissions from South-East Asia. Flights 15 – 24 were based at Yokota Air Force base near Tokyo Japan and flights were designed to intercept anthropogenic pollution plumes as well as natural volcanic and dust emissions from China, the Korean peninsula and Japan.

1.5 Asian Aerosol Characterization Experiment (ACE-Asia)

The United States' National Science Foundation (NSF) as part of the International Global Atmospheric Chemistry Project (IGAC) supported the Asian Aerosol Characterization Experiment (ACE-Asia) from March 31st to May 4th 2001. ACE-Asia had three objectives (<http://saga.pmel.noaa.gov/aceasia/ACEAsiaDescription.html>).

- ◆ Objective 1. Determine the physical, chemical, and radiative properties of the major aerosol types in the Eastern Asia and Northwest Pacific region and investigate the relationships among these properties.
- ◆ Objective 2. Quantify the interactions between aerosols and radiation in the Eastern Asia and Northwest Pacific region
- ◆ Objective 3. Quantify the physical and chemical processes controlling the evolution of the major aerosol types and in particular their physical, chemical, and radiative properties.

ACE-Asia was also a multi-national, multi-agency experiment involving multiple platforms and observations sites in conjunction with forecasting meteorology and atmospheric chemistry transport models. An overview of the ACE-Asia experiment can be found in *Huebert et al.* [submitted 2003]. Again, HiGEAR participated with instrumentation designed to assess the physical and optical properties of aerosols. This instrumentation operated aboard the NSF/NCAR C-130 during 19 research flights. The C-130 aircraft was stationed at the Marine Corps Air Station Iwakuni located in Iwakuni Japan, ~50 kilometers south of Hiroshima. Flight tracks for the NCAR C-130 are also shown in figure 1.1.

2.0 Particle Nucleation Theory

Part of the significance of secondary aerosols relative to the primary aerosols hinges on whether newly produced particles will survive coagulation processes long enough to grow by condensation to optically significant sizes and/or sizes which could affect the number and distribution of cloud condensation nuclei. In order to address this issue the following section briefly outlines a number of theoretical approaches that we have used to investigate these processes. The results of the application of this theory to our analysis are covered in the discussion (Section 7.0).

2.1 The C_{crit} Parameterization

In the atmosphere, collisions between sulfuric acid and water molecules occur at random due to Brownian motion. Stable clusters of hydrated sulfuric acid exist in equilibrium until the system is perturbed in such a way that allows a significant fraction of these clusters to remain stable and grow [Kulmala *et al.*, 2000]. In order for clusters to stabilize and grow the cluster must exceed its critical radius. The critical radius is a function of the Gibbs free energy. For the binary nucleation scenario the free energy change associated with the cluster formation is a function of temperature as well as the concentration of sulfuric acid and water molecules [Seinfeld and Pandis, 1998]. When atmospheric conditions associated with the free energy change are such that clusters can breach the saddle point for the collision iso-surface, stable clusters grow by condensation initiating a nucleation event. Free energies of formation appear to be lower by perhaps an order of magnitude for the ternary system involving H_2SO_4 , H_2O and NH_3 [Ball *et al.*, 1999; Kulmala *et al.*, 2000].

The theoretical framework for nucleating cluster formation is complicated and covered in detail in other publications [Seinfeld and Pandis, 1998]. In our discussion of secondary aerosol formation we will refer to a simpler formulation for the concentration of sulfuric acid required to produce a nucleation event. The C_{crit} parameterization of Jaecker-Voirol and Mirabel [1989] and Wexler *et al.* [1994] expresses the critical concentration of sulfuric acid necessary to achieve a binary homogeneous nucleation rate of $1 \text{ cm}^{-3} \text{ s}^{-1}$ in terms of relative humidity and temperature. The empirical formula is parameterized as:

$$C_{crit} = 0.16 \cdot \exp(0.1T - 3.5RH - 27.7) \quad (2.1)$$

where T is temperature ($^{\circ}\text{K}$), RH is relative humidity (0-1) and the units of C_{crit} are $\mu\text{g m}^{-3}$. This simple formulation has been used as an indicator for potential binary homogeneous nucleation of H_2SO_4 and H_2O in the clean marine environment near cloud outflow [Clarke *et al.*, 1999; Clarke *et al.*, 1998; Weber *et al.*, 1999]. This parameterization is based on Jaecker-Voirol and Mirabel [1989] which tends to predict nucleation at lower H_2SO_4 relative

acidities² than the *Wilemski* [1984] model due to a thermodynamic inconsistency inherent to the model (see *Weber et al.* [1999]). We employ the *Wexler et al.* formulation because of its simplicity and because it represents a conservative estimate for binary nucleation. Modeling by *Pirjola et al.* [2000] suggests that binary nucleation only occurs under extreme conditions when free tropospheric air containing very low aerosol condensation sinks and high sulfuric acid concentrations ($>10^8$ molecules cm^{-3}) is entrained into the marine boundary layer. They suggest that instead a ternary nucleation mechanism involving H_2SO_4 , H_2O and NH_3 predicts new particle formation under more realistic sulfuric acid (1.2×10^7 molecules cm^{-3}) and ammonia (>5 pptv) concentrations for the unperturbed marine boundary layer (MBL).

2.2 Flux Rate of Sulfuric Acid to the Size Distribution

Because the relative rate of diameter change for nucleation mode particles is higher than that for accumulation and coarse mode aerosols it is possible to calculate the change of particle diameter with respect to time, dD_p/dt . By adopting the method of *Kulmala et al.* [2001] we calculate the condensation sink (CS) a parameter relating the rate at which condensable vapours are lost to the existing aerosol size distribution. Calculations of this type allow us to estimate the flux rate of vapour (believed to be dominated by sulfuric acid) to the size distribution.

The differential equation:

$$\frac{dC}{dt} = Q - CS \cdot C \quad (2.2)$$

is evaluated assuming steady state $\frac{dC}{dt} = 0$, where Q is the flux rate of vapour, C is the vapour concentration and CS is the condensational sink. The growth rate is given by:

$$\frac{dD_p}{dt} = \frac{2m_v \beta_m D_p C}{\rho D_p} \quad (2.3)$$

² Like relative humidity, relative acidity is the ratio of the mixing ratio of sulfuric acid gas to its value at saturation for the same temperature and pressure.

where m_v is the molecular mass of the condensable vapour A (98.0794 g mol⁻¹), D_v is the diffusion coefficient of gas A toward a particle when both are suspended in background gas B (in this case air), ρ is the particle density (1.4 g cm⁻³), and β_m is the transitional correction factor (Eqn. 2.6) for mass flux integrated over the size distribution. We calculate the vapour concentration, C , using:

$$C = \frac{\rho}{m_v D_v \Delta t} \cdot \left[2(Dp^2 - Dp_o^2) + \lambda_{AB}(12\alpha - 0.623)\left(\frac{Dp}{2} - \frac{Dp_o}{2}\right) + 0.623\lambda_{AB}^2 \ln \left(\frac{\lambda_{AB} + \frac{Dp}{2}}{\lambda_{AB} + \frac{Dp_o}{2}} \right) \right] \quad (2.4)$$

where Dp is the particle diameter after some time interval Δt , α is the mass accommodation coefficient ($\alpha=1$) and λ_{AB} is the mean free path of gas particle A with respect to gas B.

The condensational sink CS is expressed as $2\pi D_{AB} CS'$ where:

$$CS' = \sum_i \beta_{mi} Dp_i N_i \quad (2.5)$$

and,

$$\beta_{mi} = \frac{Kn_i + 1}{0.377Kn_i + 1 + \frac{4}{3\alpha}(Kn_i + Kn_i^2)} \quad (2.6)$$

Kn is the Knudsen number (Eqn. 2.10) a dimensionless parameter relating the length scales of fluid processes (transfer of heat, momentum and mass) to the length scales associated with the particle radius [Seinfeld and Pandis, 1998].

This estimate of the condensation rate of sulfuric acid is based on the size distributions measured by the rDMA and OPC instrument systems (Section 3.0). Other methods are available and we compare some published values to those calculated by this method in the discussion (Section 7.0).

2.3 Coagulation Rate of Nucleation Mode Particles

We can also calculate the coagulation sink (CoagS) using the time rate of change of particle diameter, dD_p/dt . The method of *Kulmala et al.* [2001] allow us to calculate the expected coagulation rate of the nucleation mode particles and will provide a rough estimate of their atmospheric lifetime.

The loss rate for a given size particle is expressed as,

$$N(t) = N_0 e^{-CoagS \cdot t} \quad (2.7)$$

where the coagulation sink, CoagS, is integrated over the whole size distribution according to,

$$CoagS = \sum_j K_{ij} N_j. \quad (2.8)$$

Using the Fuchs form of the Brownian coagulation coefficient, K_{12} can be expressed as:

$$K_{12} = 2\pi(D_1 + D_2)(Dp_1 + Dp_2) \left(\frac{Dp_1 + Dp_2}{Dp_1 + Dp_2 + 2(g_1^2 + g_2^2)^{1/2}} + \frac{8(Dp_1 + Dp_2)}{(\bar{c}_1^2 + \bar{c}_2^2)^{1/2}(Dp_1 + Dp_2)} \right)^{-1} \quad (2.9)$$

where,

$$Kn_i = \frac{2\lambda_{air}}{Dp_i} \quad (2.10)$$

$$\bar{c} = \left(\frac{8kT}{\pi m_i} \right)^{1/2} \quad (2.11)$$

$$D_i = \frac{kT}{3\pi\mu Dp_i} \cdot \left(\frac{5 + 4Kn_i + 6Kn_i^2 + 18Kn_i^3}{5 - Kn_i + (8 + \pi)Kn_i^2} \right) \quad (2.12)$$

$$l_i = \frac{8D_i}{\pi\bar{c}_i} \quad (2.13)$$

$$g_i = \frac{1}{3Dp_i l_i} \cdot \left[(Dp_i + l_i)^3 - (Dp_i^2 + l_i^2)^{3/2} \right] - Dp_i \quad (2.14)$$

and where k is the boltzman constant, λ_{air} is $0.0686 \mu\text{m}$, m_i is the mass of the particle based on a density of 1.4 g cm^{-3} , and μ is the viscosity of air, $1.83 \times 10^{-5} \text{ kg m}^{-1} \text{ s}^{-1}$. All calculations are based on an unhydrated molecular mass of H_2SO_4 of $98.0794 \text{ g mol}^{-1}$, temperature (T) of $298.15 \text{ }^\circ\text{K}$ and a pressure (p) of 101.325 kPa [Kulmala *et al.*, 2001; Seinfeld and Pandis, 1998].

From theory we expect that the nucleation mode particles will coagulate with the primary aerosol on the order of 1-2 days [Raes *et al.*, 2000]. In the discussion section of the thesis we tabulate the e-folding times for the nucleation mode particles from the observed size distributions.

3.0 Research Aircraft and Instrumentation

Our research team (HiGEAR) installed a variety of aerosol instrumentation aboard the NASA P3-B and NSF/NCAR C-130 during the TRACE-P and ACE-Asia field campaigns. Two intercomparison flights between the two aircraft showed excellent agreement [Moore *et al.*, submitted 2003]. The following sections outline the research platforms and the instrumentation used during the field campaigns.

3.1 Research Aircraft

During TRACE-P HiGEAR instrumentation was installed aboard the NASA P3-B aircraft. NASA's Wallops Flight Facility located in Wallops Island Virginia manages this aircraft. The aircraft can operate between 50 and 7000 meters with a typical airspeed of $100\text{-}150 \text{ m s}^{-1}$. Aerosol instrumentation aboard the P3-B was linked to a solid diffuser type inlet and was mounted in a standard research rack. The solid diffuser inlet is designed to sample isokinetically. If the inlet is sampling isokinetically the velocity of the sample air through the cross section of the inlet tip is the same as the air speed for the aircraft. In order to achieve this the sample stream is connected to a venturi type exhaust port that increases sample flow rate as the aircraft increases speed (the venturi effect). Losses of supermicrometer particles in this type of system become significant near about $4 \mu\text{m}$ but have a negligible effect on total particle number. No significant losses of nucleation mode particles are expected.

During ACE-Asia HiGEAR instrumentation was installed aboard the National Science Foundation (NSF) C-130 research aircraft. An experimental Low Turbulence Inlet (LTI) was designed and installed aboard the C-130 by the University of Denver. This active flow system maintains laminar flow within the sample stream while sampling isokinetically. This system is expected to substantially reduce losses and even enhance the concentrations of supermicrometer particles entering the sampling systems. The OPC system (see Section 3.5) was mounted on the starboard side of the aircraft and was directly linked to LTI. Nephelometers (see Section 3.6) were mounted vertically in the second starboard rack and were operated by the University of Washington. The nephelometers were also linked directly to the LTI system by flow splitters. The condensation nuclei counters (see Section 3.2) and the DMA (see Section 3.4) aboard the C-130 sampled from a solid diffuser inlet and were located on the starboard side of the aircraft.

3.2 Condensation Nuclei Counters

Three separate models of CN counters were employed during ACE-Asia and TRACE-P. Aboard the NASA P3-B two TSI model 3010 CN counters were used. The first operates at ambient temperature the second operates at 300°C. The model 3010 CN has a 50% counting efficiency at 0.01 μm (its smallest useful size) and can detect particles up to 3 μm in size (its largest useful size). The concentration range for this instrument is 0.0001 – 10,000 cm^{-3} , with < 10% coincidence counting at 10,000 cm^{-3} [TSI, 1992]. The model 3010 CN counters operate at a 1.0 L min^{-1} flow rate. Aboard the C-130 aircraft two model 3760 CN counters operated at ambient temperature and 300°C. A third 3760 CN counter, operated by the NCAR Research Aviation Facility, is referred to as the “RAF CN”. The model 3760 CN counter measures particles > 0.01 μm with concentrations up to 9886.8 cm^{-3} ($2.8 \times 10^8 \text{ ft}^{-3}$) [TSI, 1986]. However, 50% counting efficiency for this instrument is more likely ~0.012 μm [A.D. Clarke, personal communication]. The model 3760 CN counters operate with a 1.5 L min^{-1} flow rate. A model 3025A CN counter, also aboard the C-130, operated at ambient temperature. This instrument has 50% detection efficiency at 0.003 μm and 90% detection efficiency at 0.005 μm . The model 3025A counter records concentrations with an accuracy of +/- 10% at $9.99 \times 10^4 \text{ cm}^{-3}$ and operates with a sample flow rate of 1.5 L min^{-1} [TSI, 1996].

When referring to the data from the CN counters we will use a number of acronyms. For both the P3-B and the C-130 the CN counters operating at ambient conditions are referred to as the “Cold CN” or “UH Cold CN”. For the CN counters operating at 300°C the designations are “Hot CN” or “UH Hot CN”. Volatile CN (VCN) is the difference between the Cold CN and the Hot CN and is an indication of the number of particles which contain primarily sulfates and neutralized sulfate species (ammonium sulfate and ammonium bisulfate) [Clarke *et al.*, 1998]. However, due to the polluted nature of this marine environment we note that any organic compounds with boiling points < 300°C will also be volatilized during the heating process and is a possible source of error. Refractory CN (RCN) is the same as the Hot CN and refers to the fact that those particles counted after heating to 300°C contain primary aerosols either as internally mixed soot, fly ash or externally mixed dust and/or sea salt. Refractory ratio is the ratio of Hot CN:Cold CN. RCN ratios tending toward unity indicate the aerosol is dominated by internal mixtures containing primary aerosols (soot, fly ash) or external mixtures of exclusively refractory material (sea salt and/or dust). Ratios tending toward zero indicate the aerosol is nearly completely volatile at 300°C and contains no refractory component. It is convention to define nucleation mode particles as particles with $D_p < 0.01 \mu\text{m}$ [Raes *et al.*, 2000]. However, we can estimate concentrations for nucleation mode particles by subtracting total concentration as measured by the model 3025A (referred to as the UCN) and the model 3760 CN counters. Based on the 50% counting efficiencies for these two instruments our nucleation mode particle concentrations are measured between 3 and ~12 nm. This is sometimes referred to as DCN.

3.3 Thermo-Optical Aerosol Discriminator (TOAD)

A Thermo-Optical Aerosol Discriminator (TOAD) operated by the HiGEAR team is coupled to both the DMA and OPC sampling systems (see Sections 3.4 & 3.5). This simple system of heaters and valves allows size distributions to be obtained at dry ambient³ temperature, 150°C and 300°C. We use the differences between the heated and unheated size distributions in order to measure aerosol volatility which is related to composition [Clarke, 1991]. In the clean marine atmosphere we have shown that the difference between the dry

³ Sheath flows for both the rDMA and OPC system are dried (RH < 20%) using desiccant chambers. We therefore refer to the sample streams' size distribution as being recorded at “dry ambient conditions”.

ambient and the 150°C scan represents primarily unneutralized sulfuric acid [Clarke *et al.*, 1998]. The TOAD volatilizes neutralized sulfate species such as ammonium sulfate and ammonium bisulfate ((NH₄)₂SO₄ and NH₄HSO₄) between 150°C and 300°C. We refer to the aerosol volume remaining after 300°C as the “refractory component” which typically consists of black carbon species, fly ash, sea salt and/or mineral dust. The more polluted environment of the ACE-Asia and TRACE-P study region makes the interpretation of volatile species more uncertain due to our inability to distinguish between sulfate aerosols and nitrates, organic aerosols and other components volatile at temperatures < 300°C. However, links between size-resolved volatility and rapid measurement of aerosol chemistry (PILS) aid in the interpretation of the data.

3.4 Differential Mobility Analyzer (DMA)

Radial Differential Mobility Analyzers (rDMA's) were installed aboard both the NASA P3-B and the NCAR C-130. The rDMA operates using a 90 second data scan followed by a 30 second down time (no data recorded). The rDMA effectively sizes particles between 0.007 and 0.213 µm with a resolution of 32 channels per logarithmically spaced decade. The rDMA system sizes particles using an electrical field. Particles are singly charged by a radioactive polonium source before entering the electric field. As the voltage is logarithmically ramped between 0 and 10,000 volts particles of successively larger sizes are deflected into the counting instrument (a modified TSI model 3010 CN counter). More information on the theory behind the use of the rDMA system can be found in Zhang *et al.* [1995].

In order to sample the same air over up to a 6-minute sampling period the rDMA is coupled to a Lagged Aerosol Grab (LAG) chamber. The LAG chamber samples the air mass over a 20 second period and holds the sample in a thermally stratified column [Clarke *et al.*, 1998]. During level legs the rDMA system completes three consecutive scans at dry ambient conditions, 150°C and 300°C using the TOAD (6 minute sampling time). During vertical profiles the rDMA completes single scans at dry ambient conditions (2 minute sampling time) improving vertical resolution of the size distribution.

3.4.1 DMA corrections

Of particular relevance to this thesis is the accuracy with which the number distribution of aerosols is measured. The number distribution is dominated by the smallest particles, i.e. those measured by the rDMA system. In this regard a number of important corrections were made to the rDMA data in order that the total number of particles measured by the rDMA and OPC were within a confident range of values as compared to the UCN and Cold CN counters. The UCN and Cold CN counters have slightly different cut-off sizes compared to the rDMA system but give a more accurate estimate of total aerosol number because they do not suffer the same losses as the rDMA system. The corrections applied to the rDMA system are:

- ◆ the transmission efficiency correction,
- ◆ the neutralizer charging correction for heated scans (150°C and 300°C),
- ◆ and the correction to standard atmospheric temperature and pressure (SATP, 298.15°K, 101.325 kPa).

When particles enter the rDMA system or when samples are sequestered inside the LAG chamber, nucleation mode particles can be rapidly lost to tubing walls and other surfaces due to their high rate of diffusion. In order to correct for this effect field and laboratory experiments were conducted in order to evaluate losses based on the particle sizes. The transmission efficiency curves for ACE-Asia and TRACE-P were generated based on these calculations. The transmission efficiency curves for ACE-Asia and TRACE-P are shown in figure 3.1, more information can be found in Appendix A.

Figure 3.1 – Comparison of the transmission efficiency curves applied to the rDMA data sets for ACE-Asia and TRACE-P.

The second type of correction to the size distribution applies only to the heated scans. The correction stems from the inability of the DMA data acquisition program to properly invert data to get the original size of the charged particle (before heating) based upon its size after heating. The result is a false Boltzman charge distribution being assigned to particle sizes when the inversion is applied to the heated aerosol size distribution.

In laboratory experiments we were able to evaluate the magnitude of this correction by swapping the position of the polonium source from its standard position, upstream of the TOAD heaters, to a position downstream of the heaters (i.e. the polonium source was swapped to neutralize the size distribution after heating). The left panel of figure 3.2 shows an example of over counting due to the position of the neutralizer. Dry ambient size distributions are identical regardless of the neutralizer position. For 10 nm particles the actual particle concentrations at 150°C are only ~70% of the concentration measured using the standard configuration (right panel of Figure 3.2). At 300°C 10 nm particle

concentrations are only ~60% of the concentrations measured in the standard configuration. Ratios of the difference between size distributions obtained from the standard procedure and that for the modified neutralizer position were generated for various aerosols under a range of total number concentrations. From the analysis we generated an empirical correction for the DMA charging which was then applied to all of the 150°C and 300°C DMA scans measured during ACE-Asia and TRACE-P. More detailed information regarding this correction can be found in Appendix A.

The final correction made to the rDMA size distribution is a conversion to standard atmospheric temperature and pressure (101.325 kPa and 298.15°K) from the “ambient” conditions recorded by temperature and RH sensors in the rDMA sample flow.

Figure 3.2 – Example of over-counting aerosol number due to false Boltzman charging of the heated DMA scans (left). Example of the ratio of number concentrations for neutralizer after heater vs. the standard neutralizer position before heater (right).

3.4.2 Accuracy of the total number integral

The total integral number of particles between 0.007 and 20.0 μm can be calculated by combining the DMA and OPC number distributions. We then compare the size distribution integrals to the CN counters aboard both aircraft in order to determine whether or not the total number integrals from the DMA and OPC are accurate. Figures 3.3 and 3.4 describe the statistics of the difference between calculated DMA and measured CN concentrations. Gaussian fits to the logarithm of the ratio between the total particle concentrations measured using the rDMA and OPC are compared to the CN counters.

Figure 3.3 – Gaussian fit to the logarithm of total particle number recorded by the rDMA + OPC instruments compared to; (a) the UCN, (b) the RAF CN, (c) the UH Cold CN, as well as the 300°C size distributions as compared to the UH Hot CN (d).

Since the UCN cutoff size is 3 nm and the rDMA cutoff size is 7 nm we expect that the rDMA size distribution will slightly underestimate total particle number in a comparison.

We see this in the first panel of figure 3.3 where the mean ratio of size distribution counts to UCN counts of total particle concentration is 0.8440. The half-width parameter (w) for the Gaussian fit is $10^{0.4875}$ and corresponds to a range of 0.275 – 2.59 for the ratio of the size distribution number integral to the total measured by the UCN. The RAF CN and UH CN Cold have slightly larger cutoff sizes than the rDMA so we expect a ratio > 1.0 . The ratios for the RAF CN and the UH Cold CN show values of 1.021 (0.397 – 2.57) and 1.045 (0.397 – 2.75). The ratio of the heated scans (300°C) to the UH Hot CN showed a ratio of 0.7447 (0.408 – 2.75). There is no explanation at this time for the instrument disparity. One source of error is the fact that the UH Hot CN performed well for a smaller fraction of time than either the RAF CN, or the UH CN Cold. Additionally the neutralizer correction applied to the heated scans may not be entirely appropriate. Also, due to the intermittent nature of the heated scans by the rDMA and OPC the number of samples is substantially lower than for the unheated scans.

The same comparison of total counts to integral number from size distributions was completed for the TRACE-P data. This information is summarized in figure 3.4. The ratio of size distribution integral number to the Cold CN during TRACE-P was calculated at 0.8385 (0.480 – 1.46). The corresponding Hot CN ratio is 0.7820 (0.528 – 1.16) for TRACE-P.

Figure 3.4 – Gaussian fit to the logarithm of total particle number recorded for the dry ambient rDMA + OPC size distributions as compared to the UH Cold CN (a), as well as the 300°C size distributions as compared to the UH Hot CN (b).

3.5 Optical Particle Counter (OPC)

Laser optical particle counters (PMS LAS-X with customized electronics) were used aboard both the P3-B and the C-130 to measure the aerosol size distributions. The OPC effectively sizes particles between 0.100 and 20.0 μm with a resolution of 112 logarithmically spaced channels per decade. The OPC completes scans every 30 seconds at dry ambient temperature, 150°C and 300°C during level legs. This process is computer controlled by sequential cycling of the TOAD unit. During vertical profiles we only measure the dry ambient size distribution with the OPC allowing us to obtain better vertical resolution.

The sample stream is dilution dried ($\text{RH} < 20\%$) by mixing 0.3 L min^{-1} sample and 0.3 L min^{-1} desiccated air upstream of the optical cavity. The OPC uses a Helium-Neon (He-Ne) laser operating at a wavelength of 632.8 nm inside of the optical cavity. Particles in the sample stream scatter the laser light and the intensity of the scattered light is measured by the photo-detector. The electrical response recorded by the photo-detector is calibrated in the laboratory by using polystyrene spheres and glass beads (borosilicate glass) of known uniform sizes (0.100 – 4.51 μm ; 2.5 – 15.4 μm) and refractive indices (1.588 - 0i; 1.54 - 0i). OPC response to the monodisperse aerosols is recorded for the 256 channels of the OPC and a resulting calibration curve for the OPC is generated empirically. Since the intensity of the scattered light measured by the photo-detector is a function of the aerosol size, shape and chemical composition the optical effective size of the environmental aerosol based upon the OPC calibration may differ from its physical size. The reader should keep in mind that the size distribution from the OPC represents the apparent *optical diameter* which may differ slightly from the DMA's *mobility diameter* in the region of overlap (0.100 – 0.213 μm).

3.6 Total and Submicrometer Scattering

Total scattering is measured aboard the NASA P3-B using a 3-wavelength (450, 550, 700 nm) TSI model 3563 nephelometer. Two model 3563 nephelometers aboard the NCAR C-130 were used to measure total and submicrometer scattering by installing a 1 μm impactor upstream of the second nephelometer. More information about the operation and

corrections made to the nephelometer data can be found in *Anderson et al.* [1996] and *Anderson and Ogren* [1998].

3.7 Other instrumentation

During TRACE-P a modified TSI ultrafine condensation particle counter (model 3025A) equipped with pulse height analysis (PHA-UCN) was operated by the Georgia Institute of Technology aboard the NASA P3-B aircraft. This instrument measures then calculates a one minute average of 3-8 nm particle concentrations [*Marti et al.*, 1996; *Saros et al.*, 1996; *Weber et al.*, 1998b]. Soluble ions (Na^+ , K^+ , NH_4^+ , Ca^{2+} , Mg^{2+} , Cl^- , NO_3^- , SO_4^{2-}) were measured using ion chromatography in the Georgia Institute of Technology Particle-Into-Liquid Sampling (PILS) system aboard both the NASA P3-B and the NCAR-C-130 [*Orsini and Weber*, 2002; *Weber et al.*, 2001b]. Gas phase SO_2 was measured using an atmospheric pressure ionization mass spectrometer (APIMS) using isotopically labeled internal standards. The APIMS instrument was operated by Drexel University aboard both aircraft [*Thornton et al.*, 2002]. Gas phase concentrations of H_2SO_4 , OH and MSA were measured exclusively aboard the NASA P3-B by the team from the National Center for Atmospheric Research (NCAR) in Boulder Colorado using a selected ion chemical ionization mass spectrometer (SCIMS) [*Eisele and Tanner*, 1993].

4.0 Secondary Aerosol Formation on a Synoptic Scale

Nucleation mode particles ($D_p < 63$ nm) were typically observed downwind of the urban/industrial regions of Asia with strong sources of SO_2 emissions. The top 50 $1^\circ \times 1^\circ$ SO_2 emission areas for the study region are plotted as red circles in figure 4.1. The highest SO_2 source grid has an emission rate of ~ 310 kt year⁻¹ while the 50th ranked grid has an emission rate of ~ 83 kt year⁻¹ [*Carmichael et al.*, submitted 2002; *Streets et al.*, submitted 2002]. The top 50 SO_2 point sources for the study region are plotted as numeric values in the second row of figure 4.1. Each numbered point source exceeds 9 kt SO_2 year⁻¹ with the top ten sources in the region exceeding 165 kt SO_2 year⁻¹ [*Ibid.*]. The highest concentrations of anthropogenic SO_2 recorded by the P3-B and the C-130 aircraft were in the Yellow Sea. Elevated SO_2 concentrations were also identified south of Japan where Asian outflow is advected beyond the East China Sea toward the Northwest Pacific. The Sea of Japan was

also heavily impacted by the outflow from Asia and by the strong source regions near the South Korean cities of Seoul and Pusan. In addition to the anthropogenic sources of SO₂ in the region several active volcanoes are substantial sources of regional SO₂. Miyakejima, located south of Tokyo, and Sakurajima, located in Southern Kyushu, emit 8400 and 470 kt SO₂ year⁻¹. These volcanoes are plotted as scaled black triangles in figure 4.1.

The upper panels in figure 4.1 show the spatial extent of all events recorded by the ACE-Asia rDMA where size-distributions measured on the C-130 show evidence of particles with diameter <0.063 µm and with particle concentrations > 1,000 cm⁻³. This approach makes it possible to identify secondary aerosols originating from nucleation events within the previous 24 hours. Each data point has been colour coded by SO₂ concentration at the time of observation. The right hand column shows the same data plotted with a meridional view to show the vertical distribution of these nucleation mode particles. The middle panels in figure 4.1 show where the PHA-UCN's concentration of 3-8 nm particles exceeded 100 particles cm⁻³ during TRACE-P. This measurement emphasizes recently nucleated aerosol expected to be less than a few hours old. The lower panels show the TRACE-P nucleation events as measured by the rDMA board the P3-B. Because the rDMA and PHA-UCN measure particles of different sizes locations where nucleation events were observed are also slightly different. For example, during TRACE-P flight 17 the rDMA system recorded elevated concentrations of nucleation mode particles downwind of the Miyakejima volcano (cluster of points near 135°E, 33°N). Despite strong evidence of a nucleation event from the rDMA system the PHA-UCN data shows concentrations of 3-8 nm particles were less than 100 cm⁻³. Closer examination of the rDMA size distributions show these nucleation mode particles are larger than 3-8 nm which accounts for their absence in the PHA-UCN data.

Both instruments demonstrate that the majority of newly formed secondary aerosols were found below 2500 m (typical maximum height of the MBL) and that they are associated with SO₂ concentrations in excess of 1 ppbv. Nucleation mode particles appear to be less prevalent in the free troposphere (FT) where SO₂ concentrations rarely exceed 1 ppbv.

We will now look closer at several specific cases in order to determine when, i.e. under what meteorological conditions, these events were observed and whether the observations support a binary or a ternary nucleation process for the formation of these secondary aerosols.

Figure 4.1 – Plan and meridional views of nucleation events for ACE-Asia from rDMA analysis (first row), for TRACE-P from PHA-UCN analysis (second row), and for TRACE-P from rDMA analysis (last row).

4.1 Outflow during March 18th – TRACE-P Flight 14

On March 18th meteorological data indicated that surface flow brought air over the industrialized areas of Beijing, Tianjin and Qingdao into the Yellow Sea at approximately 5-10 m s⁻¹. The outflow was due to a low pressure system centered east of Honshu Japan and a second northeast of Harbin China (near the border of Northeastern China and Siberia). These two low-pressure systems were backed by a high-pressure system located above Wuhan, to the west of Shanghai China (Figure 4.2). TRACE-P flight 14 (RF14) was designed to intercept this airmass as it was advected from the industrialized regions of Northeastern China out over the Yellow Sea. The first column of figure 4.3 shows the flight path of the NASA P3-B, location of three profiles, as well as back trajectories generated by the US National Ocean and Atmospheric Administration (NOAA) Air Resources Laboratory's HYSPLIT model (<http://www.arl.noaa.gov/ready/hysplit4.html>).

Figure 4.2 – Meteorology for the Northwest Pacific during TRACE-P RF14 on March 18th, 2001.

Figure 4.3 – Back trajectories for profiles from TRACE-P RF14 on March 18th, 2001 (left) and ACE-Asia RF07 and RF08 on April 12-13th, 2001 (right).

4.2 Outflow during April 12th and 13th – ACE-Asia Flights 7 and 8

From April 6th – April 13th of 2001 a major dust storm swept through the ACE-Asia study region. On the 12th the C-130 conducted field operations in the Yellow Sea including an intercomparison with the Gosan surface site at Jeju Island South Korea (33.28°N, 126.17°E, alt. 70 m). A subsequent flight on April 13th involved an intercomparison with the R/V Ron Brown stationed in the Sea of Japan (35.74°N, 132.50°E) followed by an intercomparison at Amami-Ohshima south of Kyushu Japan (28.44°N, 129.70°E). The flight path for ACE-Asia RF07 and RF08, the relevant profiles, the location of the R/V Ron Brown, and each of the surface sites are contained in the second column of figure 4.3.

April 12th is characterized as a post-frontal air mass undergoing synoptic scale subsidence in the wake of the passing front. The advancing cold front passed the Gosan surface site at about 16:00 UTC on April 11th (01:00 JST, April 12th). Meteorological conditions show that 5-8 m s⁻¹ winds at the 925 mb level were from the Northwest (Figure 4.4). The dust storm passed over the industrialized areas of Beijing, Tianjin and Qingdao and

into the Yellow and East China Seas on its way toward the Pacific. The same passing cold front moved over the R/V Ron Brown, located in the Sea of Japan, at approximately 06:00 UTC April 12th (15:00 JST, April 12th). For a second day the C-130 was able to sample the aerosol in the cloud free wake of the advancing front. After the Ron Brown flyby the C-130 passed over the Japanese archipelago and flew Southwest of Kyushu to the LIDAR installation at Amami-Oshima. HYSPLIT back trajectories show that the airmass, particularly near the surface, passed over the strong point source emissions of Mainland China. Based on the back trajectories from RF08 we see that the air sampled on April 13th appears to have been the same air mass sampled during April 12th. The time frame for transport of the airmass was fortuitously spaced at approximately 24 hours. This situation is similar to the case outlined on March 18th during TRACE-P. However, unlike the March 18th case the northwesterly flow behind the April 6th – 13th cold front also brought mineral dust from the desert regions China.

Figure 4.4 – Meteorology for the Northwest Pacific during ACE-Asia RF07 on April 12th, 2001.

4.3 Aircraft Profiles for March 18th and April 12th, 13th Cases

The P3-B and the C-130 can cover 1000's of kilometers during each ~9 hour flight and often complete vertical profiles anywhere between 50 and 7000 meters. Variability of thermodynamic properties as well as gas and aerosol phase parameters were routinely observed on the scale of 10's to 100's of meters during these vertical profiles.

Thermodynamic variables often reveal features that help interpret structure in the gas and aerosol fields. Figures 4.5 through 4.7 illustrate some measured thermodynamic, gas, aerosol and optical properties observed during TRACE-P RF14 and ACE-Asia flights RF07 and RF08. The first column of each figure contains water vapour mixing ratio ($\text{g H}_2\text{O kg Air}^{-1}$) as well as ambient and potential temperature ($^{\circ}\text{C}$). The second column of figure 4.5 shows SO_2 , H_2SO_4 and calculations of C_{crit} . The second column of figures 4.6 and 4.7 show SO_2 as well as *total and sub-micron scattering* (Mm^{-1} at 550 nm) because gas phase measurements of H_2SO_4 were not available aboard the NCAR C-130. The last column of figure 4.5 contains total scattering (550 nm) and particle concentrations ($> 10 \text{ nm}$) measured aboard the P3-B. The final columns of figures 4.6 and 4.7 include ultrafine ($> 3 \text{ nm}$) particle concentrations, particle concentrations $> \sim 12 \text{ nm}$ as well as their difference in order to estimate the total concentration of 3 – 12 nm particles. Each row of the three figures corresponds to the North, Central and Southern profiles indicated in figure 4.3 for TRACE-P RF14 as well as ACE-Asia RF07 and RF08. The characteristics of each profile are closely linked to the history of the airmass so when viewing figures 4.5 through 4.7 the reader will find it helpful to refer to figure 4.3.

4.3.1 TRACE-P – Flight 14 – North Profile

Back trajectories show the airmass has advected from the Beijing and Tianjin urban/industrial complex, out over the Gulf of Bo Hai and into the Yellow Sea during the previous 24 hours (left panel of Figure 4.3). A layer of elevated water vapour mixing ratio and depressed ambient and potential temperature near the surface extends to 360 m (top of Figure 4.5). Lowest particle concentrations ($25,000 \text{ cm}^{-3}$) were coincident with lowest values of water vapour mixing ratio, SO_2 and total scattering. Highest concentrations of SO_2 are

positively correlated with the peak in particle concentrations ($50,000 \text{ cm}^{-3}$) and water vapour mixing ratio at 692 m. The stable stratification (increasing potential temperature with height) and little variation in particle concentrations above 692 m suggests that new particle formation might be taking place over the entire depth of the MBL even though certain regions, such as those near the peaks in SO_2 and water vapour mixing ratio (692 m) have conditions that appear more favorable for new particle formation.

4.3.2 TRACE-P – Flight 14 – Central Profile

A layer of evaporative cooling, or an “ocean boundary layer” (OBL), exists between the surface and 507 meters (middle of Figure 4.5). The peak concentrations of aerosol number, SO_2 and H_2SO_4 occurred above the interface between the OBL and the remainder of the marine boundary layer (MBL). Total scattering increases within the OBL suggesting that pollution from the Asian landmass and/or shipping lanes as well as sea salt from the ocean surface may be trapped below the OBL. Steep gradients of aerosol surface area, relative humidity and temperature near the OBL inversion are associated with high concentrations of H_2SO_4 . The low value for C_{crit} (Eqn. 2.1) at the ocean surface indicates the most likely site for secondary aerosol formation is the high relative humidity environment over the ocean. However, the highest particle concentrations are observed at the OBL/MBL interface where the values of C_{crit} remains ~5 times larger than the observed concentrations of H_2SO_4 . This suggests that the available H_2SO_4 is insufficient to support a binary homogeneous nucleation process at the time of observation. Particle concentrations, SO_2 and H_2SO_4 decrease sharply from their peaks at 500 m toward the surface. In contrast water vapour mixing ratio and total scattering increase sharply over the same interval. This suggests that a process linked to aerosol surface area and relative humidity is responsible for the depletion of gas phase precursors and aerosols within the OBL.

4.3.3 TRACE-P – Flight 14 – South Profile

A pronounced OBL layer exists to a height of 615 m during the southern profile (bottom of Figure 4.5) similar to the structure observed in the central profile. Peak concentrations of SO_2 are found within the OBL but particle concentrations peak at the

interface between the layer of evaporative cooling and the remainder of the MBL. Within the OBL scattering is at least a factor of 4 higher than the overlying air which appears to be relatively clean. On either side of the cleanest layer (615 – 1066 meters) particle concentrations show small peaks suggesting that gradients in aerosol surface area, relative humidity and temperature create microphysical environments where new particle production is favored. Gas concentrations and aerosol number concentrations are reduced just above the ocean surface where total scattering and water vapour mixing ratio are highest. This suggests that the removal of both the gas phase precursors and aerosols is occurring in the same process and that the process appears to be linked to aerosol surface area and relative humidity.

Figure 4.5 – Thermodynamic, gas phase and aerosol properties during the North (top), Central (middle) and Southern (bottom) profiles of TRACE-P RF 14 on March 18th, 2001.

4.3.4 ACE-Asia – Flight 07 – North Profile

The northern end of this flight into the Yellow Sea (Figure 4.3) revealed a complex layered structure where submicrometer scattering increases towards the surface nearly doubling in the lowest 594 m (top of Figure 4.6). Increasing water vapour mixing ratio and near surface gradient in potential temperature suggests that the OBL (<594 m) is once again de-coupled from the remainder of the MBL. Lowest concentrations (still high) of 3 – 12 nm particles (less than $35,000 \text{ cm}^{-3}$) occur in the OBL, however, concentrations for particles greater than 12 nm are a factor of 1.3 higher than the overlying layers (75,000 versus $56,000 \text{ cm}^{-3}$). Five rDMA size distributions obtained within the MBL during the profile show the nucleation mode particles have a mode diameter between 26 and 18 nm with the smallest mode diameters being associated with the lowest aerosol surface area and SO_2 concentrations aloft. Based on the size distribution information we conclude that by the time of this profile (13:30 JST) the majority of the newly formed secondary aerosols have grown beyond 12 nm in size due to condensational growth in a layer with peak SO_2 concentration of 12 ppbv.

4.3.5 ACE-Asia – Flight 07 – Central Profile

This descent profile occurred directly above Jeju Island, South Korea between 10:15 and 10:35 am JST (1:15 – 1:30 UTC). Scattering increases from below the inversion (2400 meters) towards the surface and is dominated by the presence of supermicrometer dust in the wake of the passing cold front (middle of Figure 4.6). In the upper MBL sub-micron scattering, SO_2 and total particle concentrations increase toward the surface. Below ~1200 m these parameters remain relatively constant. The number of particles in the 3 – 12 nm size range remains relatively constant at $40,000 \text{ cm}^{-3}$ in both the upper and lower MBL. Within the lowest 700 meters the water vapour mixing ratio fluctuates between 1.90 and 3.80 g kg^{-1} corresponding to oscillations in relative humidity between 27% and 47%. Secondary aerosols are distributed more evenly due to the absence of the miniature OBL inversion and secondary aerosol formation appears to be occurring throughout the MBL.

4.3.6 ACE-Asia – Flight 07 – South Profile

This profile (33.1°N, 124.4°E) occurred between the geographic locations of the central and southern TRACE-P profiles under a similar pattern of outflow from the Chinese Mainland (Figure 4.3). A temperature inversion and layer of evaporative cooling exists below 314 m (bottom of Figure 4.6). Sharp increases in water vapour mixing ratio as well as total and submicrometer scattering are in phase with sharp decreases in SO₂ and particle concentrations near the surface. SO₂ and 3 – 12 nm particle concentrations peak (8.69 ppbv, 40,800 cm⁻³) at the OBL/MBL interface (268 m) and drop by about a factor of 2 near the surface (3.4 ppbv, 21,400 cm⁻³). Particle concentrations above the OBL are above 30,000 cm⁻³ but are separated from the OBL by a local minimum. An additional profile near this location later in the day shows 3 – 12 nm particle concentrations were elevated throughout the remainder of the MBL decreasing to 18,000 cm⁻³ at the MBL inversion (not shown). This profile shows that new particle production is probably occurring throughout the MBL. High aerosol surface area and relative humidity within the layer of evaporative cooling appears linked to reduced concentrations of newly formed secondary aerosols. Three to twelve nanometer particles peak at the transition in aerosol surface area located at 314 meters. This microphysical environment allows a greater number of the nucleation mode particles to survive compared to the layer directly below. For the remainder of the MBL a probable level where these secondary aerosols were formed could not be identified suggesting the secondary aerosols are forming throughout the MBL and surviving because of decreasing aerosol surface area with height.

Figure 4.6 – Thermodynamic, gas phase and aerosol properties during the North (top), Central (middle) and Southern (bottom) profiles of ACE-Asia RF07 on April 12th, 2001.

4.3.7 ACE-Asia – Flight 08 – North Profile

Back trajectories in figure 4.3 show the northern profile for RF08 (top of Figure 4.7) should be similar to the air mass characterized in the north profile from RF07 (top of Figure 4.6). The airmass was transported over South Korea the previous night and the Sea of Japan that morning. The absence of the stable surface layer caused by evaporative cooling and near constant water vapour mixing ratio and potential temperature (top of Figure 4.7) indicates that the column has become well mixed below 1300 m. Both total and submicrometer scattering are nearly constant with height below 1300 meters which also suggests mixing. However total scattering, and to a lesser extent submicrometer scattering, values are lower than those observed during RF07. This suggests removal of the coarse mode aerosol during transport over South Korea or that this is a slightly different airmass to that characterized upwind the previous day. Concentrations of SO₂ are approximately one half to one third the previous day's values (2.0 +/- 0.5 versus 5.9 +/- 1.1 ppbv) between the 500 and 1000 m level. These peaks are well correlated ($R^2 = 0.7395$) to 3 – 12 nm particle concentrations that are a factor of 4 lower than those recorded the previous day (10,000 cm⁻³ vs. 40,000 cm⁻³).

4.3.8 ACE-Asia – Flight 08 – Central Profile

Back trajectories (Figure 4.3) for the RF08 central profile (middle of Figure 4.7) show this airmass should have characteristics similar to the middle profile for RF07 (middle of Figure 4.6). However, the air has just crossed the Japanese island of Kyushu and the profile exhibits a layered structure. Some of these features may be due to orographic effects and/or anthropogenic gas and aerosol sources on Kyushu. A surface layer does appear to exist below 500 m and is associated with high water vapour mixing ratio and lower total and 3 – 12 nm particle concentrations. Concentrations of SO₂, total and submicrometer scattering are nearly constant to the top of the MBL. This suggests the air below 500 m has a different history or is decoupled from the layers above. This is supported by the plots of 3 – 12 nm particles which show that concentrations are much higher aloft and possibly formed near the local maximum in water vapour mixing ratio at ~1700 m or at the MBL inversion (~2300 m).

4.3.9 ACE-Asia – Flight 08 – Southern Profile

Back trajectories from the northern and central profiles from RF08 show that at some point the airmass passed over land. In contrast, back trajectories for the southern profile show that this air remained over the Yellow Sea and East China Sea before moving out towards the Pacific (Figure 4.3). This air should be similar to the airmass observed during the southern profile of RF07 (bottom of Figure 4.6). There is no hint of the OBL observed the previous day. In fact, every parameter measured during this profile suggests that the airmass has been completely mixed between the surface and the top of the MBL located at 1800 meters (bottom of Figure 4.7). If we re-examine the RF08 northern profile (top of Figure 4.7) it suggests that after leaving the Korean mainland the airmass appears to be evolving from having characteristics like those seen in the central profile (near land) towards those seen in the southern profile (open ocean). This suggests that as the airmass moves out over the Pacific we can expect its structure to become more homogeneous as convective cells and diurnal cycles turn the airmasses over. At this location the airmass has also encountered the warm Kuroshio current (Figure 4.8). During RF07 sea surface temperatures (SST) in the Yellow Sea were 8-10°C. North of Japan SST was 13-15°C and East of Kyushu the sea surface temperatures were 18-20°C. Sea surface temperature was 21-23°C at the southern profile near Amami-Oshima. The Kuroshio seems to have provided a strong source of heat and water vapour responsible for ~4°C increase in potential temperature (6°C at the surface) and a water vapour mixing ratio above 4.2 g kg⁻¹ for the entire MBL. During the southern profile of RF07 the water vapour mixing ratio only exceeded 4.2 g kg⁻¹ below 205 m in the shallow layer of evaporative cooling (OBL). This suggests that heating of the airmass by the warm surface turned the column over and is responsible for the well-mixed structure observed in the profile. Concentrations of 3 – 12 nm particles are highest (4400 cm⁻³) near the inversion (1800 m) where there is a steep gradient in aerosol surface area, RH and temperature. SO₂ concentrations have dropped from values of 8.69 ppbv at 250 m during RF07 to values near 1.40 ppbv for RF08.

Figure 4.7 – Thermodynamic, gas phase and aerosol properties during the North (top), Central (middle) and Southern (bottom) profiles of ACE-Asia RF08 on April 13th, 2001.

Figure 4.8 – Sea Surface Temperatures for April 12th (top) as well as SST's measured by infrared (IR) sensors aboard the P3-B (left) and C-130 (right) during TRACE-P RF14 on March 18th and ACE-Asia RF07 and RF08 on April 12th and 13th, 2001.

5.0 Size Distributions Measured Aboard the Aircraft

Size distributions are dynamic and evolve over time in response to processes linked to aerosol formation and removal. Changes in the size distributions can provide greater insight into processes than concentrations alone. Number, area and volume distributions at dry ambient temperature, 150°C and 300°C can be calculated by combining the thermally resolved size distributions measured by the University of Hawai'i rDMA and the OPC. Recall that the rDMA measures particle size using mobility while the OPC is an optical method (see section 3.4 and 3.5). Simple MATLAB functions were written in order to join the size distributions over their region of overlap (0.100 – 0.213 μm) and then to smooth the output. The MATLAB functions are contained in Appendix B. The size distributions are presented within the thesis as either single distributions at a particular altitude (Figures 5.1 – 5.3 and 5.5) or as contour plots to show structure over a vertical profile (Figures 5.4 & 5.6). Size distributions associated with TRACE-P flight RF14 and ACE-Asia flights RF07 and RF08 are presented in the following sections.

5.1 Size distributions from TRACE-P RF14

On March 18th during the central TRACE-P descent profile an rDMA size distribution was obtained at 663 m allowing us to evaluate the size distribution directly above the observed OBL. The SO_2 concentration at the time of observation was 9.60 ppbv, the sulfuric acid concentration was 6.03×10^7 molecules cm^{-3} and C_{crit} was 4.40×10^8 molecules cm^{-3} . This indicates that the concentration of H_2SO_4 required for binary homogeneous nucleation is low by a factor of ~ 7 according to *Wexler et al.* [1994].

Figure 5.1 shows the number, area and volume distributions obtained during this scan. Dry ambient distributions are shown in blue, distributions at 150°C are red, while the black lines correspond to scans completed at 300°C. The number distribution shows a clear nucleation mode aerosol centered at 9 nm but that after heating to 150°C nearly all the volume for this mode has been eliminated. This is consistent with the nucleation mode aerosol being composed primarily of sulfuric acid or another compound volatile at temperatures below 150°C. The accumulation mode aerosol shows a distinct pollution

signature with low volatility consistent with near complete neutralization of the sulfuric acid by ammonium. The Particle-Into-Liquid Sampling system (PILS) operated by Georgia Institute of Technology primarily measures the soluble ionic species in the accumulation mode aerosol [Orsini and Weber, 2002; Weber *et al.*, 2001b]. The molar equivalents ratio ($[\text{NH}_4^+]: 2[\text{SO}_4^{2-}]+[\text{NO}_3^-]$) as measured by the PILS instrument was 1.17. This demonstrates there is an abundant local source of ammonia and confirms our inferred near complete neutralization of the accumulation mode sulfuric acid by ammonia. This also suggests a possible ternary nucleation mechanism in the formation of the secondary aerosol due to the insufficient concentration of H_2SO_4 as calculated using the C_{crit} parameterization.

After the descent profile the P3-B completed a level leg at 118 m (Figure 5.2) where the size distribution looks much different than that obtained above the OBL. Nucleation mode particles are smaller and exist at reduced concentrations compared to those above the OBL (note change of scale for $dN/d_{\log D_p}$ by 1 order of magnitude between figures 5.1 and 5.2). Total aerosol surface area has doubled with all of the increase in the accumulation mode aerosol. Molar ratios of $[\text{NH}_4^+]:(2[\text{SO}_4^{2-}]+[\text{NO}_3^-])$ averaged 0.87 (+/- 0.06) supporting the volatility analysis which shows accumulation mode aerosol has been neutralized to a lesser degree than the accumulation mode aerosol at 663 m. SO_2 concentrations have dropped but remain high at 5.07 ppbv (+/- 1.5 ppbv), H_2SO_4 has dropped to 2.15×10^7 molecules cm^{-3} (+/- 0.80) indicating that the concentration of H_2SO_4 is still about a factor of 7 lower than that required for binary nucleation ($C_{\text{crit}} = 1.47 \times 10^8 \pm 0.69$ molecules cm^{-3}). SO_2 and H_2SO_4 concentrations drop by factors of 1.89 and 2.80 while total aerosol surface area increases by a factor of 1.90 compared to the region above. The nature of the C_{crit} parameterization (Eqn. 2.1) suggests that high relative humidity conditions would deplete H_2SO_4 but produce a vast number of nucleation mode particles. Within the OBL a process that simultaneously depletes gas phase precursors (H_2SO_4 and SO_2) as well as nucleation mode particles is required in order to explain the observations.

Figure 5.1 – Aerosol number (top), area (middle) and volume (bottom) distributions recorded at **663 m** above the Yellow Sea along 124.4°E during TRACE-P RF14, March 18th, 2001. Distribution highlights the presence of nucleation mode particles just above a shallow layer of evaporative cooling. Accumulation mode aerosol shows near complete neutralization.

Figure 5.2 – Aerosol number (top), area (middle) and volume (bottom) distributions recorded at **118 m** above the Yellow Sea along 124.4°E during TRACE-P RF14, March 18th, 2001. Distributions show doubling of surface area and reduced number (note scale change compared to Figure 5.1) and diameter of nucleation mode particles within the layer of evaporative cooling.

5.2 Size distributions from ACE-Asia RF07

ACE-Asia RF07 on April 12th involved an intercomparison with the Gosan surface site located at Jeju Island, South Korea (Figure 4.3). At 1:30 UTC (10:30 am JST) the C-130 flew west of the surface site at 40 m (the sea cliffs at Jeju are ~70 m high). Nucleation mode particle sizes at this time were centered at 13 nm (Figure 5.3). Concurrent DMA scans completed at the surface site show the peak diameter for the nucleation mode particles to be 11 nm [Buzorius *et al.*, submitted 2003]. As described during TRACE-P RF14 most of the nucleation mode particles are again eliminated after heating to 150°C but the accumulation mode aerosol shows volatility consistent with partial neutralization to ammonium sulfate/bisulfate. This suggests that an abundant source of ammonia is present for secondary aerosols to form via a ternary nucleation mechanism though the presence of NH_4^+ in the accumulation mode does not directly imply a ternary nucleation mechanism. The PILS instrument also aboard the NCAR C-130 showing a molar ratio of 0.70 supports partial neutralization of the accumulation mode aerosol. Additional evidence for the participation of ammonia in the formation of secondary aerosols comes from the Gosan surface site. Operating a humidified tandem differential mobility analyzer (HTDMA) the research group from Brookhaven National Laboratory determined that the hygroscopic growth of 25 nm particles was best explained by an ammonium sulfate/ammonium bisulfate type composition [Buzorius *et al.*, submitted 2003].

The back trajectory analysis and profile data from ACE-Asia RF07 indicate the atmospheric structure and pattern of outflow for TRACE-P RF14 and ACE-Asia RF07 are nearly identical particularly with regard to the OBL. The main difference between these cases is the absence of the coarse mode dust during March 18th (TRACE-P RF14). Size distributions from RF14 confirm that “dry” aerosol surface area in the OBL (Figure 5.2) was much higher than in the remainder of the MBL (Figure 5.1). Figure 5.4 shows combined DMA and OPC area distributions from ACE-Asia RF07 during the vertical profiles along 124.4°E on April 12th. These show few nucleation mode particles below 500 meters as seen in the more limited number of distributions from TRACE-P RF14. The accumulation mode area also has a larger mode diameter within the surface layer and is present in conjunction with coarse dust near the surface. Nucleation mode particles have their highest

concentrations above the OBL and are associated with smaller coarse and accumulation mode surface area. C_{crit} predicts that the region of secondary aerosol formation is within the OBL yet 3 – 12 nm particle concentrations are lowest within the shallow layer. It appears that nucleation mode particles (as well as SO_2 - see top and bottom of Figure 4.6) in the OBL have been depleted but that just above the layer of evaporative cooling these species still exist at peak concentrations. There is also a second peak in nucleation mode particles near the MBL inversion. C_{crit} predicts that the cold, high relative humidity environment near the inversion favours the formation of nucleation mode particles. Also, entrainment could play an important role in secondary aerosol formation by reducing aerosol surface area through dilution of MBL air with low surface area free troposphere air [Nilsson and Kulmala, 1998].

At 7:00 UTC (16:00 JST) the C-130 made a second pass by the Gosan surface site. Once again the size distributions measured on the ground were nearly identical to those measured aboard the aircraft. Nucleation mode particles aboard the aircraft were centered at 28 nm (Figure 5.5). The surface site showed a peak diameter centered at 33 nm. Integral number (as measured by the size distributions) had decreased from $32,800 \text{ cm}^{-3}$ to $18,900 \text{ cm}^{-3}$ (a factor of 1.74) and total particle concentrations measured by the ultrafine particle counter ($> 3 \text{ nm}$) were lower by a factor of 3. The size distributions measured at the Gosan site by the C-130 were not part of the same air parcel (a Lagrangian analysis) because winds from the Northwest were $5 - 8 \text{ m s}^{-1}$. Airmass heterogeneity could therefore be responsible for the differences observed at Gosan between 1:30 UTC (10:30 am JST) and 7:00 UTC (16:00 JST). While airmass heterogeneity could play a role the reduction of particle number and shifts to larger size classes suggests that instead particles are growing through condensation while particle number is being reduced through coagulation with the accumulation and coarse mode aerosols.

Figure 5.3 – Aerosol number (top), area (middle), and volume (bottom) distributions measured during the morning fly-by of the Gosan surface site during ACE-Asia RF07, April 12th, 2001. Nucleation mode particles are identical to those observed at the ground station.

Figure 5.4 – Vertical structure of aerosol surface area over the Yellow Sea along 124.4°E during ACE-Asia RF07 on April 12th, 2001. Aerosol surface area is highest within the shallow layer of evaporative cooling. Larger accumulation mode sizes and mineral dust account for approximately 60% and 40% of the surface area within the OBL. Nucleation mode particles are present in highest concentrations above the OBL where total surface area is lower and the accumulation mode area is centered at smaller particle diameters.

Figure 5.5 – Aerosol number (top), area (middle) and volume (bottom) distributions measured during the afternoon fly-by of the Gosan surface site during ACE-Asia RF07, April 12th, 2001. Nucleation mode particles are identical to those observed at the ground station and have shifted to larger size classes than those recorded during the morning fly-by (Figure 5.3).

5.3 Size distributions from ACE-Asia RF08

From 1:35 – 2:05 UTC on April 13th the C-130 completed an intercomparison with R/V Ron Brown located at 35.74°N, 132.50°E. The C-130 recorded nucleation mode particles with a peak diameter of 14 nm compared to a peak diameter of 13 nm measured aboard the Ron Brown (D. Covert, U. of Washington). The Ron Brown recorded evolving size distributions during April 13th similar to the Gosan surface site the previous day. The C-130 continued to operate in the postfrontal airmass on April 13th observing nucleation mode particles in the MBL North and South of the Japanese archipelago. The C-130 completed two vertical profiles at 7:00 UTC above the LIDAR installation at Amami-Oshima. In figure 5.6 we show the composite size distribution for these profiles from the surface to 3000 meters. C_{crit} reaches it's minimum value of $4.5 \times 10^7 \text{ cm}^{-3}$ just below the inversion located at ~1800 m. Values of C_{crit} suggest that the cold high relative humidity condition near the MBL inversion is the most favoured site for the formation of secondary aerosols via binary nucleation. Unfortunately H_2SO_4 measurements were not available aboard the C-130 so a relative comparison to C_{crit} as an indicator of binary nucleation is not possible. However, PILS data show that the molar ratios of $[\text{NH}_4^+]:([\text{SO}_4^{2-}]+[\text{NO}_3^-])$ are still between 0.83 and 0.68 for these profiles suggesting the presence of ammonia during the southern profile of RF08. The presence of nucleation mode particles (bottom of Figure 4.7) throughout the MBL suggests that in fact aerosols are forming throughout the column but that the strongest driving force arising from the highest relative acidity should be near the MBL inversion as evident by the relative minima in C_{crit} (Figure 5.6).

Figure 5.6 – Vertical structure of the aerosol number distribution near Amami-Ohshima during ACE-Asia RF08 on April 13th, 2001. Highest concentrations of nucleation mode particles exist near the MBL inversion where the C_{crit} parameterization indicates gas-to-particle conversion of sulfuric acid is favoured. Presence of nucleation mode particles throughout the marine boundary layer suggests that they are forming throughout the column or that they are being mixed after forming near the inversion.

6.0 Particle growth rates for April 12th and April 13th

The C-130 observed nucleation mode particles throughout the MBL on April 12th while traveling across 8 degrees of longitude (~720 km) and 4 degrees of latitude (~440 km). Moreover, the following day, while conducting operations in essentially the same airmass the C-130 again observed nucleation mode particles throughout the MBL while covering 6 degrees of longitude (~540 km) and 7 degrees of latitude (~770 km). These observations show that formation of secondary aerosols occurred on a scale of about 200,000 km² over a two-day period. High secondary aerosol concentrations in the wake of a passing cold front appears to be associated with steep vertical gradients in aerosol surface area, relative humidity and temperature (Figures 4.5, 4.6, 4.7, 5.4 and 5.6). Other publications [Easter and Peters, 1994; Nilsson and Kulmala, 1998] suggest that nucleation events can occur in regions where airmasses of slightly different character (e.g. relative humidity, temperature, H₂SO₄, SO₂, aerosol surface area etc.) can mix. Our observations appear to confirm that steep gradients in thermodynamic variables, gas concentrations and aerosol surface area, particularly those associated with atmospheric layers (OBL and the MBL inversion), can enhance new particle production on a synoptic scale [Nilsson *et al.*, 2001].

6.1 Growth rates as observed by the C-130

While ACE-Asia flights RF07 and RF08 were not designed as Lagrangian experiments the back trajectories suggest that the aircraft remained within the same air mass over a two-day period. If the C-130 observations reflect widespread secondary aerosol formation and growth throughout the MBL during these two days then a plot of nucleation mode diameter vs. UTC time should reveal this. All recent nucleation peaks evident below 63 nm were identified for these flights and plotted vs. time of day. The top row of figure 6.1 shows the peak diameter of the nucleation peak for the dry ambient size distributions from RF07 and RF08 along with a linear fit estimate indicative of the growth rate. The graphs show remarkable agreement between the two days with linear growth rates of 2.4 and 1.7 nm hr⁻¹ for flights seven and eight with R² statistics of 0.6294 and 0.8314. These values are consistent with other observed growth rates [Aalto *et al.*, 2001; Birmili and Wiedensohler, 2000; Birmili *et al.*, 2000; Verheggen and Mozurkewich, 2002; Weber *et al.*, 1997; Weber *et*

al., 1998a] summarized in table 6.1. The data shows a slightly higher growth rate in the Yellow Sea (RF07) as compared to the Sea of Japan and East China Sea (RF08). Intercepts for both growth plots suggest that at 00:00 UTC (9:00 JST) the particles had sizes of about ~10 nm. However, extrapolation of the growth rate indicates formation of nucleating clusters (1 nm) at 05:00 or 04:00 JST. Sunrise on the two days occurred at 06:13 and 06:11 JST indicating our linear extrapolation of particle growth is not accurate at or near the time of formation when particles are very small (< 10 nm).

Figure 6.1 – Evolution of the nucleation mode aerosols observed over a synoptic scale during ACE-Asia flights RF07 and RF08 flown on April 12th and 13th of 2001. The top row indicates the size of the peak diameter of nucleation mode particles as measured at dry conditions. Bottom row indicates the peak diameter of neutralized nucleation mode after heating to 150°C.

Table 6.1 – Particle growth rates published for other regions and environmental conditions.

Publication	Growth Rate	Environment/Location
<i>Weber et al.</i> , 1997	1.2 +/- 0.4 nm hr ⁻¹	alpine, clean continental
<i>Weber et al.</i> , 1998	2 to 5 nm hr ⁻¹	biogenically impacted clean marine
<i>Birmili and Wiedensohler</i> , 2000	4.1 +/- 2.3 nm hr ⁻¹	polluted continental
<i>Birmili et al.</i> , 2000	2.1 +/- 0.1 nm hr ⁻¹	alpine, clean continental
<i>Aalto et al.</i> , 2001	3 to 4 nm hr ⁻¹	boreal forest
<i>Verheggen and Mozurkewich</i> , 2002	4.2 +/- 0.8 nm hr ⁻¹	polluted continental
<i>McNaughton et al.</i> , 2003	1.7 to 2.4 nm hr ⁻¹	polluted marine

If sulfuric acid were the only gas phase compound condensing on the aerosol size distribution then we expect that after sunset (19:10 JST April 12th) photochemical production of OH radicals necessary for converting SO₂ to H₂SO₄ would stop and condensational growth of the nucleation mode particles would be suspended until the following morning. Since it is likely that ammonia and low vapour pressure organics⁴ continue to condense after sunset, nucleation mode particles may continue to grow overnight. Continued growth of the nucleation mode particles occurs in conjunction with the coagulation process which will deplete the total number of nucleation mode aerosols transferring their mass to larger size classes.

On April 13th the airmass North and South of Japan was the same airmass characterized the previous day over the Yellow Sea (Figure 4.3). April 13th size distributions show no distinct evidence of the nucleation mode particles formed on April 12th. The data suggests that overnight condensational growth rates are not high enough to shift the nucleation mode particles far enough into the Aitken mode size classes such that they appear as a distinct mode in the aerosol size distribution 16 – 24 hours after their formation. Thus the nucleation events on April 12th and 13th appear to represent a daily cycle of new particle production in the region. Modeling of the coagulation rate for the nucleation mode particles is discussed in Section 7.3.

⁴ Mass of organic carbon (OC) is approximately equal to the mass of sulfates for the accumulation mode aerosol in this environment (*B. Huebert, A. Clarke*, personal communication).

6.2 Evidence for Partial Neutralization of the Nucleation Mode Particles

The data obtained from the size distributions recorded at 150°C (second row of Figure 6.1) is also of interest since it reveals the development of a component refractory at 150°C as the secondary aerosols age. The data shows the nucleation mode aerosol to be less volatile at 150°C over time indicating that ternary species (ammonia and/or organics with a boiling point > 150°C) are being incorporated through condensation into the nucleation mode aerosols. However, the different slopes drawn through this data are uncertain in view of the scatter in the data.

Size distributions during RF07 and during RF08 also suggest neutralization of the nucleation mode aerosol. Examples of these size distributions are shown in figures 6.2 and 6.3. Five distributions from RF07 show 46.9 % +/- 14.8 % of the nucleation mode volume is refractory after heating to 150°C (Table 6.2). Four distributions from RF08 show 25.6 % +/- 8.3 % of the nucleation mode volume is refractory (Table 6.3). Size distributions from RF07 were obtained near the Gosan surface site in the Yellow Sea. Size distributions from RF08 were obtained South of Kyushu and near Amami. This analysis shows that the nucleation mode aerosol is becoming less volatile over time and suggests that the ternary species participating in neutralization of the particles might also participate in secondary aerosol formation during gas-to-particle conversion.

Table 6.2 – Percent neutralization of nucleation mode volume at 150°C as inferred from volatility and size distributions near Jeju Island (Yellow Sea) during ACE-Asia RF07 on April 12th, 2001.

Scan Time	Dry ambient peak DP	150°C peak Dp	% Volume Neutralization
7:00-7:08	28.4	24.6	48.0
7:08-7:17	26.4	24.6	55.3
7:18-7:25	30.5	28.4	63.3
7:33-7:41	19.8	13.8	32.3
7:41-7:49	19.8	16.0	36.8
Mean	24.1	20.7	46.9
Stdev	5.3	6.9	14.8

Table 6.3 – Percent neutralization of nucleation mode volume at 150°C as inferred from volatility and size distributions near Amami-Oshima (East China Sea) during ACE-Asia RF08 on April 18th, 2001.

Scan Time	Dry ambient peak DP	150°C peak Dp	% Volume Neutralization
4:33-4:41	16.0	15.0	37.2
4:41-5:00	16.6	12.5	25.7
5:01-5:15	13.8	12.0	21.4
5:15-5:31	19.8	14.0	18.3
mean	16.6	13.4	25.6
stdev	2.5	1.4	8.3

Figure 6.2 – Aerosol number (top), area (middle) and volume (bottom) distributions near Gosan during ACE-Asia flight RF07 shows 48.0% neutralization (inset) of the nucleation mode volume after heating to 150°C and suggests the participation of ternary species (NH₃ or organics) during gas-to-particle conversion.

Figure 6.3 – Aerosol number (top), area (middle) and volume (bottom) distributions near Amami during ACE-Asia flight RF08 shows 18.3% neutralization (inset) of the nucleation mode volume after heating to 150°C and suggests the participation of ternary species (NH₃ or organics) during gas-to-particle conversion.

6.3 Evolution of the size distribution at the surface

The ubiquity with which nucleation mode particles were observed within the MBL on April 12th and 13th show that, on average, growth rates for the nucleation mode aerosols was between 2.4 and 1.7 nm hr⁻¹. The Gosan field site and the R/V Ron Brown also obtained size distributions at the surface using differential mobility analyzers. These platforms essentially occupied a Eulerian reference frame. If the production of secondary aerosols was occurring at a single location and is then advected to the platforms we would not expect to see the same evolution in the size distributions obtained near the surface. Also if air mass heterogeneity was responsible for differences in the aerosol size distribution than the stationary surface sites should record this with better temporal resolution.

In fact, both the Gosan surface site and the R/V Ron Brown observed evolving size distributions during April 12th and April 13th (Figure 6.4). This data is consistent with our interpretation of aerosol growth from the C-130 data. The C-130, with its broad spatial resolution, demonstrates that the formation of secondary aerosol in this region occurred throughout the air mass on a synoptic scale and over a two-day period. The surface sites demonstrate condensational growth of the nucleation mode aerosol as well as reductions in total particle number over time indicating scavenging of nucleation mode aerosols by the accumulation and coarse mode aerosol. Figure 6.4 also shows that the growth rates from the C-130 are broadly consistent with those measured at the surface but that near 0:00 UTC (9:00 JST) the C-130 estimates over-predict nucleation mode diameters. The ground stations both show that near 0:00 UTC growth rates appear to be higher than 2 nm hr⁻¹. The comparison confirms that our earlier extrapolation of the intercepts (at 10 nm) to a 1 nm cluster size is inaccurate.

Figure 6.4 – Evolution of the nucleation mode aerosols as observed by the Gosan surface site on April 12th, 2001 and observed by the R/V Ron Brown on April 13th, 2001. Growth rates are broadly consistent with the linear regression of nucleation mode growth rates calculated from the C-130 while surveying the regional airmass.

7.0 Discussion

Although measurements of H_2SO_4 were limited during TRACE-P flight 14 and were not available during ACE-Asia, the C_{crit} parameterization indicates the concentration of H_2SO_4 during TRACE-P RF14 was insufficient to explain secondary aerosol formation at the time of observation. And, although no measurements of NH_3 gas were made aboard the NASA P3-B or NCAR C-130, it is likely that the large urban centers and agricultural facilities in the region have NH_3 emission rates of the same order of magnitude as the emission rates for SO_2 [Huebert *et al.*, submitted 2003; Streets *et al.*, submitted 2002]. This information suggests that NH_3 was available for a ternary nucleation mechanism.

In laboratory experiments Ball *et al.* [1999] showed that 80 pptv of NH_3 (g) increases nucleation rates in the H_2SO_4 - H_2O - NH_3 system by up to an order of magnitude at 15% RH. These findings are also consistent with Hanson and Eisele [2002] who show ammonia and sulfuric acid can play an important role in forming new particles in the atmosphere and that the ternary system has a strong dependence on relative humidity.

Field measurements of aerosols collected at Qingdao China (36.0°N, 120.3°E) in October 1996 indicated that morphology and composition of particle droplets in the 0.04 – 0.11 μm size range consisted of sulfuric acid and/or partially neutralized sulfate species [Zhang *et al.*, 1999]. Particle-into-Liquid samplers operated aboard the NASA P3-B and the NCAR C-130 show equivalent mole fractions consistent with accumulation mode aerosol dominated by neutralized sulfuric acid species. Finally, partial neutralization of the nucleation mode aerosols suggests that a plausible explanation for the observations is new particle production via a ternary nucleation mechanism involving H_2SO_4 , H_2O and NH_3 .

7.1 Fog Formation Over the Yellow Sea

Although the discussion in Section 6.0 emphasized a synoptic scale nucleation event this is due in part to large-scale similarity in air mass characteristics. It is important to keep in mind that processes that favor formation and evolution of aerosol can depend upon small-scale variations in these characteristics (microphysical environments). A marked event of boundary layer nucleation and the role of boundary layer processes on aerosol evolution was evident in TRACE-P measurements made over the Yellow Sea [Weber *et al.*, submitted

2002]. They attribute the formation of secondary aerosols to a pollution “plume” being advected from Mainland China to the Yellow Sea by the regional Southeasterly flow. In the central and southern profiles of TRACE-P flight 14 (middle and bottom rows of Figure 4.5) ambient and potential temperature as well as water vapour mixing ratio indicate that a shallow layer of evaporative cooling exists below ~500 m. After the descent at the central profile the P3-B flew at 118 m heading north between 34.25°N and 35.75°N and then ascending to complete the northern profile (top of Figure 7.1). In the northern profile (first row of Figure 4.5) the layer of evaporative cooling is less apparent and particle concentrations remain high throughout the MBL. In contrast particle concentrations are lowest in the central and southern profiles within the layer of evaporative cooling.

Relatively low variability (7-10%) was observed in unreactive gas and aerosol combustion indicators including refractory CN (RCN) and CO during the horizontal leg near the surface (top of Figure 7.1). However, reactive aerosol precursors SO₂ and H₂SO₄ as well as volatile CN (VCN), drop by factors of 3.6, 6.2 and ~30 between their maximum at 507 m and their minimum during the level leg (center and bottom of Figure 7.1). The *Wexler et al.* [1994] formulation for C_{crit} predicts that increasing relative humidity favours nucleation, however, the high relative humidity environment at the surface, prior to 4:15 UTC, shows the least number of volatile CN. Relative humidity and VCN both increase after 4:15 UTC (>35.25°N) on the approach to the northern profiles’ ascent. This is the region with a less pronounced OBL.

Figure 7.2 illustrates the relationship between relative humidity and SO₂, H₂SO₄ and VCN below 1.0 km for the central profile, the level leg at 118 meters and the northern profile shown in figure 7.1. Outside of the OBL ($w < 2.9 \text{ g kg}^{-1}$) each parameter is positively correlated to relative humidity (black lines). This suggests that the source of SO₂ is near the surface and that the production of sulfuric acid and new particle number are favoured in the high relative humidity environment. This observation is consistent with the C_{crit} formulation of *Wexler et al.* Within the OBL ($w > 2.9 \text{ g kg}^{-1}$) the relationship between SO₂, H₂SO₄ and VCN becomes negative (red lines) with R^2 statistics of 0.9095, 0.9004 and 0.9138. Such a close coupling between gas phase precursors, volatile aerosol and RH suggest that air mass history, with regard to relative humidity, may have influenced the formation of nucleation mode aerosols.

Figure 7.1 – Altitude and non-reactive tracers along 124.4°E during TRACE-P flight 14 (top). Volatile CN (VCN), SO₂ and H₂SO₄ are negatively correlated to relative humidity during the boundary layer run (middle and bottom). Calculations of C_{crit} at ambient RH indicated binary nucleation is not possible. However, calculations at 97% RH (C_{crit97}) suggest binary nucleation was possible during the initial descent over a shallow layer of fog that may have existed earlier in the day.

Figure 7.2 – Linear regressions of the relationship between SO₂ (top left), H₂SO₄ (top right), volatile CN (bottom left) and relative humidity. Positive correlations outside the OBL (black lines) indicate production of sulfuric acid and secondary aerosols is favoured in the high RH environment. Within the OBL (red lines) the formation of surface fog has depleted gas phase precursors and new particle number through aqueous phase chemistry and coagulation.

Returning to figure 4.5 we note that by extrapolating the values of water vapour mixing ratio and ambient temperature from 118 m to the surface (25 m and 101.325 kPa) RH values for the southern and central profiles exceed 100% (Table 7.1). The extrapolations of relative humidity show that fog may have existed over the Yellow Sea earlier in the day. C_{crit} calculations were made at 97% relative humidity (C_{crit97}) to estimate the potential for nucleation under near cloud (fog) conditions. This is plotted in the bottom panel of figure 7.1 and suggests that sulfuric acid concentrations at this RH could have sustained binary homogeneous nucleation at the 507 m level.

Table 7.1 – Extrapolation of thermodynamic parameters from TRACE-P RF14 on March 18th, 2001 from ~ 115 m to 25m. Coastal fog appears likely in the OBL for the Central and Southern profiles but is absent from the Northern profile (see also Figures 4.5, 7.1 and 7.2).

	Parameter	RF14 North Profile	RF14 Central Profile	RF14 South Profile
Original Data	P (mb)	986.93	987.10	987.42
	Alt. (m)	117.9	115.6	112.0
	w (g kg ⁻¹)	3.04	5.80	5.69
	Theta (°C)	14.3	10.7	10.3
	T (°C)	13.3	9.6	9.2
	es (mb)	15.23	11.97	11.66
	ws (g kg ⁻¹)	9.45	7.45	7.26
	RH (%)	32.1%	77.9%	78.4%
	H ₂ SO ₄ (molecules cm ⁻³)	-	2.68E+07	-
	C _{crit}	8.38E+08	1.22E+08	1.15E+08
Extrapolation to 25 meters	P (mb)	1013.25	1013.25	1013.25
	w (g kg ⁻¹)	3.34	7.01	7.24
	T (°C)	13.4	8.7	9.4
	ws (g kg ⁻¹)	9.29	6.84	7.15
	es (mb)	15.36	11.27	11.78
	RH (%)	36.0%	102.4%	101.3%
	C _{crit}	7.24E+08	4.43E+07	4.95E+07

Highest concentrations of nucleation mode particle were observed above the OBL (Figure 5.1) but a small nuclei mode was also evident within the layer (Figure 5.2). This indicates that nucleation was occurring in both locations under the high relative humidity conditions. However, the large reduction in SO₂, H₂SO₄ and VCN compared to unreactive CO and RCN while flying at 118 m suggests enhanced relative removal of these species within the ocean boundary layer. This presents the possibility that preferential scavenging might have occurred for SO₂ and H₂SO₄ relative to CO and the primary aerosol through cloud or fog conditions where enhanced surface area and rapid aqueous reactions can accelerate the production of sulfates [Hegg and Hobbs, 1981]. If formation of secondary aerosols within the fog layer occurred then the surface area provided by the fog droplets (D_p between 5 and 50 µm) could result in rapid coagulation of the nucleation mode aerosol. The

nucleation mode particles observed in the size distribution at 118 m (Figure 5.2) either survived the coagulation process or formed after the dissipation of the fog similar to observations by *Kerminen and Wexler* [1994b]. The smaller size of particles within the OBL could be a result of a lower rate of sulfuric acid condensation in a region where the sulfur dioxide and sulfuric acid precursors have been drawn down by aqueous phase chemistry. Cloud scavenging and enhanced production of sulfuric acid in the fog layer may also provide an explanation for less neutralization of the larger accumulation mode aerosols at 118 m (Figure 5.2) compared to the size distribution obtained at 663 m and presumed to be above the layer of morning fog (Figure 5.1).

Flight operations in the Yellow Sea during TRACE-P RF14 were centered on 4:00 UTC (1:00 pm JST) on March 18th, 2001. No clouds were evident and the crew aboard the NASA P3-B did not report observations of fog during the flight. However, local meteorology stations reported “heavy fog”, “fog”, “smoke” and “haze” across the Eastern and Western coasts of the Gulf of Bo Hai and Yellow Sea and extended past Shanghai to as far south as Hong Kong at 0:00 UTC (9:00 am JST). Figures 4.6 and 5.4 show that the OBL structure during ACE-Asia RF07 (April 12th, 2001) was similar to the conditions observed on March 18th during TRACE-P flight 14. Less extensive reports of “heavy fog”, “smoke”, “fog” and “haze” were recorded North and South of the Shandong Peninsula, at coastal sites in North Korea and as far South as Shanghai on April 12th despite the fact that fog was not reported by the crew aboard the NCAR C-130. Archived sea surface temperature (SST) from April 12th (a detailed map for March 18th was not available) show upwind coastal SST appear 1 – 5 degrees cooler than SST at the observation points during the ACE-Asia RF07 on April 12th (see Figure 4.8).

Spring fog over the Yellow Sea is not unusual. *Chung et al.* [1999] report that the 6-year average of foggy days (visibility < 1 km) from 1991 to 1996 for an inland site in South Korea are 5.2 days for March and 3.8 days for April. The number of misty or hazy (associated with pollution) days was 19.8 and 20.0. They report that radiative cooling in the cloud free regions of synoptic scale subsidence and that differences in air-sea temperatures can result in fog formation in the Yellow Sea that can then be advected inland. Synoptic scale nucleation events were only observed on 2 out of 10 flights into the Yellow Sea. Taken as a representative sample we expect this phenomenon could be occurring on ~ 6 days per

month in the spring. This is also consistent with ground station data from Gosan which showed strong nucleation events occurred on at least eight days during April of 2001.

These observations indicate that cooler conditions prevailed earlier in the day (as investigated in Table 7.1) and formation of fog enhanced the transfer of gas phase precursors to the aerosol size distribution [Kerminen and Wexler, 1995]. Within and directly above the fog layer, binary and/or ternary nucleation created the high concentrations of nucleation mode particles consistent with the post-fog nucleation of Kerminen and Wexler [1994b] and similar to conditions associated with nucleation near cloud outflow [Clarke *et al.*, 1999; Clarke *et al.*, 1998; Weber *et al.*, 2001a]. Hence, the nucleation mode particles observed just above the OBL and present at reduced concentrations and smaller sizes within the OBL are consistent with fog formation that would lower rates of condensation growth while depleting their number due to scavenging by the elevated aerosol surface area.

Because of the common presence of fog it is clear the production and growth of nuclei will vary greatly in the region even when precursors remain at similar levels. Consequently, although high RH and colder temperatures create more favorable conditions for nucleation of sulfuric acid aerosol, if these conditions lead to fog formation then the increase in surface area both scavenges gas precursors and many of the nuclei formed. This example can also be applied to conditions near the MBL inversion a common site of cloud formation for the region. Colder temperatures and higher RH at altitude tend to favor nucleation, however these secondary aerosols are expected to have very short lifetimes once clouds begin to form.

7.2 Flux Rate of Sulfuric Acid to the Size Distribution

Typical mid-day growth rates for the nucleation mode aerosols during RF07 and RF08 were estimated at 2.4 and 1.7 nm hr⁻¹. Size distributions at the Gosan surface site and aboard the R/V Ron Brown also reflect this with better temporal resolution. Figure 6.4 shows that the growth rates from the C-130 are broadly consistent with those measured at the surface but near 0:00 UTC (9:00 am JST) the C-130 estimates tend to over-predict nucleation mode diameters. Using the change of particle diameter with respect to time, dD_p/dt , we can calculate the condensation and coagulation sink (CS and CoagS) by adopting the method of Kulmala *et al.* [2001] (see Section 2.0). These calculations will allow us not only to estimate

the flux rate of vapour (believed to be dominated by sulfuric acid) to the size distribution but also to estimate the coagulation rate of the nucleation mode particles and thus their atmospheric lifetime. The MATLAB code created to evaluate the condensation and coagulation sinks as well as those used to estimate flux rates and volume of sulfuric acid added to the aerosols is contained in Appendix C.

The values for the condensation sink (CS) and the vapour flux (Q) are summarized in table 7.2. Growth rates of 2 nm hr^{-1} were used based on three size distributions from TRACE-P RF14, four size distributions from ACE-Asia RF07 and three distributions from ACE-Asia RF08. Where the nucleation mode particle concentrations were highest, calculations at 1 nm hr^{-1} and 4 nm hr^{-1} have also been included. The mean vapour flux, based on a 2 nm hr^{-1} growth rate is $2.4 \times 10^6 \text{ molecules cm}^{-3} \text{ s}^{-1} \pm 1.2 \times 10^6 \text{ molecules cm}^{-3} \text{ s}^{-1}$. These values compare favourably with sulfuric acid production rates of $0.5 - 2.0 \times 10^6 \text{ molecules cm}^{-3} \text{ s}^{-1}$ calculated by *Weber et al.* [submitted 2002] for TRACE-P RF14. This indicates that our steady state assumption for equation 2.2 appears reasonable.

Using the *Weber et al.* [submitted 2002] estimates for sulfuric acid production and the dry ambient size distributions measured aboard the NASA P3-B and the NCAR C-130 it is possible to estimate the mass added to the submicrometer and supermicrometer aerosol. We provide estimates for addition of mass based on three different aerosol size distribution scenarios. The first is a pollution dominated case from TRACE-P RF14 where total aerosol surface area is $1221 \text{ um}^2 \text{ cm}^{-3}$ with 89 % of the area in sizes $< 1.0 \text{ um}$. The second case is a mixed dust/pollution scenario from ACE-Asia RF07. Total aerosol surface area is $690 \text{ um}^2 \text{ cm}^{-3}$ with 47 % of the area in the submicrometer mode. The last case is a dust-dominated case during ACE-Asia RF06. During this case total surface area is $1278 \text{ um}^2 \text{ cm}^{-3}$ with 76% of the area in the coarse ($> 1.0 \text{ um}$) mode. The results in table 7.3 were obtained assuming condensation to the size distribution is simply related to the available aerosol surface area and using production rates of $0.5, 1.0$ and $2.0 \times 10^6 \text{ molecules cm}^{-3} \text{ sec}^{-1}$ for eight hours. The calculations indicate that after eight hours $1.8 - 7.22 \text{ um}^3 \text{ cm}^{-3}$ of sulfuric acid can be added to the size distribution. Depending on the partitioning of surface area for each scenario this amounts to between 2.4 and 24.3 % increases in submicrometer volume and between 0.1 and 1.1% increases in coarse mode volume.

Table 7.2 – Sulfuric acid flux rate to size distributions observed during TRACE-P RF14 on March 18th, 2001 and ACE-Asia RF07 and RF08 on April 12th and 13th, 2001.

Flight	UTC Time (hh:mm)	Altitude (m)	SA ($\mu\text{m}^2 \text{cm}^{-3}$)	dDp/dt (nm hr ⁻¹)	CS (s ⁻¹)	Q (molecules cm ⁻³ s ⁻¹)
TP RF14	3:53-4:00	663	644	1	3.76E-02	1.66E+06
	3:53-4:00	663	644	2	3.76E-02	3.32E+06
	3:53-4:00	663	644	4	3.76E-02	6.63E+06
	4:03-4:15	118	1221	2	3.59E-02	3.16E+06
	4:19-4:25	155	1144	2	4.90E-02	4.32E+06
AA RF07	1:36-1:45	97	690	2	1.81E-02	1.60E+06
	4:09-4:12	48	774	2	2.07E-02	1.83E+06
	4:19-4:22	677	609	1	3.81E-02	1.68E+06
	4:19-4:22	677	609	2	3.81E-02	3.36E+06
	4:19-4:22	677	609	4	3.81E-02	6.73E+06
	5:42-5:44	512	667	2	2.82E-02	2.49E+06
AA RF08	1:48-2:05	61	426	2	1.50E-02	1.32E+06
	6:59-7:01	93	389	2	1.27E-02	1.12E+06
	7:12-7:14	1295	295	1	1.11E-02	4.91E+05
	7:12-7:14	1295	295	2	1.11E-02	9.82E+05
	7:12-7:14	1295	295	4	1.11E-02	1.96E+06
$\rho \text{H}_2\text{SO}_4$		1.40	mean (2nm/hr only)		2.66E-02	2.35E+06
Mm H_2SO_4		98.08	stdev (2nm/hr only)		1.30E-02	1.15E+06

Table 7.3 – Volumetric increases to three types of aerosol size distributions based on the calculated sulfuric acid flux rates. The three distributions represent airmasses dominated by pollution (TRACE-P RF14), pollution with dust (ACE-Asia RF07) and dust (ACE-Asia RF06) as illustrated by the proportions of accumulation and coarse mode surface areas.

Flight	Time	H ₂ SO ₄ Flux (molec. cm ⁻³ s ⁻¹)	Acc. SA (μm ² cm ⁻³)	Coa. SA (μm ² cm ⁻³)	Acc. Vol. (μm ³ cm ⁻³)	Coa. Vol. (μm ³ cm ⁻³)	New Acc. Vol. (μm ³ cm ⁻³)	New Coa. Vol. (μm ³ cm ⁻³)	% Acc. Vol. Increase	% Coa. Vol. Increase
TP RF14	4:03 -4:15	5.00E+05	1085	135.5	65.57	100.4	1.60	0.20	2.4	0.2
		1.00E+06					3.21	0.40	4.9	0.4
		2.00E+06					6.42	0.80	9.8	0.8
AA RF07	1:36 -1:45	5.00E+05	325.0	365.0	14.73	353.6	0.85	0.95	5.8	0.3
		1.00E+06					1.70	1.91	11.6	0.5
		2.00E+06					3.40	3.82	23.2	1.1
AA RF06	2:00 -2:30	5.00E+05	305.5	972.7	19.31	946.1	0.43	1.37	2.3	0.1
		1.00E+06					0.86	2.75	4.5	0.3
		2.00E+06					1.73	5.49	9.1	0.6

7.3 Coagulation Rate of Nucleation Mode Particles

In order to estimate particle losses due to coagulation we have selected the peak diameter of the nucleation mode particles and the maximum diameter of the nucleation mode particles to provide a measure of particle lifetime. The maximum nucleation mode diameter was chosen as the local minima between the nucleation mode particles and the remainder of the Aitken mode particles. We note that many of the particles will have substantially smaller coagulation rates as condensation shifts the size distribution to the right. More accurate modeling of the combined condensation/coagulation processes using a discreet or modal parameterization is needed and may be the focus of future work. Results for the calculation of CoagS for the same ten size distributions as used in the estimates for the condensational sink (Table 7.2) are summarized in table 7.4. The data shows that in the high surface area environment during ACE-Asia and TRACE-P the pollution derived accumulation mode aerosols and the naturally produced dust aerosols are effective at scavenging the observed nucleation mode particles on the order of one to two days. However, the lower surface area conditions in the East China Sea observed during ACE-Asia RF08 show that these secondary aerosols could persist in significant concentrations up to 72 hours after their formation.

In section 6.1 we mention that none of the nucleation mode particles observed over the Yellow Sea during ACE-Asia RF07 appear as distinct modes in the size distributions of RF08 despite our suggestion that we remained within the same airmass over the two-day period. Peak diameters of the nucleation mode particles at 10:00 UTC (19:00 JST)⁵ are between 25 and 40 nm (Figure 6.1). Size distributions from the Gosan surface site suggest that at 12:00 UTC (21:00 JST) the nucleation mode particles are 30 – 40 nm in diameter. If condensation overnight continued at a rate of 2 nm hr⁻¹ then at 0:00 UTC on April 13th the same 30 – 40 nm particles should be 54 – 64 nm in diameter. No particles 50 – 70 nm in diameter form a distinct mode in the aerosol size distributions on April 13th.

In table 7.4 we see that particles smaller than ~40 nm in diameter will be eliminated by coagulation within ~24 hours but that particles near ~60 nm in diameter could exist for up to 48 hours for the size distributions measured on April 12th. We suggest two possible reasons for the absence of a distinct set of Aitken mode particles in the size distributions

⁵ Sunset occurred at 19:10 and 19:11 JST for April 12th and 13th, 2001.

from April 13th. Back trajectory analysis (Figure 4.3) shows most of the regional airmass sampled on April 13th passed over the landmasses of South Korea or Japan. We suggest that mixing due to topography, nighttime clouds, as well as local inputs of primary aerosols and gas phase precursors have the potential to modify the aerosol size distribution affecting the survivorship of the newly formed secondary aerosols. Second, condensational growth rates overnight could not be estimated. Condensational growth could have been lower than 2 nm hr⁻¹ and may even have been suspended overnight. If these particles remained small then the coagulation rates of the new secondary aerosols will remain high resulting in faster removal and their relative absence from the size distributions on April 13th.

Observationally we saw no evidence of the particles formed on April 12th surviving to contribute a distinct population of new particle number in size distributions on April 13th. This suggests that the coagulation rate of these particles is sufficiently high to eliminate these particles in 16 – 24 hours. This is broadly consistent with the modeled e-folding times for size distribution in the Yellow Sea summarized in table 7.4. A more detailed analysis using a modal parameterization of the size distribution that incorporates condensation and coagulation in order to evaluate particle dynamics is necessary to make more conclusive statements about the fate of these secondary aerosols.

Table 7.4 – Coagulation rates and e-folding times for the nucleation mode particles observed in size distributions from TRACE-P RF14 on March 18th, 2001 and for ACE-Asia RF07 and RF08 on April 12th and 13th, 2001.

Flight	UTC Time	Altitude	Dry ambient SA	RH = 25%			RH = 75%		
				Dp	CoagS for peak Dp	Dp e-fold	Dp	CoagS for peak Dp	Dp e-fold
	(hh:mm)	(m)	($\mu\text{m}^2 \text{cm}^{-3}$)	(μm)	(s^{-1})	(hr)	(μm)	(s^{-1})	(hr)
TP RF14	3:53-4:00	663	644	0.010	2.25E-04	1.23	0.013	1.98E-04	1.40
				0.021	5.33E-05	5.21	0.028	4.52E-05	6.15
				0.044	1.67E-05	16.6	0.058	1.31E-05	21.2
	4:03-4:15	118	1221	0.008	2.96E-04	0.94	0.010	2.61E-04	1.06
				0.025	3.74E-05	7.43	0.028	3.66E-05	7.58
	4:19-4:25	155	1144	0.010	2.56E-04	1.09	0.013	2.49E-04	1.12
0.021				6.88E-05	4.04	0.028	5.65E-05	4.91	
AA RF07	1:36-1:45	97	690	0.013	6.19E-05	4.49	0.016	5.82E-05	4.77
				0.026	1.57E-05	17.7	0.035	1.24E-05	22.5
	4:09-4:12	48	774	0.016	4.55E-05	6.11	0.021	3.63E-05	7.66
				0.035	1.19E-05	23.3	0.044	1.05E-05	26.6
	4:19-4:22	677	609	0.023	5.48E-05	5.07	0.028	5.42E-05	5.13
				0.058	5.36E-06	51.8	0.063	6.11E-06	45.5
5:42-5:44	512	667	0.026	3.24E-05	8.58	0.033	3.10E-05	8.97	
			0.054	6.42E-06	43.2	0.063	6.45E-06	43.0	
AA RF08	1:48-2:05	61	426	0.014	4.35E-05	6.38	0.017	4.01E-05	6.93
				0.028	1.21E-05	22.9	0.035	1.08E-05	25.8
	6:59-7:01	93	389	0.020	2.06E-05	13.5	0.026	1.66E-05	16.8
				0.041	5.43E-06	51.2	0.054	4.31E-06	64.4
	7:12-7:14	1295	295	0.023	1.44E-05	19.4	0.028	1.34E-05	20.7
				0.041	4.80E-06	57.9	0.054	3.86E-06	72.0

8.0 Conclusions

The ACE-Asia and TRACE-P aircraft observations provide the opportunity to study aerosol nucleation and growth over broad spatial and vertical scales. As the profiles show, these observations provide a different perspective from ground or ship based data obtained almost exclusively within 500 m thick “ocean boundary layer”. After studying the profiles and their associated back trajectories, a number of “characteristics” related to secondary aerosol formation can be stated in regard to the “Asian outflow”.

- ◆ As air is advected from the Asian mainland a shallow layer of evaporative cooling, termed the ocean boundary layer (OBL), often forms over the Yellow Sea and Sea of Japan. This layer may be associated with low-level fog over the ocean surface due to radiative cooling during cloud free subsidence events or due to differences in air and sea-surface temperatures.
- ◆ The OBL appears stably stratified and tends to trap local pollution along with gas phase precursors (SO_2 , H_2SO_4 , and possibly NH_3) below ~500 m.
- ◆ At the steep gradient of aerosol surface area, relative humidity and temperature associated with the OBL/MBL interface, peak concentrations of SO_2 and nucleation mode (3 – 12 nm) particles are often observed. The high concentrations of secondary aerosols are consistent with binary nucleation or ternary nucleation in high relative humidity conditions near the OBL/MBL interface.
- ◆ Somewhat lower concentrations of nucleation mode particles are often present throughout the MBL. These particles appear well mixed and linked to one or more of the following conditions.
 - a) Particles formed at the OBL/MBL interface are transported by mixing from the surface throughout the MBL due to convective cells and turbulent eddies.
 - b) Formation of secondary aerosols by a ternary nucleation mechanism is occurring throughout the MBL. Reductions in precursor concentrations with altitude appear somewhat offset by decreasing ambient temperature and increasing relative humidity allowing secondary aerosol formation to occur throughout the column.

- c) Particle formation is favoured near the MBL inversion in cool, high relative humidity conditions.
- ◆ Secondary aerosol formation was observed on a synoptic scale over a two-day period after up to 48 hours of transport from the gas phase precursor source regions.

Under post-frontal outflow conditions we observed growth rates for the nucleation mode particles of 2.4 and 1.7 nm hr⁻¹ aboard the C-130 during ACE-Asia flights 7 and 8. These were consistent with ground based and ship based measurements for the same time period. Applying this growth rate to a subset of size distributions from TRACE-P and ACE-Asia an average sulfuric acid flux rate of $2.4 \pm 1.2 \times 10^6$ molecules cm⁻³ s⁻¹ was obtained. This value represents an upper bound for the estimate of sulfuric acid flux as the accumulation mode aerosol suggests that ammonia and possibly low vapour pressure organics may also condense on the aerosol size distribution. This value is within a factor of two of *Weber et al.* [submitted 2002] who estimated sulfuric acid production rates of $0.5 - 2.0 \times 10^6$ molecules cm⁻³ s⁻¹ during TRACE-P flight 14. Calculations using the *Weber et al.* flux rates correspond to increases of the accumulation aerosol volume of 2.4 – 9.8 % and 2.3 – 9.1 % for area distributions dominated by accumulation mode and coarse mode aerosols respectively. Coarse mode aerosol shows volume increases of 0.2 – 0.8 % and 0.1 – 0.6 % for the same two scenarios.

The influence of fog and high RH was also shown to dramatically influence the formation, growth and survival of new nuclei. Figures 8.1 and 8.2 are conceptual diagrams of the processes believed to cause and/or influence the formation of secondary aerosols in the ACE-Asia and TRACE-P study regions. The figures are representative in nature and aerosol particles and atmospheric structure are not drawn to scale.

Figure 8.1 – Physical and meteorological conditions leading to synoptic scale secondary aerosol formation during spring in East Asia.

1. Cool dry continental air from Central Asia warms and dries further as it descends into the coastal plains of Mainland China.
2. The Beijing-Tianjin urban/industrial complex supplies SO_2 and NH_3 gases to the atmosphere through burning of high sulfur coal (power production and heating) and urban/agricultural activities. These gases are the dominant precursors for secondary aerosol formation.
3. Synoptic scale subsidence in the wake of passing cold fronts leads to cloud free conditions and a well-defined marine boundary layer inversion located at 2000 m ($\pm$ 500 m).
4. The extremely dry air moves out over coastal water bodies with sea surface temperatures lower than the ambient air temperatures. Overnight the formation of coastal fog creates an isolated layer of evaporative cooling between the surface and $\sim$ 500 m ($\pm$ 200 m). The OBL is separated from the remainder of the MBL by a miniature inversion in potential temperature.

Figure 8.2 – Interactions between primary and secondary aerosols in continental outflow from East Asia.

5. At sunrise SO_2 is oxidized to H_2SO_4 through photochemically produced OH. The high RH environment above the fog and near the MBL inversion leads to new particle production and rapid condensational growth of both new particles and existing primary aerosols.
6. While fog persists gas phase precursors are directly converted to aerosol mass by aqueous phase chemistry within the fog layer. Any nucleation mode particles are quickly scavenged in the high surface area, high relative humidity environment. By late morning/early afternoon the fog has dissipated leaving high aerosol surface areas and low concentrations of nucleation mode particles and gas phase precursors.
7. The OBL and MBL appear to remain intact until reaching warm surface waters associated with the Kuroshio Current. The high heat and vapour flux from the ocean surface to the atmosphere destabilizes the OBL and leads to mixing and increased homogeneity throughout the MBL.
8. New secondary aerosols can form after up to 48 hours of transport from Mainland China and may be important for up to 72 hours after forming. Cloud formation and precipitation are the dominant mechanisms for removing new particles that do not coagulate with the primary aerosol before growing (through condensation) to accumulation mode sizes.

Using a simple Brownian coagulation scheme, e-folding times for the peak diameters of the nucleation mode particles was 1 – 21 hours under cloud free conditions in the pollution dominated environment encountered on March 18th, 2001 during TRACE-P flight 14. E-folding times for nucleation mode particles under cloud free conditions were between 4.5 and 52 hours for ACE-Asia flight 7 (April 12th) and between 6.5 and 72 hours for flight 8 (April 13th). As airmasses are advected away from Asian source regions and while gas phase precursor concentrations are sufficient to trigger nucleation events, coagulation rates of secondary aerosols will continue to decline and secondary aerosols have increasing potential to survive as new aerosol number over the Pacific Ocean.

9.0 References

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10.0 Appendix A – DMA Corrections

10.1 Multiplication Factors for Transmission Efficiency

During ACE-Asia RF01 and RF02 the C-130 and the NASA P3-B conducted two intercomparison flights (TRACE-P RF17 & RF018). DMA and OPC size distributions from the flights showed excellent agreement [Moore *et al.*, submitted 2003]. Corrections to the TRACE-P DMA size distributions were calculated from a field evaluation of the transmission efficiency. Using the TRACE-P values as benchmark a comparison between the size distributions from the P3-B and the C-130 during the intercomparison flight was completed. The results from the intercomparison flights resulted in three possible curves for adjusting the ACE-Asia size distributions to correct for transmission efficiency losses. These curves are shown in figure 10.1 below. The TRACE-P correction curve is shown for comparison.

Figure 10.1 – Comparison of the transmission efficiency curves applied to the rDMA data sets for ACE-Asia and TRACE-P.

Results from histogram analysis of the total concentration using each of the three multiplication factor curves showed that the best fit to the UCN and CN data was for the “RF01 and RF02 all scans” curve (solid black line). This curve was applied to the dry ambient and 150°C scans. The multiplication factor curve was arbitrarily not applied to the 300°C due to the relatively large uncertainty of the charge correction after heating to 300°C. Shifts to the size distribution after heating to 150°C are substantially less and the multiplication factor was applied with some confidence. However, since no CN counter operated at 150°C there is no measure of error associated with this calculation. Based on the histograms for the 300°C scans (Figures 3.3 and 3.4) we see that the size distribution measurements are undercounting the UH Hot CN by about 25% for both TRACE-P and ACE-Asia. This suggests that some counting efficiency multiplication factor could be applied but that the curves obtained by comparing the two instruments were not adequate. As this portion of the analysis is not important to the discussion of the nucleation mode particles measured at dry ambient conditions no further corrections were made to the 300°C scans.

10.2 Heated Charging Correction

During October of 2002 a set of laboratory experiments were conducted in order to evaluate how the heated (150°C and 300°C) size distributions were being sized. This investigation was required due to the inability of the DMA inversion program to correct for changes to particle diameters during the heating process. This effect can be summarized as:

- ◆ Particle sizing is based on a boltzman distribution of charges being applied by the polonium neutralizer (β -source) to the particles entering the DMA.
- ◆ For unheated size distributions (dry ambient) this distribution is a known function and is correctly applied.
- ◆ Each particle is charged prior to heating to 150°C or 300°C.
- ◆ The charge distribution for the heated particles is based on their size before heating and the DMA inversion program assumes that particles have the same charge distribution as the unheated particles.
- ◆ Since particles do not lose their charge but do shrink in size (stripped of volatile mass) the particles have a slightly higher charge to mass ratio and the total number counted per channel ($dN/d\log D_p$) will be higher than some “true” value.

In order to quantify this effect a number of laboratory experiments were undertaken in order to evaluate this effect on the 150°C and 300°C scans. Sequentially performing scans with the neutralizer fore and aft of the heating process allowed us to evaluate the effects of heating on the size distribution. Differences between the distributions using the standard configuration ($dN/d_{\log Dp}$ Orig) and the configuration with the neutralizer aft of the heaters ($dN/d_{\log Dp}$ Neut) allow us to empirically derive the correction factor. A fifth-order polynomial fit was calculated and the results are shown in figure 10.2.

Figure 10.2 – Neutralizer charging correction factor based upon laboratory experiments and applied to the ACE-Asia and TRACE-P rDMA size distributions.

10.3 Applying Correction Factors to the DMA Size Distributions

In addition to the correction factors outlined above, size distributions were corrected to standard atmospheric temperature and pressure (SATP, 298.15 °K, 101325 Pa). All of the corrections were applied simultaneously to the DMA size distributions using a MATLAB code called *ACE_dma_MF_ver5b.m*. This code is included below.

10.4 ACE_dma_MF_ver5b.m

```
%-----
% Program for creating version 5 of the ACE-Asia DMA data files
%
% Program takes the version 3 and converts it. Three types of
% conversions are applied in order to produce the version 5 data.
%
% 1) adjustment of size distributions using the transmission efficiency curve
% 2) adjustment of 150oC and 300oC number distributions correcting for heating
% 3) adjustment to STP of all size distributions
%
% If you want to change the te multiplier then simply substitute the new 52
% column matrix in for the te matrix. The number should be the direct
% multiplier for the dN/dlogDp value contained in the log spaced size bin.
% Same procedure applies for the charging corrections
%
% We use 32 channels per decade as shown in the integral as the "/32" suffix.
%
%-----

% Loop for all 19 flights

for n=1:19

if n<=9;
    n1=['0' num2str(n)];
else;
    n1=num2str(n);
end;

% Read the flight's DMA file
dma_num=csvread(['C:\ACE\RF' n1 '\DMA\ACE_RF' n1 '_DMA_rev3_numdist.csv'], 2, 2);

dma_Dp=[5.42E-03 5.83E-03 6.26E-03 6.73E-03 7.23E-03 7.77E-03 8.35E-03 8.98E-03 ...
9.65E-03 1.04E-02 1.11E-02 1.20E-02 1.29E-02 1.38E-02 1.49E-02 1.60E-02 ...
1.72E-02 1.84E-02 1.98E-02 2.13E-02 2.29E-02 2.46E-02 2.64E-02 2.84E-02 ...
3.05E-02 3.28E-02 3.52E-02 3.79E-02 4.07E-02 4.37E-02 4.70E-02 5.05E-02 ...
5.42E-02 5.83E-02 6.26E-02 6.73E-02 7.23E-02 7.77E-02 8.35E-02 8.98E-02 ...
9.65E-02 1.04E-01 1.11E-01 1.20E-01 1.29E-01 1.38E-01 1.49E-01 1.60E-01 ...
1.72E-01 1.84E-01 1.98E-01 2.13E-01];

% Change elements with -999 to Nan's
nines=find(dma_num(:,:) == -9999);
new_dN=dma_num(:,:);
new_dN(nines)=NaN;
dma_num(:,:)=new_dN;

% Get the relay column
dmarelay=dma_num(:,13);

% Build relay dN data matrix and extract other data segments
relay1rows=find(dmarelay==1);
dma_dN_dlogd1=dma_num(relay1rows,15:66);
prelim1=dma_num(relay1rows,1:14);
```

```

flags1=dma_num(relay1rows,70);

relay2rows=find(dmarelay==2);
dma_dNdlogd2=dma_num(relay2rows,15:66);
prelim2=dma_num(relay2rows,1:14);
flags2=dma_num(relay2rows,70);

relay3rows=find(dmarelay==3);
dma_dNdlogd3=dma_num(relay3rows,15:66);
prelim3=dma_num(relay3rows,1:14);
flags3=dma_num(relay3rows,70);

% End of build dN data matrix
%-----
% Apply transmission efficiency (te) MF

% count the rows so we can take other data segments and make a multiplier matrix
rowcount1=size(relay1rows,1);
rowcount2=size(relay2rows,1);
rowcount3=size(relay3rows,1);

% MF=10^(-1.3481*logDp-1.6796)
% Derived from ACE RF01 only

% te_1a=[23.72 21.50 19.54 17.72 16.09 14.60 13.25 12.01 10.90 9.85 9.03 8.13 7.37 6.73 6.07
5.51 5.00 4.57 4.14 3.75 3.40 3.09 2.81 2.54 2.31 2.09 ...
%      1.90 1.72 1.57 1.42 1.29 1.17 1.06 1.00 1.00 1.00 1.00 1.00 1.00 1.00 1.00 1.00
1.00 1.00 1.00 1.00 1.00 1.00 1.00 1.00 1.00];

% MF=10^(-1.8603*log(col(Dp))-2.4041)
% Derived from ACE RF01 and RF02 all scans

te_12=[64.765 56.549 49.537 43.296 37.892 33.140 28.986 25.317 22.145 19.267 17.068 14.764
12.905 11.384 9.870 8.645 7.557 6.666 5.816 5.077 4.437 ...
      3.884 3.406 2.973 2.603 2.274 1.994 1.738 1.522 1.334 1.165 1.019 1 1 1 1 1 1 1 1
1 1 1 1 1 1 1 1];

% MF=10^(-1.4835*log(col(Dp))-1.8488)
% Derived from ACE RF01 and RF02 300oC scans

% te_3=[32.570 29.230 26.302 23.623 21.241 19.088 17.155 15.400 13.841 12.386 11.245 10.017
8.998 8.141 7.266 6.537 5.872 5.313 4.765 4.276 3.840 3.453 ...
%      3.110 2.791 2.510 2.254 2.030 1.819 1.636 1.472 1.322 1.188 1.070 1 1 1 1 1 1 1 1
1 1 1 1 1 1 1 1];

% Apply the te to relays 1, 2 and 3
MF1= repmat(te_12, rowcount1, 1);
MF2= repmat(te_12, rowcount2, 1);
MF3= repmat(te_3, rowcount3, 1);

% Make the new dN values
dma_dNdlogd1=MF1.*dma_dNdlogd1;
dma_dNdlogd2=MF2.*dma_dNdlogd2;
% dma_dNdlogd3=MF3.*dma_dNdlogd3;

% End MF
%-----
% Apply charging correction (this correction applies only to the 150oC and 300oC
% scans). The corrections stems from the inability of the DMA inversion program
% to know the original size of the charged particle and the associated shift in
% particle size after heating. The result is a false boltzman charge distribution
% being assigned to particle sizes. The correction factor was determined by CMC
% during laboratory trials in Oct. of 2002. - CMC - 10/28/02

charge2=[0.47885 0.47885 0.47885 0.47885 0.47885 0.48194 0.48541 0.48936 0.49376 0.4987
0.50422 0.51043 0.51736 0.52513 0.53388 0.54346 0.55418 0.56605 0.57921 0.59367 0.60951
0.62672 ...
      0.64556 0.66584 0.68766 0.71086 0.73552 0.76136 0.78813 0.81558 0.84346 0.87109
0.89808 0.92369 0.9474 0.96851 0.98635 1 1 1 1 1 1 1 1 1 1 1 1];

```

```

charge3=[0.30482 0.30482 0.30482 0.30482 0.30482 0.3111 0.318 0.32568 0.33405 0.34325 0.35332
0.36441 0.37656 0.38993 0.4047 0.42058 0.43802 0.45703 0.47774 0.5001 0.52422 0.54999 ...
0.57773 0.60712 0.63821 0.6707 0.70464 0.73954 0.77499 0.81058 0.8459 0.87997
0.91228 0.94186 0.96807 0.99014 1 1 1 1 1 1 1 1 1 1 1 1 1];

adjust2= repmat(charge2, rowcount2, 1);
adjust3= repmat(charge3, rowcount3, 1);

% Make the new dN values
dma_dNdlogd2=adjust2.*dma_dNdlogd2;
dma_dNdlogd3=adjust3.*dma_dNdlogd3;

% End charge efficiency adjustment
%-----
% Make the correction to SATP (25oC, 101325 Pa)
% Sample temperature (oC) is column 4
% Sample pressure (mb) is column 5

% dry-ambient
satp1=((prelim1(:,4)+273.15)/298.15).*(1013.25./prelim1(:,5));
satp1=repmat(satp1, 1, size(dma_dNdlogd1,2));
dma_dNdlogd1=satp1.*dma_dNdlogd1;

% 150oC
satp2=((prelim2(:,4)+273.15)/298.15).*(1013.25./prelim2(:,5));
satp2=repmat(satp2, 1, size(dma_dNdlogd2,2));
dma_dNdlogd2=satp2.*dma_dNdlogd2;

% 300oC
satp3=((prelim3(:,4)+273.15)/298.15).*(1013.25./prelim3(:,5));
satp3=repmat(satp3, 1, size(dma_dNdlogd3,2));
dma_dNdlogd3=satp3.*dma_dNdlogd3;

% End SATP adjustment
%-----
% Build integrals

% Dry ambient scans
for i=1:rowcount1
    % Area and Volume Distributions
    dma_dAdlogd1(i,:)=pi*dma_Dp.^2.*dma_dNdlogd1(i,:);
    dma_dVdlogd1(i,:)=pi/6*dma_Dp.^3.*dma_dNdlogd1(i,:);

    % N, A, and V integrals
    dma_Nint1(i)=nansum(dma_dNdlogd1(i,:))./32;
    dma_Aint1(i)=nansum(dma_dAdlogd1(i,:))./32;
    dma_Vint1(i)=nansum(dma_dVdlogd1(i,:))./32;
end

% 150oC scans
for j=1:rowcount2
    % Area and Volume Distributions
    dma_dAdlogd2(j,:)=pi*dma_Dp.^2.*dma_dNdlogd2(j,:);
    dma_dVdlogd2(j,:)=pi/6*dma_Dp.^3.*dma_dNdlogd2(j,:);

    % N, A, and V integrals
    dma_Nint2(j)=nansum(dma_dNdlogd2(j,:))./32;
    dma_Aint2(j)=nansum(dma_dAdlogd2(j,:))./32;
    dma_Vint2(j)=nansum(dma_dVdlogd2(j,:))./32;
end

% 300oC scans
for k=1:rowcount3
    % Area and Volume Distributions
    dma_dAdlogd3(k,:)=pi*dma_Dp.^2.*dma_dNdlogd3(k,:);
    dma_dVdlogd3(k,:)=pi/6*dma_Dp.^3.*dma_dNdlogd3(k,:);

    % N, A, and V integrals
    dma_Nint3(k)=nansum(dma_dNdlogd3(k,:))./32;
    dma_Aint3(k)=nansum(dma_dAdlogd3(k,:))./32;
    dma_Vint3(k)=nansum(dma_dVdlogd3(k,:))./32;
end

```



```

end

% End build integrals
%-----
% Build output matrices

% Transpose integrals for insertion to final matrix
dma_Nint1=dma_Nint1';
dma_Aint1=dma_Aint1';
dma_Vint1=dma_Vint1';

dma_Nint2=dma_Nint2';
dma_Aint2=dma_Aint2';
dma_Vint2=dma_Vint2';

dma_Nint3=dma_Nint3';
dma_Aint3=dma_Aint3';
dma_Vint3=dma_Vint3';

% Start matrix assemblies

num_output={prelim1 dma_dNdlogd1 dma_Nint1 dma_Aint1 dma_Vint1 flags1; ...
             prelim2 dma_dNdlogd2 dma_Nint2 dma_Aint2 dma_Vint2 flags2; ...
             prelim3 dma_dNdlogd3 dma_Nint3 dma_Aint3 dma_Vint3 flags3};

area_output={prelim1 dma_dAdlogd1 dma_Nint1 dma_Aint1 dma_Vint1 flags1; ...
              prelim2 dma_dAdlogd2 dma_Nint2 dma_Aint2 dma_Vint2 flags2; ...
              prelim3 dma_dAdlogd3 dma_Nint3 dma_Aint3 dma_Vint3 flags3};

vol_output={prelim1 dma_dVdlogd1 dma_Nint1 dma_Aint1 dma_Vint1 flags1; ...
             prelim2 dma_dVdlogd2 dma_Nint2 dma_Aint2 dma_Vint2 flags2; ...
             prelim3 dma_dVdlogd3 dma_Nint3 dma_Aint3 dma_Vint3 flags3};

num_output=sortrows(num_output, 3);
area_output=sortrows(area_output,3);
vol_output=sortrows(vol_output,3);

% End build matrix
%-----
% Output matrix

save(['C:\ACE\RF' n1 '\DMA\ACE_RF' n1 '_DMA_rev5b_numdist'], 'num_output', '-ascii');
% save(['C:\ACE\ACE_RF' n1 '_DMA_rev5_numdist'], 'num_output', '-ascii');

save(['C:\ACE\RF' n1 '\DMA\ACE_RF' n1 '_DMA_rev5b_areadist'], 'area_output', '-ascii');
% save(['C:\ACE\ACE_RF' n1 '_DMA_rev5_numdist'], 'area_output', '-ascii');

save(['C:\ACE\RF' n1 '\DMA\ACE_RF' n1 '_DMA_rev5b_voldist'], 'vol_output', '-ascii');
% save(['C:\ACE\ACE_RF' n1 '_DMA_rev5_numdist'], 'vol_output', '-ascii');

clear

end

```

11.0 Appendix B – MATLAB Size Distribution Function

Radial DMA and OPC number size distributions can be combined and then integrated to produce the second and third moments (area and volume distributions). In order to facilitate this process two codes, *ACE_sizedist_2dplot_ver5.m* and *TRACE_sizedist_2dplot_ver5.m* were created. Both of the MATLAB functions need flight number, start time, stop time, maximum plotting values for the y-axis of the number, area and volume distribution, as well as a smoothing switch in order to run. The start and stop times correspond to the period of time that the user is interested in combining distributions over. This can be a short period of time or over a level leg. The total number of scans for the rDMA and the OPC are contained in a small matrix located in the volume panel (panel 3) of the 2d plot. In order to facilitate identical plotting ranges, the option to include maxima for the number, area and volume distributions are available. If smoothing is desired the *boxfilt.m* function is invoked in order to apply a 5 bin smoothing to the rDMA distribution and a 19 bin smoothing for the OPC distributions. The selection of 5 bins and 19 bins is based on the logarithmically spaced bins for each instrument such that,

$$\frac{19}{5}(32DMAchannelsperdecade) \approx 112OPCchannelsperdecade .$$

The rDMA and OPC size distributions overlap between 0.100 and 0.213 mm. Over this region the *joindists.m* function is invoked. This function can be tailored to weight the averaging. In our application the weighting is such that 50% weighting is applied at the bin occupying the centroid of the logarithmic spacing between 0.100 and 0.213 mm. The MATLAB functions *ACE_sizedist_2dplot_ver5.m*, *TRACE_sizedist_2dplot_ver5.m*, *boxfilt.m* and *joindists.m* follow.

11.1 ACE_sizedist_2dplot_ver5.m

```
function ACE_sizedist_2dplot_ver5(fn, starthour, stophour, ymaxN, ymaxA, ymaxV, smooth)

%-----
% ACE_sizedist_2dplot_ver4(8, 1.67, 1.9167, 0, 0, 0)
% ACE_sizedist_2dplot.m
% Program written by Cam and Yohei 05/07/02
% Program to read then format DMA and OPC size distributions for plotting Number, Area and
Volume
% distributions
%
% Input Parameters
%
% fn          = flight number, RF11=11
% starthour   = start time for plotting interval 5:30=5.5
% stophour    = stop time for plotting interval 5:30=5.5
% ymaxN       = optional max for y-axis for standardized plots, if not specified make zero "0"
% ymaxA       = optional max for y-axis for standardized plots, if not specified make zero "0"
% ymaxV       = optional max for y-axis for standardized plots, if not specified make zero "0"
% smooth      = optional box-filter smoothing of distributions

%-----
% parameters

% starthour='1:30'
% stophour='2:00'
% fn=7;
% ymaxN=0;
% ymaxA=0;
% ymaxV=0;

%-----
% Convert flight numbers and times

if fn<=9;
    fn1=['0' num2str(fn)];
else;
    fn1=num2str(fn);
end;

starthour=datetime(starthour)*24
stophour=datetime(stophour)*24

%-----
% DMA Start

% dma_num=load(['C:\ACE\RF' fn1 '\DMA\ACE_RF' fn1 '_DMA_rev4_numdist']);
% dma_num=load(['C:\ACE\RF' fn1 '\DMA\ACE_RF' fn1 '_DMA_rev5b_numdist']);

% Old format
% dma_num=csvread(['C:\ACE\rf' fn1 '\DMA\ACE_RF' fn1 '_DMA_rev5_numdist.csv'], 2, 2);

dma_num(find(dma_num==-9999))=NaN;

DMA_Dp=csvread('C:\ACE\DMA_Dp.csv');

dmastarthour=24.*dma_num(:,1);
dmastophour=24.*dma_num(:,2);
dmarelay=dma_num(:,13);

tDMA_flag=dma_num(:,14);
find(dma_num(:,14)==2);

relayrows=find(dmarelay==1 & dmastarthour>=starthour & dmastophour<= stophour &
dma_num(:,14)~=2);
dma_dndlogd1=dma_num(relayrows,15:66);
```

```

relay2rows=find(dmarelay==2 & dmastarthour>=starthour & dmastophour<= stophour &
dma_num(:,14)~=2);
dmdndlogd2=dma_num(relay2rows,15:66);

relay3rows=find(dmarelay==3 & dmastarthour>=starthour & dmastophour<= stophour &
dma_num(:,14)~=2);
dmdndlogd3=dma_num(relay3rows,15:66);

% Number distribution
if size(dmdndlogd1,1)==1; % Check for vector which doesn't plot properly
    dN_meandmaR1=dmdndlogd1;
elseif size(dmdndlogd1,1)==0; % Also check for empty, make it 'Nan'
    dN_meandmaR1= repmat(NaN, 1, 52);
else; % Otherwise, fine
    dN_meandmaR1=nanmean(dmdndlogd1);
end;

if size(dmdndlogd2,1)==1; % Check for vector which doesn't plot properly
    dN_meandmaR2=dmdndlogd2;
elseif size(dmdndlogd2,1)==0; % Also check for empty, make it 'Nan'
    dN_meandmaR2= repmat(NaN, 1, 52);
else; % Otherwise, fine
    dN_meandmaR2=nanmean(dmdndlogd2);
end;

if size(dmdndlogd3,1)==1; % Check for vector which doesn't plot properly
    dN_meandmaR3=dmdndlogd3;
elseif size(dmdndlogd3,1)==0; % Also check for empty, make it 'Nan'
    dN_meandmaR3= repmat(NaN, 1, 52);
else; % Otherwise, fine
    dN_meandmaR3=nanmean(dmdndlogd3);
end;

% End DMA
%-----
% Start OPC

opc_dp = opcdiams(112);

% load distributions

opc_num=load(['c:\Ace\Rf' fnl '\OPC\rf' fnl 'opc.num']);
load(['c:\Ace\Rf' fnl '\OPC\rf' fnl 'opc.mat']);

% opc_int_fmt = ['%s' '%s' repmat('%f',1,24)];
% [opc_date1, opc_date2, opc_temp, opc_RH, Dcut, Ntot, Ndma, Nacc, Nsubhalf, Nsubum,
Nsubaero, Nsubl0, Atot, Adma, Aacc, Asubhalf, Asubum ...
% Asubaero, Asubl0, Vtot, Vdma, Vacc, Vsubhalf, Vsubum, Vsubaero, Vsubl0] =
textread(['c:\Ace\Rf' fnl '\OPC\rf' fnl 'opc.int'], opc_int_fmt, 'whitespace', ',');

% start: [388x1 double] date and time (will need to convert to dec hour)
% stop: [388x1 double] date and time (will need to convert to dec hour)
% relay: [388x1 double] dry-ambient, 150oC, 300oC
% refvolt: [388x1 double]
% RH: [388x1 double] at the OPC
% T: [388x1 double] at the OPC
% p: [388x1 double] at the OPC
% minidx: [388x1 double]
% minok: [388x1 double]
% Ntot: [388x1 double] Total number distribution
% Ndma: [388x1 double] Number > 0.2 um
% Nacc: [388x1 double] Number < Dcut
% Nsubhalf: [388x1 double] Number < 0.52 um (median Dcut)
% Nsubum: [388x1 double] Number < 1 um
% Nsubaero: [388x1 double] Number < 0.75 um (about 1 um aerodynamic)
% Nsubl0: [388x1 double] Number < 10 um
% Atot: [388x1 double] Area (same series as number)
% Adma: [388x1 double]
% Aacc: [388x1 double]
% Asubhalf: [388x1 double]
% Asubum: [388x1 double]

```

```

%   Asubaero: [388x1 double]
%   Asub10: [388x1 double]
%   Vtot: [388x1 double]      Volume (same series as number)
%   Vdma: [388x1 double]
%   Vacc: [388x1 double]
%   Vsubhalf: [388x1 double]
%   Vsubum: [388x1 double]
%   Vsubaero: [388x1 double]
%   Vsub10: [388x1 double]

% End load distributions
%-----
% Convert date & time to a useable decimal hour time

opcstarthour=24.*(stats.start-floor(stats.start));
opcstophour=24.*(stats.stop-floor(stats.stop));

% End convert date string to a useable decimal hour time
%-----
% Create number, area and volume distributions for defined time interval

opcrow1=find(opcstarthour>=starthour & opcstophour<=stophour & stats.relay==1);
opcrow2=find(opcstarthour>=starthour & opcstophour<=stophour & stats.relay==2);
opcrow3=find(opcstarthour>=starthour & opcstophour<=stophour & stats.relay==3);

opcdndlogd1=opc_num(opcrow1,:);
opcdndlogd2=opc_num(opcrow2,:);
opcdndlogd3=opc_num(opcrow3,:);

% Number distribution
% dN_meanopcR1=nanmean(opcdndlogd1);
% dN_meanopcR2=nanmean(opcdndlogd2);
% dN_meanopcR3=nanmean(opcdndlogd3);

if size(opcdndlogd1,1)==1;          % Check for vector which doesn't plot properly
    dN_meanopcR1=opcdndlogd1;
elseif size(opcdndlogd1,1)==0;     % Also check for empty, make it 'Nan'
    dN_meanopcR1=repmat(NaN, 1, 256);
else;                               % Otherwise, fine
    dN_meanopcR1=nanmean(opcdndlogd1);
end;

if size(opcdndlogd2,1)==1;          % Check for vector which doesn't plot properly
    dN_meanopcR2=opcdndlogd2;
elseif size(opcdndlogd2,1)==0;     % Also check for empty, make it 'Nan'
    dN_meanopcR2=repmat(NaN, 1, 256);
else;                               % Otherwise, fine
    dN_meanopcR2=nanmean(opcdndlogd2);
end;

if size(opcdndlogd3,1)==1;          % Check for vector which doesn't plot properly
    dN_meanopcR3=opcdndlogd3;
elseif size(opcdndlogd3,1)==0;     % Also check for empty, make it 'Nan'
    dN_meanopcR3=repmat(NaN, 1, 256);
else;                               % Otherwise, fine
    dN_meanopcR3=nanmean(opcdndlogd3);
end;

% End OPC
%-----
% Apply smoothing if desired

if smooth==1;
    dN_meandmaR1=boxfilt(dN_meandmaR1, 5);
    dN_meandmaR2=boxfilt(dN_meandmaR2, 5);
    dN_meandmaR3=boxfilt(dN_meandmaR3, 5);
    dN_meanopcR1=boxfilt(dN_meanopcR1, 19);
    dN_meanopcR2=boxfilt(dN_meanopcR2, 19);
    dN_meanopcR3=boxfilt(dN_meanopcR3, 19);
end

```

```

% End smoothing
%-----
% Call the "joindists.m" function to merge DMA and OPC size distributions

% % % if nargin < 8
% % %     max_DMA = max(DMA_Dp);
% % %     min_OPC = min(opc_dp);
% % % end
% % %
% % % 'mindiam', [min(DMA_Dp) min_OPC], 'maxdiam', [max_DMA max(opc_dp)],

% % % keyboard

[diam, dNdlogDp1] = joindists(DMA_Dp, dN_meandmaR1, opc_dp, dN_meanopcR1, 'overlap',
'smooth');
[diam, dNdlogDp2] = joindists(DMA_Dp, dN_meandmaR2, opc_dp, dN_meanopcR2, 'overlap',
'smooth');
[diam, dNdlogDp3] = joindists(DMA_Dp, dN_meandmaR3, opc_dp, dN_meanopcR3, 'overlap',
'smooth');

% Use "getdlogDp.m" function in order to compute new number integrals
dlogDp=getdlogd(diam);

% Number integrals
Nint1=nansum(dlogDp.*dNdlogDp1);
Nint2=nansum(dlogDp.*dNdlogDp2);
Nint3=nansum(dlogDp.*dNdlogDp3);

% Use "dN2dA.m" function to create area distribution
dAdlogDp1=dN2dA(diam, dNdlogDp1);
dAdlogDp2=dN2dA(diam, dNdlogDp2);
dAdlogDp3=dN2dA(diam, dNdlogDp3);

% Area Integrals
Aint1=nansum(dlogDp.*dAdlogDp1);
Aint2=nansum(dlogDp.*dAdlogDp2);
Aint3=nansum(dlogDp.*dAdlogDp3);

% Use "dN2dV.m" function to create volume distribution
dVdlogDp1=dN2dV(diam, dNdlogDp1);
dVdlogDp2=dN2dV(diam, dNdlogDp2);
dVdlogDp3=dN2dV(diam, dNdlogDp3);

% Volume Integrals
Vint1=nansum(dlogDp.*dVdlogDp1);
Vint2=nansum(dlogDp.*dVdlogDp2);
Vint3=nansum(dlogDp.*dVdlogDp3);

% End call the "joindists.m"
%-----
% Get CN data to check accuracy of integrals
load(['c:\Ace\ACE_C130_MergeV4.mat']);

% Convert time coordinates
cnhour=mod(data.UTC_Time,1);

% Select only time interval from flight of interst
CNrows=find(data.Flight_Number==fn & cnhour>=(starthour/24) & cnhour<=(stophour/24));

% Construct means and standard deviations of the CN data for the time interval

meanUCN=nanmean(data.UHC_UCN(CNrows));
stdevUCN=nanstd(data.UHC_UCN(CNrows));

meanRAFCn=nanmean(data.NC_CONCN(CNrows));
stdevRAFCn=nanstd(data.NC_CONCN(CNrows));

meanCNcold=nanmean(data.UHC_CNcold(CNrows));
stdevCNcold=nanstd(data.UHC_CNcold(CNrows));

meanCNhot=nanmean(data.UHC_CNhot(CNrows));

```

```

stdevCNhot=nanstd(data.UHC_CNhot(CNrows));

% End get CN data for check
%-----
% Plotting

figure;

% Number distribution plot
subplot(3,1,1);
graph1=semilogx(diam, dNdlogDp1,'b-', diam, dNdlogDp2,'r-', diam, dNdlogDp3,'k-');

xlabel('diameter (\mum)');
ylabel(['dN/dlogD']);
title(['ACE-Asia Flight ' fnl ' ' datestr(datetime(0,0,0,starthour,0,0),15) ' - '
datestr(datetime(0,0,0,stophour,0,0),15) ...
', Averaged Number, Area and Volume Distributions']);
if ymaxN==0;
    j=axis;
    axis([0.005 20 0 j(4)]);
    ymaxN=j(4);
else;
    axis([0.005 20 0 ymaxN]);
end;

set(graph1,'linewidth',3);

% Integral Text Boxes
int_handle_N1=text(4, 0.9*ymaxN,['IntNum = ' num2str(Nint1, '%.0f') ' #/cm^3']);
int_handle_N2=text(4, 0.8*ymaxN,['IntNum = ' num2str(Nint2, '%.0f') ' #/cm^3']);
int_handle_N3=text(4, 0.7*ymaxN,['IntNum = ' num2str(Nint3, '%.0f') ' #/cm^3']);

set(int_handle_N1, 'FontSize', 8);
set(int_handle_N2, 'FontSize', 8);
set(int_handle_N3, 'FontSize', 8);

% CN data Text Boxes
% Integral Text Boxes
UCN_handle=text(4, 0.4*ymaxN,['UCN = ' num2str(meanUCN, '%.0f') '+/-' num2str(stdevUCN,
'%.0f') ' #/cm^3']);
RAFCn_handle=text(4, 0.3*ymaxN,['RAFCn = ' num2str(meanRAFCn, '%.0f') '+/-'
num2str(stdevRAFCn, '%.0f') ' #/cm^3']);
CNcold_handle=text(4, 0.2*ymaxN,['UHCold = ' num2str(meanCNCold, '%.0f') '+/-'
num2str(stdevCNCold, '%.0f') ' #/cm^3']);
CNhot_handle=text(4, 0.1*ymaxN,['UHhot = ' num2str(meanCNhot, '%.0f') '+/-'
num2str(stdevCNhot, '%.0f') ' #/cm^3']);

set(UCN_handle, 'FontSize', 8);
set(RAFCn_handle, 'FontSize', 8);
set(CNcold_handle, 'FontSize', 8);
set(CNhot_handle, 'FontSize', 8);

% Area distribution plot
subplot(3,1,2);
graph2=semilogx(diam, dAdlogDp1,'b-', diam, dAdlogDp2,'r-', diam, dAdlogDp3,'k-');

xlabel('diameter (\mum)');
ylabel(['dA/dlogD']);

if ymaxA==0;
    j=axis;
    axis([0.005 20 0 j(4)]);
    ymaxA=j(4);
else;
    axis([0.005 20 0 ymaxA]);
end;

set(graph2,'linewidth',3);
legend('dry ambient', '150 ^oC', '300 ^oC', 2);

% Integral Text Boxes

```

```

int_handle_A1=text(0.006, 0.5*ymaxA,['Intarea = ' num2str(Aint1, '%.1f') ' \mu^2/cm^3']);
int_handle_A2=text(0.006, 0.4*ymaxA,['Intarea = ' num2str(Aint2, '%.1f') ' \mu^2/cm^3']);
int_handle_A3=text(0.006, 0.3*ymaxA,['Intarea = ' num2str(Aint3, '%.1f') ' \mu^2/cm^3']);

set(int_handle_A1, 'FontSize', 8);
set(int_handle_A2, 'FontSize', 8);
set(int_handle_A3, 'FontSize', 8);

% Volume distribution plot
subplot(3,1,3);
graph3=semilogx(diam, dVdlogDp1,'b-', diam, dVdlogDp2,'r-', diam, dVdlogDp3,'k-');

xlabel('diameter (\mu)');
ylabel(['dV/dlogD']);

if ymaxV==0;
    j=axis;
    axis([0.005 20 0 j(4)]);
    ymaxV=j(4);
else;
    axis([0.005 20 0 ymaxV]);
end;

set(graph3,'linewidth',3);

% Integral Text Boxes
int_handle_V1=text(0.006, 0.9*ymaxV,['Intvol = ' num2str(Vint1, '%.2f') ' \mu^3/cm^3']);
int_handle_V2=text(0.006, 0.8*ymaxV,['Intvol = ' num2str(Vint2, '%.2f') ' \mu^3/cm^3']);
int_handle_V3=text(0.006, 0.7*ymaxV,['Intvol = ' num2str(Vint3, '%.2f') ' \mu^3/cm^3']);

set(int_handle_V1, 'FontSize', 8);
set(int_handle_V2, 'FontSize', 8);
set(int_handle_V3, 'FontSize', 8);

% Scan number statistics Text Boxes
scan_handle_DMA=text(0.006, 0.5*ymaxV,[num2str(size(relay1rows,1), '%.0f') ' '
num2str(size(relay2rows,1), '%.0f') ' ' num2str(size(relay3rows,1), '%.0f')]);
scan_handle_OPC=text(0.006, 0.4*ymaxV,[num2str(size(opcrow1,1), '%.0f') ' '
num2str(size(opcrow2,1), '%.0f') ' ' num2str(size(opcrow3,1), '%.0f')]);

set(scan_handle_DMA, 'FontSize', 8);
set(scan_handle_OPC, 'FontSize', 8);

% Set page and stamp
stamp(['ACE-RF' fn1 '-' num2str(round(100*starthour)) 'to' num2str(round(100*stophour)) '-
sizedist.jpg, ACE-sizedist-2Dplot.m']);
orient landscape;

% End make figure
%-----
% Export figure

% % % print('-djpeg95', '-r120', ['ACE-RF' fn1 '-' num2str(round(100*starthour)) 'to'
num2str(round(100*stophour)) '-sizedist'])

extract1=[diam; dNdlogDp1; dNdlogDp2; dNdlogDp3]';
extract2=[diam; dAdlogDp1; dAdlogDp2; dAdlogDp3]';
extract3=[diam; dVdlogDp1; dVdlogDp2; dVdlogDp3]';

save(['C:\ACE\RF' fn1 '\dN_extract' num2str(round(100*starthour)) 'to'
num2str(round(100*stophour)) 'v5b'], 'extract1', '-ascii');
save(['C:\ACE\RF' fn1 '\dA_extract' num2str(round(100*starthour)) 'to'
num2str(round(100*stophour)) 'v5b'], 'extract2', '-ascii');
save(['C:\ACE\RF' fn1 '\dV_extract' num2str(round(100*starthour)) 'to'
num2str(round(100*stophour)) 'v5b'], 'extract3', '-ascii');

```


11.2 TRACE_sizedist_2dplot_ver5.m

```
function TRACE_sizedist_2dplot_ver5(fn, starthour, stophour, ymaxN, ymaxA, ymaxV, smooth)

% Cam, June 7, 2002
%-----
% Yohei, Nov. 19, 2001
% CHECK IF OPC IS CORRECTED FOR STP (I GUESS NOT)!
% DMA IS CORRECTED FOR STP.

% Input Parameters
%
% fn          = flight number, RF11=11
% starthour   = start time for plotting interval 5:30=5.5
% stophour    = stop time for plotting interval 5:30=5.5
% ymaxN       = optional max for y-axis for standardized plots, if not specified make zero "0"
% ymaxA       = optional max for y-axis for standardized plots, if not specified make zero "0"
% ymaxV       = optional max for y-axis for standardized plots, if not specified make zero "0"
% smooth      = optional box-filter smoothing of distributions
%-----

% parameters

% % % fn=14
% % % starthour='3:53'
% % % stophour='4:00'
% % % ymaxN=0
% % % ymaxA=0
% % % ymaxV=0
% % % smooth=1
% % % max_DMA = 0.149
% % % min_OPC = 0.10857
%-----

% convert times
starthour=datetime(starthour)*24
stophour=datetime(stophour)*24
%-----

% DMA bins

% version (see TP_dma.m)
dmaver=5;

% diameter in um
dmad=[7.23E-03 7.77E-03      8.35E-03      8.98E-03      9.65E-03      1.04E-02 ...
      1.11E-02      1.20E-02      1.29E-02      1.38E-02      1.49E-02      1.60E-02
      ...
      1.72E-02      1.84E-02      1.98E-02      2.13E-02      2.29E-02      2.46E-02
      ...
      2.64E-02      2.84E-02      3.05E-02      3.28E-02      3.52E-02      3.79E-02
      ...
      4.07E-02      4.37E-02      4.70E-02      5.05E-02      5.42E-02      5.83E-02
      ...
      6.26E-02      6.73E-02      7.23E-02      7.77E-02      8.35E-02      8.98E-02
      ...
      9.65E-02      1.04E-01      1.11E-01      1.20E-01      1.29E-01      1.38E-01
      ...
      1.49E-01      1.60E-01      1.72E-01      1.84E-01      1.98E-01      2.13E-01];

%-----

% load DMA data

dma=load(['C:\TRACE\DMA\TPf' num2str(fn) 'dma' num2str(dmaver)]);

% Substitute 1 in order to match relay signals to that in OPC (0 for unheated, 1 for 150C, and
% 2 for 300C).
dmarelay=dma(:,65)-1;
```

```

% End load DMA data
%-----
% DMA averaging & integrals

% Change elements with -999 to Nan's
nines=find(dma(:,8:55)==-999)
new_dN=dma(:,8:55);
new_dN(nines)=NaN;
dma(:,8:55)=new_dN;

% Get the rows for the time interval
dmarow0=find(dma(:,2)/3600>=starthour & dma(:,3)/3600<=stophour & dmarelay==0);
dmarow1=find(dma(:,2)/3600>=starthour & dma(:,3)/3600<=stophour & dmarelay==1);
dmarow2=find(dma(:,2)/3600>=starthour & dma(:,3)/3600<=stophour & dmarelay==2);

% Find and count rows with -999 for integrals (used later to tell you the number of good/bad
scans)
dmabad0=size(find(dma(dmarow0,56)==-999),1);
dmabad1=size(find(dma(dmarow1,56)==-999),1);
dmabad2=size(find(dma(dmarow2,56)==-999),1);

% Number distribution
if size(dma(dmarow0,8:55),1)==1; % Check for vector which doesn't plot properly
    dma_dndlogd0=dma(dmarow0,8:55);
elseif size(dma(dmarow0,8:55),1)==0; % Also check for empty, make it 'Nan'
    dma_dndlogd0= repmat(NaN, 1, 48);
else; % Otherwise, fine
    dma_dndlogd0=nanmean(dma(dmarow0,8:55));
end;

if size(dma(dmarow1,8:55),1)==1; % Check for vector which doesn't plot properly
    dma_dndlogd1=dma(dmarow1,8:55);
elseif size(dma(dmarow1,8:55),1)==0; % Also check for empty, make it 'Nan'
    dma_dndlogd1= repmat(NaN, 1, 48);
else; % Otherwise, fine
    dma_dndlogd1=nanmean(dma(dmarow1,8:55));
end;

if size(dma(dmarow2,8:55),1)==1; % Check for vector which doesn't plot properly
    dma_dndlogd2=dma(dmarow2,8:55);
elseif size(dma(dmarow2,8:55),1)==0; % Also check for empty, make it 'Nan'
    dma_dndlogd2= repmat(NaN, 1, 48);
else; % Otherwise, fine
    dma_dndlogd2=nanmean(dma(dmarow2,8:55));
end;

% End DMA averaging & integrals
%-----
% load OPC data

opc=load(['C:\TRACE\OPC\TPf' num2str(fn) '.num']); % number distribution
opctim=load(['C:\TRACE\OPC\TPf' num2str(fn) '.tim']); % time
opcanc=load(['C:\TRACE\OPC\TPf' num2str(fn) '.anc']); % ancillary data to get relay
opcrelay=opcanc(:,1);
clear opcanc;

% End load OPC data
%-----
% OPC Number distribution
opcd = opcdiams(112);

opcrow0=find(opctim(:,2)/3600>=starthour & opctim(:,3)/3600<=stophour & opcrelay==0);
opcrow1=find(opctim(:,2)/3600>=starthour & opctim(:,3)/3600<=stophour & opcrelay==1);
opcrow2=find(opctim(:,2)/3600>=starthour & opctim(:,3)/3600<=stophour & opcrelay==2);

% Construct the number integrals
if size(opc(opcrow0,:),1)==1; % Check for vector which doesn't plot properly
    opc_dndlogd0=opc(opcrow0,:);
elseif size(opc(opcrow0,:),1)==0; % Also check for empty, make it 'Nan'
    opc_dndlogd0= repmat(NaN, 1, 256);

```

```

else; % Otherwise, fine
    opc_dndlogd0=nanmean(opc(opcrow0,:));
end;

if size(opc(opcrow1,:),1)==1; % Check for vector which doesn't plot properly
    opc_dndlogd1=opc(opcrow1,:);
elseif size(opc(opcrow1,:),1)==0; % Also check for empty, make it 'Nan'
    opc_dndlogd1=repmat(NaN, 1, 256);
else; % Otherwise, fine
    opc_dndlogd1=nanmean(opc(opcrow1,:));
end;

if size(opc(opcrow2,:),1)==1; % Check for vector which doesn't plot properly
    opc_dndlogd2=opc(opcrow2,:);
elseif size(opc(opcrow2,:),1)==0; % Also check for empty, make it 'Nan'
    opc_dndlogd2=repmat(NaN, 1, 256);
else; % Otherwise, fine
    opc_dndlogd2=nanmean(opc(opcrow2,:));
end;

% End OPC Number Distributions
%-----
% Apply smoothing if desired

if smooth==1;
    dma_dndlogd0=boxfilt(dma_dndlogd0, 5);
    dma_dndlogd1=boxfilt(dma_dndlogd1, 5);
    dma_dndlogd2=boxfilt(dma_dndlogd2, 5);
    opc_dndlogd0=boxfilt(opc_dndlogd0, 19);
    opc_dndlogd1=boxfilt(opc_dndlogd1, 19);
    opc_dndlogd2=boxfilt(opc_dndlogd2, 19);
end

% End smoothing
%-----
% Call the "joindists.m" function to merge DMA and OPC size distributions

% % % if nargin < 8
% % %     max_DMA = max(dmad);
% % %     min_OPC = min(opcd);
% % % end
% % %
% % % 'mindiam', [min(dmad) min_OPC], 'maxdiam', [max_DMA max(opcd)],

[diam, dNdlogDp0] = joindists(dmad, dma_dndlogd0, opcd, opc_dndlogd0, 'overlap', 'smooth');
[diam, dNdlogDp1] = joindists(dmad, dma_dndlogd1, opcd, opc_dndlogd1, 'overlap', 'smooth');
[diam, dNdlogDp2] = joindists(dmad, dma_dndlogd2, opcd, opc_dndlogd2, 'overlap', 'smooth');

% Use "getdlogDp.m" function in order to compute new number integrals
dlogDp=getdlogd(diam);

% Number integrals
Nint0=nansum(dlogDp.*dNdlogDp0);
Nint1=nansum(dlogDp.*dNdlogDp1);
Nint2=nansum(dlogDp.*dNdlogDp2);

% Use "dN2dA.m" function to create area distribution
dAdlogDp0=dN2dA(diam, dNdlogDp0);
dAdlogDp1=dN2dA(diam, dNdlogDp1);
dAdlogDp2=dN2dA(diam, dNdlogDp2);

% Area Integrals
Aint0=nansum(dlogDp.*dAdlogDp0);
Aint1=nansum(dlogDp.*dAdlogDp1);
Aint2=nansum(dlogDp.*dAdlogDp2);

% Use "dN2dV.m" function to create volume distribution
dVdlogDp0=dN2dV(diam, dNdlogDp0);
dVdlogDp1=dN2dV(diam, dNdlogDp1);
dVdlogDp2=dN2dV(diam, dNdlogDp2);

```

```

% Volume Integrals
Vint0=nansum(dlogDp.*dVdlogDp0);
Vint1=nansum(dlogDp.*dVdlogDp1);
Vint2=nansum(dlogDp.*dVdlogDp2);

% End call the "joindists.m"
%-----
% Get CN data to check accuracy of integrals

load(['c:\Trace\TRACE_Merge.mat']);

% Convert time coordinates
cnhour=data.UTC./86400;

% Select only time interval from flight of interst
CNrows=find(data.FLIGHT==fn & cnhour>=(starthour/24) & cnhour<=(stophour/24));

% Construct means and standard deviations of the CN data for the time interval

meanCNcold=nanmean(data.CNcoldSTP(CNrows));
stdevCNcold=nanstd(data.CNcoldSTP(CNrows));

meanCNhot=nanmean(data.CNhotSTP(CNrows));
stdevCNhot=nanstd(data.CNhotSTP(CNrows));

% End CN data
%-----
% 3-panel plot

figure;

% Number distribution plot
subplot(3,1,1);
graph1=semilogx(diam, dNdlogDp0,'k--', diam, dNdlogDp1,'k:', diam, dNdlogDp2,'k-');
set(graph1,'linewidth',3);
xlabel('diameter (\mum)');
ylabel(['dN/dlogDp']);

if ymaxN==0;
    j=axis;
    axis([0.005 20 0 j(4)]);
    ymaxN=j(4);
else;
    axis([0.005 20 0 ymaxN]);
end;

title(['TRACE-P flight ' num2str(fn) ', ' datestr(datenum(0,0,0,starthour,0,0),15) ' - '
datestr(datenum(0,0,0,stophour,0,0),15) ...
', Averaged Size Distributions']);

int_handle_N0=text(4, 0.9*ymaxN,['IntNum = ' num2str(Nint0, '%.0f') ' #/cm^3']);
int_handle_N1=text(4, 0.8*ymaxN,['IntNum = ' num2str(Nint1, '%.0f') ' #/cm^3']);
int_handle_N2=text(4, 0.7*ymaxN,['IntNum = ' num2str(Nint2, '%.0f') ' #/cm^3']);

set(int_handle_N0, 'FontSize', 8);
set(int_handle_N1, 'FontSize', 8);
set(int_handle_N2, 'FontSize', 8);

% CN data Text Boxes
% Integral Text Boxes
CNcold_handle=text(4, 0.2*ymaxN,['UHcold = ' num2str(meanCNcold, '%.0f') '+/-'
num2str(stdevCNcold, '%.0f') ' #/cm^3']);
CNhot_handle=text(4, 0.1*ymaxN,['UHhot = ' num2str(meanCNhot, '%.0f') '+/-'
num2str(stdevCNhot, '%.0f') ' #/cm^3']);

set(CNcold_handle, 'FontSize', 8);
set(CNhot_handle, 'FontSize', 8);

```

```

% Area distribution plot
subplot(3,1,2);
graph2=semilogx(diam, dAdlogDp0,'k--', diam, dAdlogDp1,'k:', diam, dAdlogDp2,'k-');
set(graph2,'linewidth',3);
xlabel('diameter (\mum)');
ylabel(['dA/dlogDp']);

legend('dry ambient', '150 ^oC', '300 ^oC', 2);

if ymaxA==0;
    j=axis;
    axis([0.005 20 0 j(4)]);
    ymaxA=j(4);
else;
    axis([0.005 20 0 ymaxA]);
end;

% Integral Text Boxes
int_handle_A0=text(0.006, 0.5*ymaxA,['Int Area = ' num2str(Aint0, '%.0f') ' \mum^2/cm^3']);
int_handle_A1=text(0.006, 0.4*ymaxA,['Int Area = ' num2str(Aint1, '%.0f') ' \mum^2/cm^3']);
int_handle_A2=text(0.006, 0.3*ymaxA,['Int Area = ' num2str(Aint2, '%.0f') ' \mum^2/cm^3']);

set(int_handle_A0, 'FontSize', 8);
set(int_handle_A1, 'FontSize', 8);
set(int_handle_A2, 'FontSize', 8);

% Volume distribution plot
subplot(3,1,3);
graph3=semilogx(diam, dVdlogDp0,'k--', diam, dVdlogDp1,'k:', diam, dVdlogDp2,'k-');
set(graph3,'linewidth',3);
xlabel('diameter (\mum)');
ylabel(['dV/dlogDp']);

if ymaxV==0;
    j=axis;
    axis([0.005 20 0 j(4)]);
    ymaxV=j(4);
else;
    axis([0.005 20 0 ymaxV]);
end;

% Integral Text Boxes
int_handle_V0=text(0.006, 0.9*ymaxV,['Int Vol = ' num2str(Vint0, '%.0f') ' \mum^3/cm^3']);
int_handle_V1=text(0.006, 0.8*ymaxV,['Int Vol = ' num2str(Vint1, '%.0f') ' \mum^3/cm^3']);
int_handle_V2=text(0.006, 0.7*ymaxV,['Int Vol = ' num2str(Vint2, '%.0f') ' \mum^3/cm^3']);

set(int_handle_V0, 'FontSize', 8);
set(int_handle_V1, 'FontSize', 8);
set(int_handle_V2, 'FontSize', 8);

% Scan number statistics Text Boxes
scan_handle_DMA=text(0.006, 0.5*ymaxV,[num2str((size(dmarow0,1)-dmabad0), '%.0f') ' '
num2str((size(dmarow1,1)-dmabad1), '%.0f') ' ' num2str((size(dmarow2,1)-dmabad2), '%.0f')]);
scan_handle_OPC=text(0.006, 0.4*ymaxV,[num2str(size(opcrow0,1), '%.0f') ' '
num2str(size(opcrow1,1), '%.0f') ' ' num2str(size(opcrow2,1), '%.0f')]);

set(scan_handle_DMA, 'FontSize', 8);
set(scan_handle_OPC, 'FontSize', 8);

% Stamp and orient
stamp(['TPf' num2str(fn) 'sizedisthour' num2str(starthour) 'to' num2str(stophour) '.fig,
TRACE-sizedist-2dplot-ver4.m']);
orient landscape;

% Save as JPG
% print('-djpeg95', '-r120', ['ACE-RF' fn1 '-' num2str(round(100*starthour)) 'to'
num2str(round(100*stophour)) '-sizedist'])
print('-djpeg95', '-r120', ['TRACE-RF' num2str(fn) '-' num2str(round(100*starthour)) 'to'
num2str(round(100*stophour)) '-sizedist-v4'])

```

```

extract1=[diam; dNdlogDp0; dNdlogDp1; dNdlogDp2]';
extract2=[diam; dAdlogDp0; dAdlogDp1; dAdlogDp2]';
extract3=[diam; dVdlogDp0; dVdlogDp1; dVdlogDp2]';

save(['C:\TRACE\RF14\dN_extract_' num2str(round(100*starthour)) 'to'
num2str(round(100*stophour)) 'v4'], 'extract1', '-ascii');
save(['C:\TRACE\RF14\DA_extract_' num2str(round(100*starthour)) 'to'
num2str(round(100*stophour)) 'v4'], 'extract2', '-ascii');
save(['C:\TRACE\RF14\DV_extract_' num2str(round(100*starthour)) 'to'
num2str(round(100*stophour)) 'v4'], 'extract3', '-ascii');

```

11.3 boxfilt.m

```

function yf = boxfilt(y, bl)
% function yf = boxfilt(y, bl)
% Apply a boxcar filter, first padding the ends of the series
% with constant values to reduce end effects.
% The filter length, bl, must be an odd integer.
% y must be a vector, either row or column.

if rem(bl,2) ~= 1,
    error('Boxcar length must be an odd integer');
end

[nrows, ncols] = size(y);

nr = max(nrows, ncols);

npad = (bl-1)/2;
box = ones(bl,1)/bl;

yf = conv([ones(npad,1)*y(1); y(:); ones(npad,1)*y(nr)], box);
yf = yf(bl:(nr+bl-1));

% If the input is a row vector, convert output to row also.
if nrows == 1, yf = yf';
elseif ncols ~= 1, error('input to boxfilt is a matrix');
end

```

11.4 joindists.m

```

function [outdiam,dist] = joindists(varargin)
% Join size distributions from different instruments
%
% syntax:
%   diststruct = joindists(dist1struct,dist2struct,...,options);
%   or
%   [diams,dist] = joindists(dist1diams,dist1dN,dist2diams,...,options);
%
% inputs:
%   If using structures, they should have the following fields
%
%   diam  1 by m vector of diameters (or n by m vector where n is the
%         number of samples
%   dNdlogd  n by m vector of distribution heights. Values can actually
%         be any moment, but must be called dNdlogd.
%   mindiam  minimum diameter to believe (optional, default is min(diam)).
%         Can be scalar or n by 1.
%   maxdiam  maximum diameter to believe (optional, default is max(diam)).
%         Can be scalar or n by 1.
%   weight  Weighting to apply (optional, default 1). Can be scalar,
%         1 by m, n by 1, or m by n.
%
%   If using matrices, the mindiam, maxdiam, and weight options can be
%   indicated as parameter, value pairs. Values must be length p
%   vectors, where p is the number of instruments.
%
% Other options include
%

```

```

% outdiam Output diameter vector. After joining, the distributions are
% interpolated to outdiam. Default is to use diameters from
% each instrument where it is the only one contributing to that
% size range. Where overlaps exist, instrument 1 diameters take
% precedence over instrument 2, etc. Lower priority instruments
% are interpolated onto the diameters of higher priority
% instruments within the overlap region.
%
% overlap Whether to attempt to join distributions smoothly. If
% 'smooth', 'y', or nonzero, then weights at the ends of the
% distribution are adjusted for a relatively smooth transition
% between instruments. Otherwise, data are just averaged by
% whatever weight was entered. NOTE: This only makes sense for
% comparatively narrow overlap regions.
%
% outputs:
% if structures are input, a structure is output with fields diam and
% dNdlogd. Otherwise outdiam and dNdlogd are returned as matrices.
%
% Note: If each instrument has the same number (n) of samples, then each
% will be joined and the returned distribution will have n lines. If
% there are different numbers of samples, then I average all samples
% from each instrument before joining the distributions and the returned
% distribution will have 1 line.

%Parse input variables
args = length(varargin);
if isstruct(varargin{1})
    structmode = 1;
    p = 1;
    for ii=1:args
        if isstruct(varargin{ii})
            inst{ii,1} = varargin{ii};
            p = ii;
        else
            break
        end
    end
else
    structmode = 0;
    p = 0;
    for ii = 1:2:args
        if ischar(varargin{ii})
            break
        else
            p = p+1;
            tmpinst.diam = varargin{ii};
            tmpinst.dNdlogd = varargin{ii+1};
            inst{p,1} = tmpinst;
        end
    end
end

%Now get any parameter,value pairs
outdiam = [];
overlapmode = 0;
if ii<args
    for jj = ii:2:args
        switch lower(varargin{jj})
            case {'outdiam'}
                outdiam = varargin{jj+1};
            case {'overlap'}
                val = varargin{jj+1};
                if (ischar(val) & ismember(val(1),'sSyY')) | ...
                    (isnumeric(val) & val>0.5)
                    overlapmode = 1;
                end
            case {'mindiam'}
                md = varargin{jj+1};
                for kk = 1:p
                    inst{kk}.mindiam = md(kk);
                end
            default
                % Do nothing
        end
    end
end

```

```

        end
        case {'maxdiam'}
            md = varargin{jj+1};
            for kk = 1:p
                inst{kk}.maxdiam = md(kk);
            end
        case {'weight'}
            md = varargin{jj+1};
            for kk = 1:p
                inst{kk}.weight = md(kk,:);
            end
        end
    end
end
end

% Go through each instrument and make a few adjustments as necessary
for jj = 1:p
    ndist(jj) = size(inst{jj}.dNdlogd,1);
    % Is there a minimum channel? If so, exclude affected data.
    %Note that no provision is made for 2-d diameter. Later.
    if isfield(inst{jj},'mindiam')
        badcol = find(inst{jj}.diam<inst{jj}.mindiam);
        inst{jj}.diam(badcol) = [];
        inst{jj}.dNdlogd(:,badcol) = [];
    end
    % Is there a maximum channel? If so, exclude affected data.
    if isfield(inst{jj},'maxdiam')
        badcol = find(inst{jj}.diam>inst{jj}.maxdiam);
        inst{jj}.diam(badcol) = [];
        inst{jj}.dNdlogd(:,badcol) = [];
    end
    %Is there a weight? If not, assign 1.
    if ~isfield(inst{jj},'weight')
        inst{jj}.weight = ones(size(inst{jj}.dNdlogd));
    elseif all(size(inst{jj}.weight)==1) % if weight is scalar, expand
        inst{jj}.weight = ones(size(inst{jj}.dNdlogd)).*inst{jj}.weight;
    elseif size(inst{jj}.weight,2) == size(inst{jj}.dNdlogd,2) & ...
        size(inst{jj}.weight,1) == 1 & ndist(jj) > 1
        %If weight is a vector, expand it to a matrix the same size as dNdlogd
        inst{jj}.weight = repmat(inst{jj}.weight, ndist(jj), 1);
    end
end

% If each instrument has the same number of distributions, then join
% corresponding distributions. Otherwise, average each instrument's
% distributions together.
if all(ndist==ndist(1))
    ndist = ndist(1);
else
    for jj=1:p
        if ndist(jj)>1 % Nanmean backfires if just 1 row!
            inst{jj}.dNdlogd = nanmean(inst{jj}.dNdlogd);
            inst{jj}.weight = nanmean(inst{jj}.weight);
        end
    end
    ndist = 1;
end

% If an output diameter vector was specified, use it.
% Otherwise, build the output diameters piecemeal
if isempty(outdiam)
    outdiam = inst{1}.diam;
    for jj=2:p
        smaller = inst{jj}.diam<outdiam(1);
        if any(smaller)
            outdiam = [inst{jj}.diam(smaller) outdiam];
        end
        larger = inst{jj}.diam>outdiam(end);
        if any(larger)
            outdiam = [outdiam inst{jj}.diam(larger)];
        end
    end
end

```



```

    end
    end
end

% Interpolate each instrument on to the output diameter. NaNs will occur
% outside the instrument range. Substituting zero for NaN works because a
% weight of zero is applied.
for jj=1:p
    dNdlogd(:, :, jj) = interp1(log10(inst{jj}.diam), inst{jj}.dNdlogd, ...
                                log10(outdiam));
    weight(:, :, jj) = interp1(log10(inst{jj}.diam), inst{jj}.weight, ...
                                log10(outdiam));
end

% If there's no data, just return an array of NaNs with the right size. Otherwise, continue.
if all(isnan(dNdlogd))
    dist.dNdlogd = zeros(size(dNdlogd,1), size(dNdlogd,2)) * NaN;
else

    weight(isnan(weight) | isnan(dNdlogd)) = 0;
    dNdlogd(isnan(dNdlogd)) = 0;

    % If in overlap mode, adjust weights of each instrument
    if overlapmode
        % Overlap is where more than one instrument has data. Can find that
        % through the weight.
        hasdata = sum(weight,1) ~= 0;
        nwithdata = sum(hasdata,3);
        overlap = nwithdata > 1;
        olstart = find(diff([0 overlap]) == 1);
        olstop = find(diff([overlap 0]) == -1);
        % Smooth joining doesn't work if at beginning or end of distribution
        if olstart(1) == 1
            olstart(1) = [];
            olstop(1) = [];
        end
        if olstop(end) == size(nwithdata,2)
            olstart(end) = [];
            olstop(end) = [];
        end

        for jj=1:length(olstart) % Go through the overlaps
            for kk=1:p
                % Is instrument kk involved in overlap jj?
                if any(hasdata(1, olstart(jj):olstop(jj), kk))
                    % Is overlap at the high end of the instrument? If so, then the
                    % instrument should have data smaller than olstart.
                    top = any(hasdata(1, 1:olstart(jj)-1, kk));
                    bottom = any(hasdata(1, olstop(jj)+1:end, kk));
                    % Overlap smoothing works only if bottom or top, not both
                    if xor(top, bottom)
                        olist = zeros(size(nwithdata));
                        olist(olstart(jj):olstop(jj)) = 1;
                        olist = find(olist & hasdata(1, :, kk));
                        fracwt = (1:length(olist))/(length(olist)+1);
                        if top
                            fracwt = fliplr(fracwt);
                        end
                        weight(:, olist, kk) = repmat(fracwt, ndist, 1) .* weight(:, olist, kk);
                    end
                end
            end
        end

        % Now take the weighted mean
        dist.diam = outdiam;
        warning off % Zero weights yielding NaNs are expected
        dist.dNdlogd = sum(dNdlogd.*weight,3)/sum(weight,3);
        warning on
        dist.weight = sum(weight,3);
    end
end

```

```

end %of if all(isnan(dNdlogd))

%If not in structure mode, output the diameters and dNdlogd
if structmode
    if nargout == 1
        outdiam = dist;
    end
else
    dist = dist.dNdlogd
end

```

12.0 Appendix C – MATLAB Condensation and Coagulation Modeling

Kulmala et al. [2001] use a simple formulation based on the size distribution and dDp/dt to estimate the condensation of sulfuric acid to the size distribution. *Seinfeld and Pandis* [1998] have summarized the work of Fuchs for calculating the coagulation rate for a particle of given size when the remainder of the size distribution is known. The theory associated with these calculations is contained in Section 2.0. Section 12.1 contains the MATLAB function *ACE_Condensable_Vapours.m*. This code was used to calculate the sulfuric acid flux rates summarized in table 7.2. Section 12.2 contains the MATLAB function *ACE_Fuchs_Coagulation.m*. This code was used to calculate the coagulation rates for the nucleation mode particles as summarized in table 7.4

12.1 ACE_Condensable_Vapours.m

```
% ACE_Condensable_Vapours.m
%
% Program written by Cam 01/02/03
%
% A number of formulae are contained in Kulmala et al. 2001 pertaining to our
% work on the nucleation paper. We use this program to calculate the concentrations
% of gas phase precursors that are available to condense onto the size distribution
% based on the observed growth rate of the nucleation mode particles obtained by
% shifts in the size distribution over time.
%
% Reference:
% Kulmala, M., M. Dal Maso, J.M. Makela, L. Pirjola, M. Vakeva, P. Aalto, P. Miikkulainen, K.
% Hameri, and C.D. O'Dowd,
% On the formation, growth and composition of nucleation mode particles, Tellus, 53B (4),
% 479-490, 2001.
%
%-----
% Parameters
lambda_air=0.0686;           % um
k=1.38065*10^(-23);          % J/oK
R=8.31447;                   % J/mol/oK
mu=0.0000183;                % kg/m/s
T=298.15;                    % oK
rho=1400;                    % kg/m3
alpha=1.0;                   % (-)
Mm_H2SO4=98.0794/1000;       % kg/mol
Na=6.022*10^23;
%
%-----
% Variables
Dp1 = 0.003;                 % um
Dp2 = 0.01;                  % um
GR = 0.002;                  % um/hr
r1 = Dp1/2
r2 = Dp2/2
del_t=((Dp2-Dp1)/GR)*3600     % s
%
%-----
% Mean free path for diffusion of vapour molecule A toward particle in gas B
```

```

p=101325 % Pa
Mm_Air=28.97/1000 % kg/mol

sigma_H2SO4=0.51545; % using estimate of S-O bond length of 1.4321 angstroms

sigma_N2=0.31; % nm^2
sigma_O2=0.27; % nm^2
sigma_Ar=0.26; % nm^2
sigma_Air=(0.78*sigma_N2+0.21*sigma_O2+0.01*sigma_Ar);

sigma_AB=((sigma_Air+sigma_H2SO4)/2)/(10^18) % m^2

lambda_AB=(10^6)/(((1+Mm_H2SO4/Mm_Air)^0.5)*(p/(k*T))*(pi*sigma_AB)) % um

%-----
% Calculate the diffusion constant for gas in a binary mixture S&P page 457

c_H2SO4=((8*R*T)/(pi*Mm_H2SO4))^0.5 % m/s (Page 454
S&P)

D_AB=(3*pi/32)*(1+Mm_H2SO4/Mm_Air)*(lambda_AB/10^6)*c_H2SO4 % m^2/s

%-----
% Condensable vapour Calculations based on page 480 of Kulmala et al.

C_a=(Na*rho)/(del_t*D_AB*Mm_H2SO4); % molecules/m^5
C_b=((r2^2-r1^2)/2+(4*(3*alpha)-0.623)*lambda_AB*(r2-
r1)+0.623*(lambda_AB^2)*log((lambda_AB+r2)/(lambda_AB+r1))); % um^2

C=C_a*(C_b/(10^12))/(10^6) % molecules/cm^3

%-----
% Part II
%-----
% Load the size distribution of interest

% % % dN = load('c:\TRACE\RF14\dN_extract_388to400v4');
% % % dN = load('c:\TRACE\RF14\dN_extract_405to425v4');
% % % dN = load('c:\TRACE\RF14\dN_extract_432to442v4');

% % % dN = load('c:\ACE\RF07\dN_extract_160to175v5b');
% % % dN = load('c:\ACE\RF07\dN_extract_415to421v5b');
% % % dN = load('c:\ACE\RF07\dN_extract_433to437v5b');
% % % dN = load('c:\ACE\RF07\dN_extract_570to574v5b');

% % % dN = load('c:\ACE\RF08\dN_extract_180to208v5b');
% % % dN = load('c:\ACE\RF08\dN_extract_698to702v5b');
% % % dN = load('c:\ACE\RF08\dN_extract_720to724v5b');

dN = load('c:\ACE\RF07\dN_extract_160to175v5b');

Dp = dN(1:end, 1);
dlogDp = getdlogD(Dp);
dN_dlogDp = dN(1:end, 2);

dN = dN_dlogDp.*dlogDp;

%-----
% Calculation of condensational sink

% Knudsen number calculation
Kn=2*lambda_AB./Dp;

% Transitional correction factor
Bm=(Kn+1)./(0.377.*Kn) + 1 + ((4*alpha^-1).*Kn.^2)/3 + ((4*alpha^-1).*Kn)/3);

CS_prime = nansum(Bm.*(Dp/2).*dN); % um/cm^3

```

```

CS = 4*pi*(D_AB*10^4)*(CS_prime/10^4) % cm^3/cm^3/s

%-----
% Vapour Source Rate (Q)

Q=CS*C % molecules/cm^3/s

```

12.2 ACE_Fuchs_Coagulation.m

```

%-----
% ACE_Fuchs_Coagulation.m
%
% Program written by Cam 01/02/03
%
% A number of formulae are contained in Kulmala et al. 2001 pertaining to our
% work on the nucleation paper. We use this program to calculate the coagulation
% sink for particles of a given size. The theory is based on Fuchs, published in
% Kulmala and S&P in Section 12.3.
%
% Reference:
% Kulmala, M., M. Dal Maso, J.M. Makela, L. Pirjola, M. Vakeva, P. Aalto, P. Miikkulainen, K.
% Hameri, and C.D. O'Dowd,
% On the formation, growth and composition of nucleation mode particles, Tellus, 53B (4),
% 479-490, 2001.
%
% Seinfeld, J.H., and S.N. Pandis, Atmospheric Chemistry and Physics, John Wiley & Sons,
% Inc., New York, 1998.
%-----
% Parameters

lambda_air=0.0686; % um
k=1.38065*10^(-23); % J/oK
mu=0.0000183; % kg/m/s
T=298.15; % oK
rho=1400; % kg/m3
alpha=1.0; % (-)

%-----
% Load the size distribution

% % % dN1 = load('c:\TRACE\RF14\dN_extract_388to400v4');
% % % dN1 = load('c:\TRACE\RF14\dN_extract_388to400v4_RH25');
% % % dN1 = load('c:\TRACE\RF14\dN_extract_388to400v4_RH75');

% % % dN1 = load('c:\TRACE\RF14\dN_extract_405to425v4');
% % % dN1 = load('c:\TRACE\RF14\dN_extract_405to425v4_RH25');
% % % dN1 = load('c:\TRACE\RF14\dN_extract_405to425v4_RH75');

% % % dN1 = load('c:\TRACE\RF14\dN_extract_432to442v4');
% % % dN1 = load('c:\TRACE\RF14\dN_extract_432to442v4_RH25');
% % % dN1 = load('c:\TRACE\RF14\dN_extract_432to442v4_RH75');

% % % dN1 = load('c:\ACE\RF07\dN_extract_160to175v5b');
% % % dN1 = load('c:\ACE\RF07\dN_extract_160to175v5b_RH25');
% % % dN1 = load('c:\ACE\RF07\dN_extract_160to175v5b_RH75');

% % % dN1 = load('c:\ACE\RF07\dN_extract_415to421v5b');
% % % dN1 = load('c:\ACE\RF07\dN_extract_415to421v5b_RH25');
% % % dN1 = load('c:\ACE\RF07\dN_extract_415to421v5b_RH75');

% % % dN1 = load('c:\ACE\RF07\dN_extract_433to437v5b');
% % % dN1 = load('c:\ACE\RF07\dN_extract_433to437v5b_RH25');
% % % dN1 = load('c:\ACE\RF07\dN_extract_433to437v5b_RH75');

% % % dN1 = load('c:\ACE\RF07\dN_extract_570to574v5b');
% % % dN1 = load('c:\ACE\RF07\dN_extract_570to574v5b_RH25');
% % % dN1 = load('c:\ACE\RF07\dN_extract_570to574v5b_RH75');

```

```

% % % dN1 = load('c:\ACE\RF07\dN_extract_700to714v5b_RH25');
% % % dN1 = load('c:\ACE\RF07\dN_extract_700to714v5b_RH75');

% % % dN1 = load('c:\ACE\RF08\dN_extract_180to208v5b');
% % % dN1 = load('c:\ACE\RF08\dN_extract_180to208v5b_RH25');
% % % dN1 = load('c:\ACE\RF08\dN_extract_180to208v5b_RH75');

% % % dN1 = load('c:\ACE\RF08\dN_extract_698to702v5b');
% % % dN1 = load('c:\ACE\RF08\dN_extract_698to702v5b_RH25');
% % % dN1 = load('c:\ACE\RF08\dN_extract_698to702v5b_RH75');

% % % dN1 = load('c:\ACE\RF08\dN_extract_720to724v5b');
% % % dN1 = load('c:\ACE\RF08\dN_extract_720to724v5b_RH25');
% % % dN1 = load('c:\ACE\RF08\dN_extract_720to724v5b_RH75');

dN1 = load('c:\TRACE\RF14\dN_extract_388to400v4_RH25');

% Input 4 times to be displayed on plot of number/area/volume distribution
times = [1 241 481 721]

Dp      = dN1(1:end, 1);
dlogDp  = getdlogd(Dp);
dN_dlogDp = dN1(1:end, 2);

dN      = dN_dlogDp.*dlogDp;

%-----
% Find the minimum between the nucleation and Aitken mode (21.3 nm & 62.6 nm)

[min_dN1 row_min1]=min(dN_dlogDp(20:35));      % 20:35 11:20
row_min1=row_min1+19;                          % 19 10
min_Dp1=Dp(row_min1)

% Find the maximum below the minimum

[max_dN1 row_max1]=max(dN_dlogDp(20:row_min1));
row_max1=row_max1+19;                          % 19 10
max_dN1
max_Dp1=Dp(row_max1)

%-----
% Calculations are based on information in Table 12.1 on page 661 of S&P

% Knudsen number
Kn=(2*lambda_air)./Dp;

% Cunningham correction factor - These values are accurate as per S&P page 464, Table 8.3
Cc_K=1+Kn.*(1.142+0.558*exp(-0.999./Kn));
% % % Cc_K(10)
% % % Cc_K(42)
% % % Cc_K(128)
% % % Cc_K(240)

Cc_F=(5.+4.*Kn+6.*Kn.^2.+18.*Kn.^3)./(5.-Kn+(8+pi).*Kn.^2);
% % % Cc_F(10)
% % % Cc_F(42)
% % % Cc_F(128)
% % % Cc_F(240)

% Now convert the Dp to meters instead of um !!!
Dp=Dp./(10^6);

% Diffusion - These values are accurate as per S&P page 480, Table 8.5
D=(k*T.*Cc_F)./(3*pi*mu.*Dp);                % m^2/s
% % % D(10)*10^4
% % % D(42)*10^4
% % % D(128)*10^4
% % % D(240)*10^4

```

```

% Particle Mass
m=(rho*pi/6).*(Dp.^3); % kg

% Thermal velocity - - These values are accurate as per S&P page 480, Table 8.5
c=((8*k*T)./(pi.*m)).^(1/2); % m/s
% % % c(10)*100
% % % c(42)*100
% % % c(128)*100
% % % c(240)*100

% flux matching distance
L=(8*D)./(pi*c); % m

% flux matching distance 2
G=(1./(3*Dp.*L)).*(((Dp+L).^3)-((Dp.^2)+(L.^2)).^(3/2))-Dp; % m

%-----
% Create Brownian Coagulation Coefficient Matrix

K12=[];
K_a=[];
K_b=[];
K_c=[];

for ii=1:size(Dp, 1);
    for jj=1:size(Dp,1);

        K_a=2*pi*(D(ii)+D(jj))*(Dp(ii)+Dp(jj));
        K_b=(Dp(ii)+Dp(jj))/(Dp(ii)+Dp(jj)+2*((G(ii)^2+G(jj)^2)^0.5));
        K_c=(8*alpha*(D(ii)+D(jj)))/(((c(ii)^2+c(jj)^2)^0.5)*(Dp(ii)+Dp(jj)));

        K12(ii, jj)=K_a*((K_b+K_c)^(-1)); % m^3/s

        clear K_a
        clear K_b
        clear K_c

    end
end

K12 = triu(K12);
K12 = K12/2;

%-----
% Calculate the Dp1=Dp2 curve
equal=[];

for ss=1:size(Dp, 1);
    equal(ss, 1)=K12(ss, ss);
end

% % % %-----
% % % % Want to check by plotting and compare to S&P page 662 Figure 12.5
% % % Dp=Dp.*(10^6);
% % %
% % % figure;
% % %
% % % graph1=loglog(Dp, K12(10, :).*(10^6), Dp, K12(42, :).*(10^6), Dp, K12(128, :).*(10^6),
% % % Dp, K12(240, :).*(10^6), Dp, equal.*(10^6))
% % %
% % % legend('0.01 \mum', '0.1 \mum', '1 \mum', '10 \mum', 'Dp1=Dp2');
% % %
% % % %-----
% % % % Data is Table 12.3, S&P page 662
% % %
% % % CHECK1=[K12(10, 10).*(10^6) K12(42, 10).*(10^6) K12(128, 10).*(10^6) K12(240, 10).*(10^6); ...
% % % K12(10, 42).*(10^6) K12(42, 42).*(10^6) K12(128, 42).*(10^6) K12(240, 42).*(10^6); ...
% % % K12(10, 128).*(10^6) K12(42, 128).*(10^6) K12(128, 128).*(10^6) K12(240, 128).*(10^6);
% % % ...
% % % K12(10, 240).*(10^6) K12(42, 240).*(10^6) K12(128, 240).*(10^6) K12(240, 240).*(10^6)];

```

```

% % %
% % % CHECK2=[9.0*10^-10 1.2*10^-8 1.6*10^-7 1.6*10^-6; ...
% % % 1.2*10^-8 7.2*10^-10 2.4*10^-9 2.2*10^-8; ...
% % % 1.6*10^-7 2.4*10^-9 3.4*10^-10 1.0*10^-9; ...
% % % 1.6*10^-6 2.2*10^-8 1.0*10^-9 3.0*10^-10];
% % %
% % % ratio=CHECK1./CHECK2
%-----
% Calculate CoagS for Size dist

% % % keyboard

% First convert the Dp back to micrometers instead of meters !!!
Dp=Dp.*(10^6);

% Need to replace Nan's with zeros for the matrix multiplication
replace = find(isnan(dN));
dN(replace) = 0;

% Create matrix for saving evolving size dists
dN_new=[dN];

% Make the coagulation sink matrix
CoagS = K12*dN*10^6; % m^3/s * #/cm^3 * cm^3/m^3 = #/s

for jj=2:721
    for ii=1:size(Dp)
        % Determine the number of particles lost in each bin
        dN_new(ii, jj) =dN_new(ii, jj-1)*exp(-CoagS(ii)*360);
    end
end

N_new = nansum(dN_new)';

%-----
% Calculate CoagS for peak Dp

CoagS_prime = nansum(K12(row_max1, :).'*dN)*10^6 % s^-1
CoagS_prime2 = nansum(K12(row_min1, :).'*dN)*10^6 % s^-1

%-----
% Check the number and area integrals

for kk=1:size(N_new)
    dA_check(kk) = nansum((pi*Dp.^2).*dN_new(:, kk));
    dV_check(kk) = nansum(((pi/6)*Dp.^3).*dN_new(:, kk));
end

display = [N_new dA_check' dV_check'];

% Calculate the number conc. for nucl., Aitken, accum. and coarse modes

for pp=1:4
    % Break it up by Raes et al. [2000] structure

    N_nuc(pp) = nansum(dN_new( 1:10 , times(1, pp)));
    N_ait(pp) = nansum(dN_new( 11:42 , times(1, pp)));
    N_acc(pp) = nansum(dN_new( 43:128, times(1, pp)));
    N_coa(pp) = nansum(dN_new(128:end, times(1, pp)));

    % Look only at what "was" the nucleation mode, and what's "left"

    N_mode(pp) = nansum(dN_new(1:row_min1, times(1, pp)));
end

percents = [100*N_nuc(1)/(N_new(times(1))) 100*N_nuc(2)/(N_new(times(2)))
100*N_nuc(3)/(N_new(times(3))) 100*N_nuc(4)/(N_new(times(4)))]; ...

```



```

100*N_ait(1)/(N_new(times(1))) 100*N_ait(2)/(N_new(times(2)))
100*N_ait(3)/(N_new(times(3))) 100*N_ait(4)/(N_new(times(4))); ...
100*N_acc(1)/(N_new(times(1))) 100*N_acc(2)/(N_new(times(2)))
100*N_acc(3)/(N_new(times(3))) 100*N_acc(4)/(N_new(times(4))); ...
100*N_coa(1)/(N_new(times(1))) 100*N_coa(2)/(N_new(times(2)))
100*N_coa(3)/(N_new(times(3))) 100*N_coa(4)/(N_new(times(4))); ...
100*N_mode(1)/(N_new(times(1))) 100*N_mode(2)/(N_new(times(2)))
100*N_mode(3)/(N_new(times(3))) 100*N_mode(4)/(N_new(times(4)));

percents(5, :)

% % % a=[find(~isnan(Dp)) Dp dN_new(:, 1)]

%-----
% Generic Plotting

% % % keyboard

figure;

subplot (3, 1, 1)
graph1 = semilogx(Dp, dN_dlogDp, 'k-', Dp, (dN_new(:, (times(2)))/dlogDp), 'b-', Dp,
(dN_new(:, (times(3)))/dlogDp), 'g-', Dp, (dN_new(:, (times(4)))/dlogDp), 'r-');
axis([0.005 20 0 100000]);

ylabel(['dN/dlogDp']);
set(graph1,'linewidth',1.5);

% Integral Text Boxes
a=get(gca,'ylim');

int_handle_N1=text(2, 0.9*a(2), ['IntNum(' num2str(times(1)) ' ) = ' num2str(N_new(times(1)),
'%0f') ' #/cm^3']);
int_handle_N2=text(2, 0.8*a(2), ['IntNum(' num2str((times(2)-1)/10) ' hours) = '
num2str(N_new(times(2)), '%0f') ' #/cm^3']);
int_handle_N3=text(2, 0.7*a(2), ['IntNum(' num2str((times(3)-1)/10) ' hours) = '
num2str(N_new(times(3)), '%0f') ' #/cm^3']);
int_handle_N4=text(2, 0.6*a(2), ['IntNum(' num2str((times(4)-1)/10) ' hours) = '
num2str(N_new(times(4)), '%0f') ' #/cm^3']);

set(int_handle_N1, 'FontSize', 8, 'Color', 'k');
set(int_handle_N2, 'FontSize', 8, 'Color', 'k');
set(int_handle_N3, 'FontSize', 8, 'Color', 'k');
set(int_handle_N4, 'FontSize', 8, 'Color', 'k');

%-----
subplot (3, 1, 2)
graph2 = semilogx(Dp, (pi*Dp.^2).*dN_dlogDp, 'k-', Dp, (pi*Dp.^2).*dN_new(:,
(times(2))/dlogDp), 'b-', Dp, (pi*Dp.^2).*dN_new(:, (times(3)))/dlogDp), 'g-', Dp,
(pi*Dp.^2).*dN_new(:, (times(4)))/dlogDp), 'r-');
axis([0.005 20 0 700]);

legend('Initial', 'Time 2', 'Time 3', 'Time 4', 2);
ylabel(['dA/dlogDp']);
set(graph2,'linewidth',1.5);

% Integral Text Boxes
b=get(gca,'ylim');

int_handle_A1=text(0.006, 0.4*b(2), ['IntArea Initial = ' num2str(dA_check(1), '%0f') '
\mum^2/cm^3']);
int_handle_A2=text(0.006, 0.3*b(2), ['IntArea Final = ' num2str(dA_check(end), '%0f') '
\mum^2/cm^3']);

set(int_handle_A1, 'FontSize', 8, 'Color', 'k');
set(int_handle_A2, 'FontSize', 8, 'Color', 'k');

%-----
subplot (3, 1, 3)

```

```

graph3 = semilogx(Dp, ((pi/6)*Dp.^3).*dN_dlogDp, 'k-', Dp, ((pi/6)*Dp.^3).*dN_new(:,
(times(2)))./dlogDp), 'b-', Dp, ((pi/6)*Dp.^3).*dN_new(:, (times(3)))./dlogDp), 'g-', Dp,
((pi/6)*Dp.^3).*dN_new(:, (times(4)))./dlogDp), 'r-');
axis([0.005 20 0 1000]);

xlabel('diameter (\mum)');
ylabel(['dV/dlogDp']);
set(graph3,'linewidth',1.5);

% Integral Text Boxes
c=get(gca,'ylim');

int_handle_V1=text(0.006, 0.4*c(2),['IntVol Initial = ' num2str(dV_check(1), '%.0f') '
\mum^3/cm^3']);
int_handle_V2=text(0.006, 0.3*c(2),['IntVol Final = ' num2str(dV_check(end), '%.0f') '
\mum^3/cm^3']);

set(int_handle_V1, 'FontSize', 8, 'Color', 'k');
set(int_handle_V2, 'FontSize', 8, 'Color', 'k');

%-----
% Save the number evolution over time and the percentage matrix

% % % save(['c:\TRACE\RF14\dN_evolve_432to442v4_RH75'], 'N_new', '-ascii');
% % % save(['c:\TRACE\RF14\dN_percents_432to442v4_RH75'], 'percents', '-ascii');

```