RELATIONS BETWEEN CLOUD CONDENSATION NUCLEI AND
AEROSOL OPTICAL PROPERTIES RELEVANT TO REMOTE SENSING

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ABSTRACT

Clouds affect the Earth’s energy balance by reflecting incoming sunlight and trapping outgoing heat. It has been hypothesized that various cloud properties (e.g., reflectivity, coverage, lifetime and precipitation efficiency) partly depend on the number concentration of aerosols that serve as cloud condensation nuclei (CCN) during cloud growth. The CCN number varies widely throughout the world over time, and is poorly known. Therefore, a means to convert satellite derived aerosol optical properties to CCN concentration would help evaluate this important indirect effect of aerosols on radiation balance. In order to assess whether remote sensing of CCN is feasible, this dissertation explores the relationships among aerosol size distribution, chemical composition and optical properties measured during aircraft experiments over USA and Mexico.

The aircraft data illuminate four reasons why remote sensing of CCN concentration can potentially achieve a small relative error (<20%) over Mexico. First, many pollution particles are large enough to significantly affect light extinction. They even dominate it in absence of dust. Consequently, the correlation between extinction and CCN number is high, once the extinction due to dust is excluded using the wavelength dependence of extinction. Second, the ambient humidity is usually low, which reduces the error in the estimated response of particle extinction to humidity changes. Third, because many CCN contain black carbon, light absorption also provides a measure of the CCN concentration. The fourth reason is pertinent to the chemical properties of CCN. The organic fraction of volatile mass of submicron particles (OMF) was found to be anti-correlated with the wavelength dependence of v
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All of these four features are weaker over USA and the surrounding oceans than in Mexico.
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1 INTRODUCTION

1.1 Aerosols, Cloud Condensation Nuclei and The Radiative Effects

Aerosols, which are generally defined as particles suspended in the atmosphere in sizes between few nanometers and tens of micrometers, arise from various natural and anthropogenic sources. Most of the aerosol mass in the global atmosphere is sea salt and dust generated at sea surface and deserts, respectively, but these large particles are not necessarily numerous. Human activities are often more important sources with regard to particle number concentration than are the natural sources. Through fossil fuel combustion, cars and factories generate ionic (e.g., sulfate, nitrate) and carbonaceous (e.g., volatile organic compounds, refractory organic compounds not volatile at 300 – 800 °C, and black carbon) particles as well as gases that are precursors of aerosols. Biomass burning from agriculture and cooking also produces submicron particles, often with different chemical compositions from the industrial / urban pollution aerosols. Numerous natural sources such as forest fires and volcanic eruptions can also contribute significantly to aerosol number.

The concentration of atmospheric aerosols is determined not only by their source strengths but also by transport and removal mechanisms. Fine particles smaller than 100 nm typically grow to the accumulation mode, between 100 – 1000 nm, via condensation of gases and coagulation of other particles. The particles in the accumulation mode are deposited to the surface by rain (wet deposition) or, to a smaller extent, by gravity (dry deposition). Larger particles in the coarse mode (> 1
μm) usually settle down at the surface by dry deposition. The residence time of particles in the troposphere varies widely but is in the order of days to weeks. These relatively short residence times lead to inhomogeneous distribution of aerosols over the spatial and temporal scales, hindering the comprehensive observation of their concentration and characteristics as well as the calculation of their effects.

Changes in the concentration of aerosols can perturb Earth’s radiative balance. In the so-called “direct effect”, the aerosols scatter and absorb the incoming solar radiation [Bohren and Huffman, 1983; Coakley et al., 1983; Charlson et al., 1992]. The scattering reduces the energy supplied to the earth-atmosphere system, while the absorption warms the atmosphere. IPCC [2007] quantifies the direct effect in the form of radiative forcing, defined as the change from 1750 to 2005 in the balance between solar radiation entering the atmosphere and the Earth’s radiation going out. On a global average, the radiative forcing due to the direct effect is uncertain between -0.9 and -0.1 W/m² (Figure 1.1). This estimate is much less constrained than that for the greenhouse effect, between +1.49 and +1.83 W/m² [IPCC, 2007]. Furthermore, the IPCC estimate does not include the so-called semi-direct effect where some absorbing aerosols change the atmospheric temperature structure and weaken the hydrological cycle [Ramanathan et al., 2001; Koren et al., 2004].

More uncertain and likely larger is the indirect effect of aerosols on clouds. This is caused by cloud condensation nuclei (CCN), the particles that are capable of initiating drop formation at given supersaturation [Pruppacher and Klett, 1980]. The aerosol indirect effect stems from the fact that as CCN number increases, available water vapor per droplet decreases and, as a result, the cloud droplet size usually
decreases. This phenomenon was first demonstrated by means of cloud chamber experiments (e.g., [Gunn and Phillips, 1957]), and later supported by in-situ measurements [Garrett and Hobbs, 1995; Borys et al., 1998], satellite observations [Kaufman and Nakajima, 1993; Kaufman and Fraser, 1997; Breon et al., 2002; Sekiguchi et al., 2003; Quaas et al., 2004] and model calculations [Lohmann and Lesins, 2002].

One consequence of smaller droplet sizes for a given liquid water content is generally higher cloud optical depth and reflectivity (the first indirect effect), as first hypothesized by Twomey [1974]. More specifically, he concluded that cloud optical depth increases as the third root of cloud droplet number, when the cloud height and liquid water content are kept constant. The sensitivity of cloud reflectance (cloud albedo, \(R\)) to changes in the droplet number concentration \((N)\), termed the susceptibility \((dR/dN)\), was shown to be:

\[
dR/dN = R(1-R) / 3N
\]

The fact that the susceptibility is inversely proportional to \(N\) means that changes in the cloud reflectance is most responsive to increases in droplet number when the number is low as in marine clouds (typically 100 – 300 particles per cm\(^3\)). This inverse relationship poses a big challenge in estimating the Twomey effect: the CCN concentration needs to be identified with high accuracy when it is small hence difficult to measure. Estimated to be between \(-1.8\) and \(-0.3\) W/m\(^2\), the radiative forcing due to this Twomey effect is even less constrained than the aerosol direct effect. It should also be noted that an exception to the positive relationship between
the droplet number and cloud albedo occurs when absorbing particles darken bright clouds and lower their reflectivity [Kaufman and Nakajima, 1993].

Another consequence of the smaller droplet sizes is decreased precipitation efficiency and prolonged cloud lifetime (second indirect effect) [Albrecht, 1989]. Satellite and in-situ observations have revealed some aspects of this effect but not a comprehensive picture. The increased cloud fractional cover and increased liquid water may produce much more cooling than the Twomey effect, as analyses of satellite observations suggested [Sekiguchi et al., 2003; Kaufman et al., 2005].

The cloud cover may decrease with the aerosol loading under the presence of high absorbing particles [Kaufman and Koren, 2006]. Under the influence of smoky air, rain drops may not form until the updrafts reach at ~6.5 km, as opposed to the usual height of <3 km [Rosenfeld, 1999]. Biomass burning smoke may completely shut off precipitation under certain conditions [Rosenfeld, 1999; Andreae et al., 2004]. Urban and industrial aerosols show similar effects [Rosenfeld and Lensky, 1998; Rosenfeld, 2000; Rosenfeld et al., 2002]. Cloud physics models have shown that clean marine conditions, with low CCN concentrations, can be very efficient at producing rain, but total rainfall amount decreases sharply when the CCN concentration is above ~150 cm\(^{-3}\) [Takahashi, 1976; Porter, 1988].

### 1.2 Kohler Equation

Not all aerosols are CCN. In order for particles as small as ~100 nm to grow to cloud droplets >~10 \(\mu\)m, water vapor molecules in the surrounding air must continually condense upon the surface of the particles. The question is, then, what
level of water vapor pressure is required for the condensation. The equilibrium water vapor pressure at the air/water interface of bulk pure water is a rather simple function of temperature (the Clausius-Clapeyron equation). However, that of atmospheric particles is different due to, as Kohler theory describes, the curvature and solutes of the particles.

The increase in particle surface tension (impeding condensation) due to curvature, termed Kelvin effect, is inversely proportional to particle diameter ($\sim D^{-1}$). The decrease in intra-molecular affinity (promoting condensation) due to the presence of solutes, termed Raoult effect, is inversely proportional to soluble particle volume ($\sim D^{-3}$). The balance between these two effects is expressed in the right-hand side of the following equation, and determines the equilibrium vapor pressure, $e$, over the droplet:

$$\ln \frac{e}{e_s(T)} = \ln S_v = \frac{A}{D} - \frac{B}{D^3}$$

$$A = \frac{4M_w \sigma}{RT \rho_w}$$

$$B = \frac{6\nu m_s M_v}{M_s \rho_w \pi}$$

where $e_s(T)$ is the equilibrium vapor pressure of pure bulk water at temperature $T$, $S_v$ is the water vapor saturation ratio, $D$ the droplet diameter, $M_w$ the molecular weight of pure water, $\rho_w$ the density of water, $\sigma$ the surface tension at the air/water interface, $m_s$ the solute mass, $M_s$ the solute molecular weight, and $\nu$ the number of ions resulting from the dissociation of one solute molecule.
The left panel of Figure 1.2 illustrates the relationship between particle diameter and supersaturation defined as $S_{w}=1$. Where the diameter is relatively small, the Raoult effect proportional to $D^{-1}$ is dominant and lowers the saturation below 1 (supersaturation below 0). As the diameter increases, the Kelvin effect with the $D^{-1}$ proportionality becomes noticeable. An important feature of the Kohler curves is the local maximum caused by these two terms. Particles smaller than the diameter at the maximum require, upon condensation, higher saturation for further growth. Thus, the particle size does not grow in the increasing side of the Kohler curves, unless supersaturation is higher than that at the local maximum. For larger particles, on the contrary, the supersaturation becomes lower as the diameter increases, thereby allowing spontaneous condensation. The saturation and diameter at the local maximum are, therefore, critical. Mathematically, the critical supersaturation ($S_c$) and the critical activation diameter ($D_{wc}$) are given as

$$S_c = (3B/A)^{1/2}$$

$$D_{wc} = (4A^3/27B)^{1/2}$$

Note that the critical supersaturation, $S_c$, is expressed with the properties of water and the mole number of the (dissociated) solutes, and not with the particle diameter. The solute mass concentration can be substituted with an expression including dry particle diameter $D_d$:

$$m_s = \frac{\pi D_d^3 \rho_s}{6}$$

Therefore,
Thus, the relationship between critical supersaturation and dry particle diameter is solely determined by qualitative properties of water and solutes at any given temperature. Equivalently, given supersaturation and temperature, the dry diameter required for CCN activation, hereafter referred to as $D_{dc}$ where the subscript "c" indicates critical, is solely determined by the qualitative properties of water and solutes. Dry particles larger than $D_{dc}$ at a given supersaturation are called CCN in the present study. The last equation also indicates that $\ln S_c$ and $\ln D_{dc}$ are linearly correlated with a slope of -3/2, a relationship useful in adjusting $D_{dc}$ to a reference supersaturation. More generally, compared to the Kohler curves drawn against wet diameter ($D$), these relationships involving the dry diameter ($D_d$) are more useful for the present study which uses aerosol measurements conducted under dry conditions.

1.3 Cloud Processing and CCN proxy

The dry particle diameter required for cloud activation, $D_{dc}$, is the key parameter in identifying the subset of the particles that can grow to cloud droplets. In-cloud aqueous-phase chemistry during cycling through non-precipitating clouds causes a minimum in number size distribution near $D_{dc}$. Cloud droplets can accumulate sulfate mass via gas to particle conversion, and, upon evaporation, are larger than before cloud activation [Hoppel et al., 1994]. Small particles, which have higher critical supersaturations and are less likely to nucleate, acquire much less additional mass; thus a size differential develops between the two populations over
time. As a result, the easiest way to find $D_{dc}$ for aerosols processed by non-precipitating clouds is to look for a minimum near 80 - 100 nm in the dry number distribution.

$D_{dc}$ is not constant but varies with the supersaturation and the particle solubility, as explained in the subsequent section. The supersaturation typically rises sharply in the lowest tens of meters from cloud base, and gradually settles down above. Because the supersaturation controls the number of condensation nuclei that are activated, the cloud droplet concentration is thus determined in the lowest cloud layer. The maximum supersaturation is usually between 0.1 and 0.6 %. The supersaturation decreases to its steady value when a balance is reached between the rate of condensation on the droplets that have formed and the updraft-produced rate of increase of supersaturation [Rogers and Yau, 1976].

Near marine stratocumulus on the Washington coast, Vong and Covert [1998] found the so-called Hoppel minima between 90 and 100 nm (dry diameter), while near the Oregon coast, Frick and Hoppel [1993] observed the minima in particle distributions at about 120 nm or larger. The size distributions sampled over the Pacific Ocean near Hawaii near the surface during our experiments (described in Chapter 2) sometimes show the minima, typically when marine aerosols such as sea-salt and sulfate were dominant. One of them, sampled on April 25, 2006 and shown in Figure 1.3, has the minimum near 70 nm. The low diameter may be a consequence of high supersaturation occurring due to stronger cloud updrafts in that region, hygroscopic components, or both. Only a minor fraction (<10% over Mexico) of our size distributions analyzed in this study showed such clear minima, presumably
because many air masses were fresh and had not been processed in clouds. Therefore, $D_{dc}$ can rarely be identified by inspecting our size distributions only.

The number of particles larger than 100 nm, illustrated in Figure 1.3, is referred to as CCN proxy in this study. The choice of 100 nm as the average threshold diameter is supported by our aircraft in-situ data, as detailed in Chapter 4. This threshold diameter is higher than many traditionally selected values (e.g., 80 nm) because a wide range of species including hydrophobic organic compounds was sampled during the experiments. The CCN proxy is employed to examine the relationships between the particle number and the optical properties (Chapter 6). Meanwhile, it should be noted that the CCN proxy is not an exact expression of CCN but an approximation, as the $D_{dc}$ for the atmospheric aerosols is not constant at 100 nm but varies. The variation in $D_{dc}$ has been intensively studied elsewhere (briefed in the subsequent section) as well as in the present study (Chapter 4).

### 1.4 Sensitivity of CCN to Chemical Composition

Aerosol emissions are considered a large source of error in calculating the direct and indirect aerosol effects in global climate models. However, the uncertainty associated with the dry critical diameter may result in similarly erroneous estimates of the aerosol radiative effects [Spracklen et al., 2005]. The right panel of Figure 1.2 highlights the variability among hygroscopic (red curve), hydrophobic (grey) and fully soluble (black) substances as a function of the supersaturation (right axis) [Rissler et al., 2004]. The dry critical diameter at 0.2% supersaturation varies between
80 nm and 300 nm in this data. The number integral of a number size distribution, such as the example shown in the figure (blue curve, left axis), from the critical diameter yields the CCN concentration. Failure to capture the variability in the critical diameter leads to a substantial error in the estimate of the CCN concentration.

According to the Kohler equation the critical activation diameter, \((3B/A)^{1/2}\), is determined by the solubility (represented by the variable \(B\)) and the surface tension (represented by \(A\)) of the particles, at any given supersaturation and temperature (section 1.2). Numerous field and laboratory experiments have been devoted to specifying each of these two terms.

The solubility is, in principle, represented by the number of molecules per unit solution, but calculating this single parameter in practice requires four input variables: soluble volume fraction, solute density, solute molecular weight and the van't Hoff factor (or the degree of ion dissociation). All of these factors depend on the particle chemical composition. These parameters are often poorly constrained, particularly for the various organic compounds.

To simplify the estimation, many studies, including recent ones by Rissler et al. [2006] and Petters and Kreidenweis [2007], instead report parameters that are essentially the ratio of the last three of the four properties specified above. They assume that the parameters are constant for a given species over a range of saturation ratio and other conditions. This simplification facilitates the assessment of critical diameter sensitivity to the aerosol chemistry, as well as the use of the particle hygroscopicity measured below saturation for estimating the solute effect above saturation.
The surface tension of particles has been studied less. Organic compounds have attracted increased attention recently [Shulman et al., 1996; Facchini et al., 1999; Nenes et al., 2002; Raymond and Pandis, 2002; Kanakidou et al., 2005; Hartz et al., 2006]. A modified version of Kohler theory incorporating both limited solute solubility and surface tension depression for slightly soluble species were first presented by Shulman et al. [1996]. Facchini et al. [2000] showed that the surface tension depression could be important for water soluble organic carbon (WSOC) typically found in polluted environments. However, in areas with a relatively small variation in organic mass fraction, the chemical effect may appear small [Dusek et al., 2006] (see a relevant discussion in section 4.3).

1.5 Measuring the CCN

In light of the importance and the uncertainty associated with the aerosol indirect effect on clouds, many attempts have been made to measure the CCN concentration, primarily by means of activation in a chamber and optical counters of cloud droplets. The chamber method traditionally achieved supersaturation of 0.3% or higher due to the limited residence time of the air and the opportunity for condensational growth. The recent development of a continuous-flow streamwise thermal-gradient CCN chamber [Roberts and Nenes, 2005; Lance et al., 2006] may achieve lower supersaturations found in some marine stratus clouds (0.1% or below). Fountoukis et al. [2007] found agreement between in-situ CCN concentration measured with a forward scattering spectrometer probe and modeled values. As these authors point out, the in-situ CCN measurements usually suffers a significant error.
The present study employs a CCN chamber measurement, but complements the analyses of water activity with an independent measurement of particle hygroscopicity which is subject to smaller error related to saturation ratio (Chapter 4).

It is challenging to derive the aerosol number distribution from remote sensing. This is because the aerosol optical signals that satellites detect usually arise from a fraction of aerosol number concentration. As the example distribution in Figure 1.3 illustrates, most particle number reside near 100 nm (top panel) whereas most light extinction reside near 1 μm (middle panel). (The extinction coefficient was calculated for the distribution using Mie theory with the refractive index of 1.59, the value for polystyrene latex spheres used for calibration.) Because this optically active size range overlaps with a considerable fraction of the particle volume (middle panel), the light extinction coefficient can show a good correlation with the particle volume, as Shinozuka et al. [2007] found from aircraft experiments over the North America (see Appendix). The sizes barely overlap, however, between the CCN proxy and the light extinction.

Higurashi and Nakajima [1999] developed an algorithm that translates the reflectance measured at two wavelengths to the aerosol size distribution. Of principal importance to their technique is the wavelength dependence of light extinction, represented by the Angstrom exponent, as a size indicator. The Angstrom exponent is defined as \(-\frac{d\log\sigma}{d\log\lambda}\), where \(\sigma\) is the scattering, and \(\lambda\), the wavelength. This parameter takes values near 0 for large particles such as dust and sea salt but values near 2 or greater for small particles such as those from industrial/urban pollution and biomass burning wavelengths (bottom panel of Figure 1.3). More elaborate remote
sensing techniques with angular and polarization measurements have been developed. For example, Dubovik and King [2000b] built an algorithm to derive the size distribution and other aerosol properties from ground-based measurements of the spectra of visible light not only directly detected from the sun but also diffused through the aerosols in the sky, the latter providing constraint on the angle dependence of aerosol scattering. Yet, these efforts to retrieve the size distribution have not been vigorously validated.

In addition to the particle size, the aerosol chemistry also affects the CCN concentration. No algorithms provide the aerosol chemistry, because many aerosol components near the critical diameter, volatile organic and ionic compounds in particular, generally exhibit similar extinction efficiency and cannot be distinguished optically from each other (see Chapter 5 for related discussions).

In spite of the inadequately tested size distribution retrieval and non-existent chemistry retrieval, NASA satellite instruments may potentially be a powerful tool in monitoring the concentration of CCN in the troposphere. They include the Moderate Resolution Imaging Spectroradiometer (MODIS) [Remer et al., 2006], the Multiangle Imaging SpectroRadiometer (MISR) [Kahn et al., 1998], the Ozone Monitoring Instrument (OMI) [Levelt et al., 2006] and the Cloud-Aerosol Lidar and Infrared Pathfinder Satellite Observation (CALIPSO) [Winker et al., 2003; Winker et al., 2007]. Satellite platforms mounting these optical sensors orbit around the Earth and cover its almost entire surface every week, frequency and spatial coverage impossible to achieve with the expensive and time-consuming aircraft/ship experiments or the fixed ground measurements. If the optical signals that the satellites detect can be
interpreted in terms of the ambient CCN concentration, the product will be extremely valuable in calculating the indirect effect on clouds.

1.6 Summary of the Introduction and Goal of This Study

CCN are essential for cloud droplet formation. Knowledge of the CCN concentration in the atmosphere for common cloud fields is crucial in calculating the indirect effect and understanding the Earth's climate. However, the relatively short residence time of aerosols in the troposphere makes the CCN concentration too variable over time and too inhomogeneous over space to comprehensively measure from aircraft, ship or ground. In this regard, satellites, with the wide spatial and temporal coverage, are a preferred platform from which to monitor the CCN concentration.

The remote sensing of CCN is challenging for two reasons. First, most CCN are too small to be optically detected by the satellite instruments. Second, the chemical properties of particles, determinant of the subset of aerosols that function as CCN, are not retrieved. These limitations exist for the aerosol properties averaged over vertical columns, and retrievals for local air masses (no vertical integral) would be even more challenging. These general limitations may be, however, overcome under specific conditions where the aerosol optical properties resolve the microphysical and chemical properties particularly well.

The goal of this study is to assess whether the CCN concentration can be observed from satellites. If yes, then we need to know how, with what accuracy, and under what conditions. If no, what future satellite capabilities might help? To address
these questions, this dissertation explores the relationships among aerosol size distribution, chemical composition and optical properties measured during aircraft experiments over North America.
Figure 1.1 Global-average radiative forcing (RF) estimates and ranges in 2005 relative to 1750 for anthropogenic carbon dioxide (CO2), methane (CH4), nitrous oxide (N2O) and other important agents and mechanisms, together with the typical geographical extent (spatial scale) of the forcing and the assessed level of scientific understanding (LOSU), according to Intergovernmental Panel On Climate Change (IPCC). The radiative forcing is the change in the balance between solar radiation entering the atmosphere and the Earth’s radiation going out. The net anthropogenic radiative forcing and its range are also shown. These require summing asymmetric uncertainty estimates from the component terms, and cannot be obtained by simple addition. Additional forcing factors not included here are considered to have a very low LOSU.
Volcanic aerosols contribute an additional natural forcing but are not included in this figure due to their episodic nature. Range for linear contrails does not include other possible effects of aviation on cloudiness. Copied from Climate Change 2007: The Physical Science Basis, published by IPCC [2007].
Figure 1.2  (left) Supersaturation as functions of the particle diameter. These Kohler curves represent the combined effects of the curvature and solute of the particles.  (right) The relationship between the supersaturation (right axis) and the dry critical diameter (bottom axis) identified by Rissler et al. [2004] for three groups of aerosol species specified in the legend. An example size distribution of aged biomass burning particles is also given (left axis).
Figure 1.3 (top) An example number distribution of marine aerosols measured at 200 m high near Hawaii on 20:50 UTC, April 25, 2006. A Hoppel minimum is evident near 70 nm. The green shade indicates the number integral referred to as CCN proxy in the text. (middle) The size distribution of aerosol light extinction (red curve) and the volume (blue) calculated for the same number distribution. The area below the curve gives the extinction coefficient (Mm⁻¹) and the volume (μm³/cm³), respectively. The extinction was calculated for a refractive index of 1.59 for a wavelength of 550 nm. (bottom) The Angstrom exponent of scattering, calculated for a refractive index of 1.59.
2 Experiments and Instruments

2.1 Experiments

Here I use the in-situ data collected from 2 aircraft over 3 regions during 4 experiments as shown in Figure 2.1. The Megacities Impact on Regional and Global Environment (MIRAGE, http://www.eol.ucar.edu/projects/milagro/) Experiment took place in March 2006 as a part of the Megacity Initiative: Local and Global Research Observations Campaign. The goal of MIRAGE is to characterize the chemical/physical transformations and the ultimate fate of pollutants exported from urban areas, and to assess the current and future impacts of these exported pollutants on regional and global air quality, ecosystems, and climate. The NCAR C130 aircraft was employed to sample the aerosols and gases directly above Mexico City and the surrounding regions.

INTEX-B (http://cloud1.arc.nasa.gov/intex-b/) was conducted during the 10-week period from March 1 to May 15, 2006. The NASA DC8 aircraft was employed. The first phase of the study was performed during March and focused on the Mexico City pollution outflow over the Gulf of Mexico and occasionally over Mexico City, while the second phase was performed during April and May and focused on Asian pollution outflow over the northeastern Pacific Ocean.

During the second part of INTEX-B, the C130 flew over the US west coast and the northwestern edge of the Pacific Ocean with the same instruments as those employed during MIRAGE. Atmospheric constituents arising from anthropogenic
and biomass burning emissions in the local area and Asia were sampled. This C130 experiment is referred to as IMPEX (Intercontinental and Megacity Pollution Experiment), while INTEX-B is used specifically for the concurrent experiment with the DC8.

We also collected data during the Intercontinental Chemical Transport Experiment – North America (INTEX-A) experiment, a major NASA science campaign conducted from July 1 to August 15, 2004 over North America and the Atlantic [Singh et al., 2006]. The main goals of INTEX-A were to (1) characterize the composition of the troposphere over North America, (2) characterize the outflow of pollution from North America and determine its chemical evolution during transatlantic transport, (3) validate satellite observations of tropospheric composition, (4) quantitatively relate atmospheric concentrations of gases and aerosols with their sources and sinks, and (5) investigate aerosol properties and their radiative effects. The NASA DC-8 research aircraft was deployed mostly over the eastern half of the continental US and the Atlantic Ocean off the US East Coast, and was equipped to measure detailed gas and aerosol composition.

Shinozuka et al. [2007] (see Appendix) analyzed the aerosol optical depth (AOD) and its association with the mass of dry aerosol up to 2.5 μm aerodynamic (PM2.5) and water uptake using the in-situ observations made during INTEX-A. The AOD is related to the aerosol direct radiative effect and readily available as a satellite product. The PM2.5 is a common measure of surface aerosol pollution at selected regional sites. A link between these two parameters would provide a way to infer PM 2.5 and its change over extensive regions observed by satellites. The ambient AODs
determined from the aircraft measurements, and confirmed for 3 profiles near surface AOD measurements, were generally below 0.4 except in the presence of a humid boundary layer with high aerosol loading. The fraction of ambient AOD due to water uptake, Wf, was found to be $37 \pm 15\%$ (average and standard deviation). Boundary layer PM2.5 was estimated (PM2.5$_{\text{proxy}}$) from low altitude size distributions measured from the aircraft. Despite the large variety of vertical aerosol structure, the ambient AOD was found correlated with the PM2.5$_{\text{proxy}}$ with $R^2 = 0.77$, after 4% of data with AOD $> 0.8$ for $>90\%$ RH were removed. These results support the application of remote sensing to retrievals of surface PM 2.5 mass. The wavelength dependence of ambient AOD was found to be less effective in stratifying the mass vs. extinction relationship on the column integral basis than on a layer by layer basis.

2.2 Instrumentation

Aerosols were collected and conveyed to the aerosol instrumentation aboard the C130 and DC8 aircraft through the University of Hawaii solid diffuser inlet. This inlet and sample plumbing has recently been shown to pass dust and sea-salt particles with dry aerodynamic diameter of 5.0 $\mu$m with a better than 50% efficiency during DC-8 Inlet/Instrument Characterization Experiment conducted over and near California [McNaughton et al., 2007]. Quantitative measurements of optical properties can be effectively studied using the UH inlet because aerosol particles smaller than 4 $\mu$m in aerodynamic diameter typically dominate aerosol optical properties even for air masses containing dust and sea-salt. The submicron accumulation-mode pollution that dominates most CCN are sampled with nearly
100% efficiency. However, a few exceptional cases with heavy dust and sea-salt concentrations were encountered during the experiments, and in these cases the extinction measured in the air masses is more uncertain than in the rest of data.

An optical particle counter (OPC, a modified LAS-X, Particle Measurement Systems, Boulder, Colorado) measured the dry (RH < 30%) aerosol size distribution between 0.1 μm and about 10 μm [Clarke, 1991]. The He-Ne laser operates at 633 nm detecting light scattered by individual particles over 35 – 145 degrees. The particle size was calibrated with polystyrene latex spheres whose refractive index is 1.59. For calibrating the coarse mode, glass beads with a refractive index of 1.54 were also used. The data was obtained every 3 seconds, but averaged over 30 – 45 seconds to reduce error due to low counting statistics at about 1 μm or larger.

Smaller sizes with mobility diameters between 10 to 250 nm were measured with a Radial Differential Mobility Analyzer (DMA) under dry conditions. DMA samples were collected over 20 s and held in a lagged aerosol grab chamber [Clarke et al., 1998] for subsequent DMA analysis. In this instrument, an electric field of known magnitude is induced in order to separate particles within a narrow electrical mobility range. For particles possessing a single elementary charge, there is a unique relationship between electrical mobility and particle size: the electrical mobility is inversely proportional to the square of the particle diameter when the mean free path of the molecules of the medium are large compared to the particle diameter. The measured mobility distribution was inverted to an aerosol size distribution by taking into account the sampling line losses, bipolar charging probabilities, calibrated DMA transfer functions regarding DMA diffusion broadening and losses, CPC counting
efficiencies [Zhou, 2001; Zhou et al., 2002]. Both DMA and OPC measurements allowed for real-time thermal analysis of particles at near 40 °C, 150 °C, 300 °C and, for some cases, 360 °C to resolve the volatile (sulfate, nitrate, some organic compounds) and refractory (soot, dust, sea salt) size distributions continuously throughout the aircraft campaigns.

The optical properties of aerosols relevant to atmospheric extinction as governed by the Beer-Lambert law were measured too. The extinction coefficient, $b$, indicates the attenuation of incident light per unit length of layer, such that

$$\frac{dF}{dx} = -bF$$

where $F$ is the intensity of radiation propagating through a layer of medium, and $x$ is the distance along the path of propagation. The extinction coefficient has units of inverse length such as $\text{Mm}^{-1}$ ($10^6 \text{m}^{-1}$), and is the sum of scattering and absorption coefficients. The integral of the extinction coefficient between two points of medium is known as the optical depth. Here I focus on the aerosol component of atmospheric extinction. Its vertical integral over the atmospheric column is termed the aerosol optical depth (AOD).

Total and submicrometer aerosol scattering coefficients were measured using two TSI model 3563 3-wavelength integrating nephelometers [Anderson et al., 1996b; Heintzenberg and Charlson, 1996; Anderson et al., 2003]. The submicrometer TSI nephelometer employed a 1-μm aerodynamic impactor designed after Berner et al. [1979], maintained at 30 lpm by an Alicat Scientific volumetric flow controller. While the measurements were made every second, the data were averaged over the sample air residence time inside the nephelometers of about 10 seconds or longer.
The relative humidity in the instrument was usually lower than 30%, often near 20%. The noise for 60 second averages is reported to be 0.4, 0.2, 0.1 Mm\(^{-1}\) at 450, 550 and 700 nm, respectively [Anderson et al., 1996a]. For particle scattering coefficients above about 1 Mm\(^{-1}\) and averaging times at 60 seconds, systematic rather than random sources of uncertainty become dominant. The systematic error is dominantly caused by the angular truncation, discussed in section 3.3. The relative error arising from gas calibration is estimated at about 1% [Anderson et al., 1996a].

On the DC8, two single-wavelength (near 540 nm) Radiance Research model M903 nephelometers were operated in parallel, one at about 80% (RH\(_1\)) and the other at <40% (RH\(_2\)) to determine the response of aerosol scattering to RH [Howell et al., 2006]. The measurement is important, as the other instruments measure dry sizes and scattering. Section 7.2 of the Appendix discusses the impact of water uptake on the light extinction observed during INTEX-A. Anderson et al. [2003] estimate that the noise averaged over 4 minutes is 0.46 – 0.58 Mm\(^{-1}\). To ensure that our 1-minute f(RH) data suffers little error due to the noise, the data with the dry scattering coefficient lower than 4 Mm\(^{-1}\) were removed. Also, the f(RH) data taken during the first 6 flights of INTEX-B are not used because of a nephelometer leak. The wet to dry scattering ratio, f(RH), was averaged for 60 seconds and used to calculate \(\gamma\) based on the following equation.

\[
f(RH) = \left(\frac{(1-RH_1/100)}{(1-RH_2/100)}\right)^\gamma
\]

\(\gamma\) characterizes scattering response that is determined by the aerosol chemistry, mixing state, sizes and refractive index. These are primarily determined by source type and location as well as transport and scavenging processes, and not directly...
related to ambient RH. Using the calculated $\gamma$, we can derive $f(RH)$ for the ambient RH, or $f(ambRH)$, by replacing $RH_1$ and $RH_2$ with the measured ambient RH and the TSI nephelometer RH (<40%), respectively. The resulting $f(ambRH)$, when multiplied by the total dry scattering coefficient gives the scattering coefficient at ambient RH.

The errors in $\gamma$ and $f(ambRH)$ were estimated by means of Monte Carlo simulation. In so doing, excursions were given to the scattering and humidity terms based on assumed measurement precision. The manufacture's stated error of RH measurement, 3.5%, is used, after Anderson et al. [2003]. The precision in each Radiance Research nephelometer scattering measurement was assumed to be 5% such that the relative error in the ratio of two scattering coefficients is 7% ($5% \times 2^{1/2}$). With these hypothetical errors included, a Monte Carlo iteration confined $\gamma$ within 18% of the true value for a true value of 0.4, and within 14% for a true value of 0.6. The derived $\gamma$ values were subsequently used to calculate $f(ambRH)$. The standard deviation of the relative difference of the resulting $f(ambRH)$ from its true value represents the relative error expected in our measurement-based $f(ambRH)$ derivation. The dependence of the derived $f(ambRH)$ error on the ambient RH and $\gamma$ is presented in Figure 2.2. The $f(ambRH)$ error exceeds 20% at 90% ambient RH for moderately hygroscopic particles ($\gamma > 0.3$). For drier air typical over Mexico (<70% RH), the error is below 10%.

A prototype 3-wavelength Radiance Research particle soot absorption photometer (PSAP) was provided by Dr. David Covert (University of Washington) to measure aerosol light absorption at 470, 530 and 660 nm. The PSAP produces a continuous measurement of absorption by monitoring the change in transmittance.
across a filter using an alternating 3-wavelength LED. This filter-based method is known to report an artifact absorption if transmission through the loaded filter is reduced by particulate light scattering [Bond et al., 1999]. The scattering artifact is a function of the ratio of the scattering coefficient to the extinction coefficient (i.e., single scattering albedo, SSA) and the wavelength. We correct our data for the scattering artifact as well as calibration error after Virkkula et al. [2005] which provides the only correction scheme available at this point for the three-wavelength PSAP. This correction is larger than the classic correction scheme widely used for a single-wavelength (at 530 nm) prototype of the PSAP [Bond et al., 1999]. We are unaware of the reason why the two correction schemes at an identical wavelength can differ by as much as 40% of the uncorrected absorption. The Virkkula et al. correction is more complex than the Bond et al. correction, but whether this is more accurate is difficult to determine.

In the present study the absorption coefficient at 530 nm is used to relate the scattering coefficient to extinction. Because the absorption rarely exceeded 10% of the extinction integrated over vertical profiles (i.e., SSA was seldom lower than 0.9), the measurement error results in a 4% or less error in estimated aerosol optical depth. The absorption coefficients are also used for calculating SSA. Absolute errors up to 0.04 in SSA are expected. The ambient scattering coefficient was adjusted to establish the ambient extinction coefficient under the assumption that the particle absorption measured with the PSAP does not depend on the humidity [Nessler et al., 2005].

The CCN concentration was measured with a continuous-flow streamwise thermal-gradient CCN chamber [Roberts and Nenes, 2005; Lance et al., 2006].
Sampled particles were exposed to supersaturation achieved by a constant temperature gradient in the stream wise direction in the vertical CCN column. Activated particles are detected by an optical particle counter at the exit of the column. The supersaturation was controlled to in 0.10 - 0.25% during MIRAGE, roughly corresponding to the lower end of the typical range of supersaturation found in the global troposphere [Pruppacher and Klett, 1980; Hudson and Svensson, 1995; Hoppel et al., 1996].

An Aerodyne aerosol mass spectrometer (AMS) of the University of Colorado provided the chemical mass of submicron non-refractory aerosol. The development of this instrument is reported by DeCarlo et al. [2006]. In brief, the sample particles are vaporized at resistively heated surface near 600 °C, ionized by electron impact, and accelerated in the electric field. The resulting mass spectra are interpreted into the masses of organic compounds and inorganic ions (sulfate, nitrate, ammonium and chloride). Detection limits are 0.05 µg/m^3 for SO_4, NO_3 and Cl, 0.35 µg/m^3 for the organics and NH_4. The AMS is also capable of aerodynamically sizing the particles by measuring the time of flight from the aerodynamic lens, but this capability was not used in this study.

Size-resolved particle hygroscopicity (growth in response to water uptake) was measured with the tandem differential mobility analyzer (TDMA) of Texas A&M University [Gasparini et al., 2004; Tomlinson et al., 2007]. Sequential measurements were made to characterize the growth of selected particles with dry (~20%RH) diameters including 50, 100 and 300 nm. The voltage applied in the first DMA was fixed in order to select a monodisperse aerosol. This aerosol was then
exposed to an elevated RH of about 84% as it passed through a second Nafion tube bundle. Subsequent to this conditioning, the initially monodisperse aerosol was introduced into the second DMA downstream, which scanned through the particle sizes. The measured size distribution is described in terms of the relative change in diameter of the particles or the growth factor. For a given aerosol distribution, several growth factor modes may be observed when multiple particle types are present. Any scan in which the relative humidity deviated by more than 5% below or 7% above 84% RH was discarded. The “growth” factor for dry (~20%RH) particles was usually found to be within 5% of the expected value (1) [Gasparini et al., 2004], and provides an indication of the measurement accuracy.
Figure 2.1 Flight tracks of the C130 and DC8 aircraft during the 4 experiments.
The relative error of $f(RH)$ estimated for the ambient and dry humidity (indicated in the parentheses), $\gamma$ (numbers between 0.1 and 0.7 noted above data points) and true values (horizontal axis). The million Monte Carlo iterations employed for this estimation appear to have returned statistically robust results in general. The only exception is the cases with 90% ambient RH and moderate particle hygroscopicity values ($\gamma>0.3$) which caused unexpected fluctuations in the estimated error. The insert shows $f(RH)$ as a function of the ambient RH.
3 Uncertainty Analyses and Data Processing

The accuracy of our in-situ measurements is examined in this section. Because

\[(\text{observed variability})^2 = (\text{measurement error})^2 + (\text{natural variability})^2\]

the measurement error needs to be separated from the observed variability of the aerosol properties – be it number concentration or light extinction – to estimate the natural variability. The measurement error is assessed through comparisons of independent measurements made aboard the aircraft. During the course of the data evaluation, the scattering coefficient is corrected for the detection angle non-ideality and the response to humidity changes.

3.1 Aerosol Number

The number of aerosol particles between 100 nm and 20 \(\mu\text{m}\) measured with the OPC, \(N_{100\text{nm}}\), is important to this study as it is used as a proxy for the CCN concentration. In this section the measurement error in \(N_{100\text{nm}}\) is assessed in two steps. Because the random error in optical sizing near 100 nm is the dominant source of the error, an upper bound of the error is estimated through comparison of number integral with the DMA distribution near this diameter. A more realistic error estimate is then acquired by minimizing the DMA error.

The error in the upper size limit, the sizing of relatively large particles and number counting efficiency of the OPC contributes little error to the number integral. Of the number integral up to 20 \(\mu\text{m}\), 99% lies below 1 \(\mu\text{m}\) for almost all (>99%) of our C130 measurements over Mexico, at 5 km above sea level or below. This is
evident in the examples of the number distributions shown in Figure 3.1. A large sizing error near or above 1 μm, if any, would result in a relative error of the number by 1% or less. Counting error can be only marginally more significant: The OPC number counts are subject to an error comparable to the relative error in flow rate (~3%).

As a result, the accuracy of \( N_{>100\text{nm}} \) depends primarily on the sizing near the small diameter limit (100 nm). One way to assess this accuracy is to compare the number of dry particles in 100 – 200 nm overlap size range between the OPC and the DMA. For each 30-second OPC cycle, the OPC distribution was averaged and compared with the DMA scan that fell into the time period. Our C130 data (the top panel of Figure 3.2) shows favorable agreement, with a linear regression of

\[
N_{\text{DMA}} (\text{cm}^{-3}) = N_{\text{OPC}} (\text{cm}^{-3}) \times 0.91 + 9.7, \quad R^2 = 0.88.
\]

If the number is limited up to 500 cm\(^{-3}\), the slope is even closer to 1 (not shown in figure):

\[
N_{\text{DMA}} (\text{cm}^{-3}) = N_{\text{OPC}} (\text{cm}^{-3}) \times 0.96 + 5.4, \quad R^2 = 0.87.
\]

Means of the regressions both ways (one from OPC to DMA, the other from DMA to OPC) are given here because neither instrument is presumed to be more accurate than the other in this size range.

Errors in OPC sizing and DMA multiple charge correction are expected to explain most of the deviations from perfect agreement. Optical sizing near 100 nm can be distorted by the nonlinear voltage amplifier implemented in the OPC detector. Variations in the aerosol refractive index and shape also pose sizing errors, though they are insignificant as demonstrated below. The DMA inversion, mentioned in
section 2.2, is subject to gradually increasing error as the size approaches the large diameter detection limit near 200 nm [Zhou, 2001]. The overall DMA relative sizing error is reported to be about ±2% [Mikhailov et al., 2004; McMeeking et al., 2005]. Because the apparent disagreement in the integral number reflects the combination of the independent errors of the two instruments, the error in the OPC number integral \(N_{100\text{nm}}\) alone must be smaller.

Another approach was taken in order to estimate the error of \(N_{100\text{nm}}\) alone. To minimize the DMA error, the DMA number counts above 100 nm were disregarded. The DMA number integral between 10 and 100 nm was calculated, and was subtracted from the size-unresolved aerosol number measured with one of the condensation nuclei (CN) counters. Logically, the result should be the number of particles larger than 100 nm, provided the CN count includes few particles smaller than 10 nm. This is frequently the case because the lower detection size limit of this particular CN counter was set at 10 nm. To constrain this comparison, we removed the cases with numerous particles near 10 nm, i.e., the cases where the ultrafine (>3 nm) particle count measured with another CN counter exceeded the CN count above 10 nm by 50% or more. This essentially excluded regions of recent nucleation. We also removed the cases where the DMA number was more than half of the DMA+OPC number. This reduces the chance that the DMA number count errors due to poor counting efficiency non-ideal charging, transmission efficiency and multiple charge correction are mistaken as the OPC number error. These criteria select 20% of the entire valid data.
The comparison of the two number integrals from 100 nm is centered near the 1:1 line, though the one-way regression is tilted by a few outlying data points (Figure 3.3):

$$N_{\text{OPC}} \ (\text{cm}^{-3}) = N_{\text{CN-DMA}} \ (\text{cm}^{-3}) \times 0.79 + 36.0, \ R^2 = 0.84.$$  

One standard deviation of $N_{\text{OPC}} / N_{\text{CN-DMA}}$ is ±27%. Note that the number difference partially reflects the (reduced) DMA error and the CN counter error. We believe each of these is as negligible as the relative error in flow rate (~3%).

The apparent number difference is partly due to the natural aerosol variability over the different sample intervals used for the DMA and OPC measurements. Each DMA sample period took 20 seconds to fill the lag chamber. Each OPC measurement cycle took 30 seconds. The change in the ambient aerosol concentration during the ~10 second gap inhibits number agreement. This natural variability can be assessed by taking the autocorrelation of the total aerosol number concentration over time. The CN (>10 nm) number counts separated by 10 seconds differed from each other by about 10% or less for most (two thirds) of the cases during MIRAGE. Because the CN counter measurement is highly precise, this temporal variation is almost entirely attributable to the natural variability of aerosol number concentration. This should be independent of the true OPC instrument error, and needs to be differentiated from the apparent OPC relative error, 27%. As a result, the relative error (one standard deviation) in the $N_{>100\text{nm}}$ measurement is 25%.

In addition to the precision of the OPC number itself, its trend with chemical composition becomes important in the discussions later. The particle size measurement could be systematically biased by, for example, variation in the
refractive index, a parameter dependent on the particle chemistry. Hence, it is reasonable to ask whether certain aerosol species bias the OPC measurements toward larger or smaller numbers. The bottom panel of Figure 3.2 shows the DMA-OPC comparison color-coded with the single scattering albedo and AMS organic mass fraction. No clear trend is evident with these parameters representative of the chemical composition. The same holds true for the dry scattering and absorption wavelength dependencies (not shown). To be sure, both the OPC and the DMA number concentrations tend to be high for large scattering wavelength dependence as expected for pollution air masses, but what matters here is the relative difference between the two independent measurements. The OPC performance was also found to be insensitive to variations in the reference voltage indicative of the laser power (not shown). Generally, no evidence exists to suggest possible operational errors, such as reference voltage maladjustment, affected the OPC number count.

The OPC measurement aboard the DC8 during INTEX-B is a little more complicated because the smallest diameters up to 130 nm were truncated electronically. We estimate the number between 100 and 130 nm by scaling the number between 130 and 300 nm \((N_{130-300\text{nm}})\) by the number fraction in this size range adapted from the C130 measurement. Figure 3.4 demonstrates that this correction factor, \(\frac{N_{100-130\text{nm}}}{N_{130-300\text{nm}}}\), is negatively correlated with the measured wavelength dependence of dry scattering coefficient, or the Angstrom exponent \(\alpha\), defined in section 1.5). The correction factor is \(-0.18\alpha+0.79\), and one standard deviation of the number ratio falls within 25% of this value. This relationship is likely driven by the fact that increasing number between 130 and 300 nm tends to raise the Angstrom
exponent but not necessarily the aerosol concentration over 100 - 130 nm, the consequence of which is reduced number ratio. The use of 300 nm as the threshold diameter is optimum. For larger threshold diameters the correlation weakens while the standard deviation of the number ratio does not decrease further. Also, the magnitude of correction relative to the total CCN proxy, $N_{100-130\text{nm}} / N_{>100\text{nm}}$, is $0.30 \pm 0.13$ (mean and one standard deviation). All this translates into 8% relative error associated with the truncation correction. The overall relative error in $N_{>100\text{nm}}$ including the 25% error intrinsic to the normal OPC mentioned above turns out to be 26%.

To evaluate the DC8 OPC correction, Figure 3.5 compares the OPC number integrals measured during the 3 intercomparison flights where the two aircraft flew generally within 100 m of each other. The corrected DC8 OPC integral agrees within about 20% of that of the C130 for most cases with concentrations larger than 100 cm$^{-3}$, good agreement in view of the estimated relative error of 25 – 26%. Note that the difference is partly attributable to air mass differences between the two samples. Thus, the two OPCs may be even more consistent with each other than what this intercomparison suggests.

### 3.2 OPC Size Distribution Validation

The goal of this study is to assess the link between the CCN concentration and the aerosol optical properties under ambient conditions. We have evaluated the error in the CCN proxy concentration measured in-situ during the experiments. Here we
shift our attention to the other part of this link, and examine the scattering coefficient, a parameter that dominates the aerosol optical properties.

Neither the nephelometer nor the OPC size distribution provides a fast and complete measurement of the scattering coefficient. The nephelometer detects scattering with a relative error of about 1% [Anderson et al., 1996a], but the detection angle is limited to 7° – 170° ([Anderson and Ogren, 1998]). The lack of forward scattering measurement causes an underestimate of the full-angle scattering coefficient by about 30% for coarse particles, less for submicron particles. The OPC size distribution can provide the scattering integrated over both 7° – 170° and 0° – 180° based on Mie theory, but with low temporal resolution. Also, the OPC sizing error could pose a significant error on the derived scattering. To correct the two scattering measurements for these non-idealities, we first validate the OPC-derived scattering against the nephelometer measurement over 7° – 170° (described below) and then use the OPC size distribution to correct the nephelometer data to 0° – 180° (in the next section). Our discussion here is directly relevant to the goal of this study, to assess whether the aerosol optical properties as seen by satellites can be linked to CCN number concentration.

The scattering derived from the OPC size distribution over the nephelometer detection angle at 550 nm slightly exceeds the nephelometer scattering coefficient on average over Mexico (Figure 3.6a):

$$\sigma_{neph} \text{ (Mm}^{-1}) = 1.11 \times \sigma_{OPC} \text{ (Mm}^{-1}) - 1.14, \ R^2 = 0.85.$$  
These two scattering coefficients agree well with each other over the northeastern Pacific Ocean flown during IMPEX (Figure 3.6b):
The comparisons at the other two nephelometer wavelengths are similar, as indicated in Table 1. As an approximation, the refractive index of calibration particles, 1.59, was used for these Mie calculations. This value is expected to be near the average for the aerosols encountered during our experiments: The refractive index may be smaller for ionic compounds, and larger (with a non-zero imaginary part) for pollution containing soot. The deviation is moderate (centered at \(-10\%\) at 550 nm during MIRAGE), and does not significantly affect the subsequent nephelometer correction. The degree of overestimation/underestimation shows little trend with the single scattering albedo (the ratio of scattering to the sum of scattering and absorption) or the organic mass fraction measured with the AMS (not shown). This implies no significant measurement bias due to specific aerosol species.

We also compare the wavelength dependence of scattering (Angstrom exponent) determined from the OPC and the nephelometer. This parameter turns out to be a useful tool in correcting the nephelometer data, particularly in the absence of a simultaneous OPC measurement. As mentioned in section 1.5, the Angstrom exponent is defined as \(-d\log \sigma /d\log \lambda\), where \(\sigma\) is the scattering, and \(\lambda\), the wavelength. This parameter takes values near 0 for dust and sea salt but values near 2 or greater for small particles such as those from industrial/urban pollution and biomass burning. This parameter also exhibits reasonable agreement within about 0.2 between the two instruments (Figure 3.7). The difference is partly explained by the natural variability of particle refractive index which is ignored in the OPC calculation. Therefore, the absolute error in the nephelometer-based scattering Angstrom exponent is expected to
be 0.1 or smaller. The differences in scattering Angstrom exponent between the nephelometer and the OPC do not show any clear trend with the SSA, implying no measurement bias due to absorbing particles.

### 3.3 Scattering Correction for Angular Truncation

The most readily available satellite aerosol product, the optical depth, is dominated by the vertical integral of the scattering coefficient over the full angle range between 0 and 180° under ambient humidity. During our aircraft experiments, the aerosol scattering was measured over an incomplete angle range under dry conditions. Before being compared to relevant in-situ or remotely sensed properties, the measured scattering coefficient needs to be corrected for ambient conditions, by calculating both the effect of the angular truncation (discussed in this section) and the humidity response of particle light scattering (next section). These calculations add uncertainties to the resulting ambient scattering coefficient.

The measured dry scattering coefficient needs to be adjusted for the scattered light over the angles in which in the TSI nephelometer has no detector (0 - 7° and 170 - 180°). The correction factor was calculated using the aerosol size distribution measured with the OPC. The angular truncation correction factor is the ratio of two scattering coefficients, one integrated over the full angle range (0 - 180°) and the other over the nephelometer angles (7 - 170°). As is expected from Mie theory (Figure 3.8a), the correction is a function of aerosol size: Large for coarse particles (a correction factor up to ~2) and small for accumulation mode particles (<10%).
The correction factors calculated for MIRAGE data at 550 nm using a refractive index (1.59) are shown in Figure 3.9a. The correction factor was averaged over Angstrom exponent bins of 0.1 between 1.1 and 2.1, and was linearly extrapolated to smaller and larger Angstrom exponent values. These bin limits (1.1 – 2.1) were selected in such a way that two thirds of the data fall between them. For IMPEX (Figure 3.9b), the relationship is less well defined than for MIRAGE, presumably because of the smaller OPC number counts (higher relative error) indicated by the smaller derived scattering coefficient (smaller markers). The bins between 0.4 and 1.6 contained two thirds of the data, and were used to linearly extrapolate the relationship to values of Angstrom exponent out of these limits.

The relationship observed during IMPEX is distinctively different from MIRAGE, represented with a less negative slope of the best fit line. The difference over the small Angstrom exponent can be explained by the subtle difference in the coarse mode size distribution. Proportionally more dust particles appeared to exceed 10 μm compared to the sea-salt (Figure 3.10). This is because of the upper size cut-off imposed by our inlet. Sea-salt particles lost water molecules and shrank upon heating through the inlet and transmission to the instruments, while the dust is insensitive to the associated humidity drop. Also, more dust than sea salt may have bounced at the inner wall of the inlet to enter the instruments.

The difference in the shape of the size distribution within the coarse mode affects the nephelometer angular truncation correction factor much more than it affects the Angstrom exponent. Mie calculations in Figure 3.8 show the angular correction factor is sensitive to size in the coarse mode whereas the Angstrom
exponent is insensitive. In contrast, the angular correction factor is small and size-insensitive over the accumulation mode where the Angstrom exponent is high and sensitive.

This difference in size sensitivity between the wavelength dependence and angular truncation hinders the use of former in correcting the latter. For example, the Angstrom exponents calculated for dust and sea-salt distributions in Figure 3.10 are only slightly different from each other (-0.25 and -0.22, respectively). This difference translates into an 11-percentage-point (absolute difference) difference in the correction factor at 550 nm (2.14 and 2.03 for the dust and sea-salt distributions, respectively) based upon Mie calculations. This can be compared to a small 0.3 percentage point difference (1.371 and 1.368) based on the Angstrom-based approximation after Anderson and Ogren [1998] (grey lines, dashed for total aerosols and solid for submicron aerosols, in Figure 3.9). They calculated the correction factors for combinations of 2 lognormal distributions, both with geometric standard deviations of 1.8, with volume mean diameters ranging between 2 and 4 μm for the coarse mode and 200 and 400 nm for the fine mode. These boundary distributions are indicated with dashed and dotted curves in Figure 3.10, with arbitrary heights. Their range of fine mode distribution covers the accumulation-mode peak (near 200 nm) of our measured distributions, but their range of coarse mode distribution does not cover the coarse-mode peak (highly variable, the example sea-salt distribution peaks near 10 μm) of our distributions. Even if a wider variety of coarse mode distributions is taken into consideration, coupling them with accumulation mode distributions, and therefore determining the Angstrom exponent, would require additional constraints.
and careful analysis. Note that the scattering coefficient we observed was mostly contributed by submicron particles, and the extremely high coarse-mode volumes exemplified in Figure 3.10 were exceptions.

Despite the magnitude of the angular correction, it remains tightly related to the Angstrom exponent provided the dominant type of coarse mode particles (i.e., dust vs. sea salt) is known. For MIRAGE, the root mean square of the correction factors is 5 – 8% depending on the wavelength. For IMPEX it increases to 9 – 10%, presumably because of the lower signal and higher relative noise. These ranges of variability are interpreted as the relative error introduced when the measured Angstrom exponent is translated into an angular truncation correction factor. They exceed the nephelometer precision before the angular correction, estimated to be 1% [Anderson et al., 1996a], and dominate the overall error in the dry scattering coefficient. The fit was used to derive the correction factor for individual data from the nephelometer-based Angstrom exponent. The use of the Angstrom exponent, instead of comparing the simultaneous OPC and nephelometer measurements one by one, minimizes the unfavorable impact of the OPC’s poor counting statistics and the frequent absence of measurements of unheated particles.

Absorbing particles may be subject to different relationships between the Angstrom exponent and the correction factor. To find the sensitivity of the relationship to the imaginary part of refractive index, a refractive index of 1.55 - 0.1i was used up to 300 nm (and 1.59 for larger diameters) to run the Mie calculation on the OPC size distributions measured during MIRAGE. The derived correction factor was lower by 5 - 7 percentage points than the value estimated for the non-absorbing
refractive index of 1.59 over the Angstrom exponent of 1.5 - 2.0. The difference due to absorption is mostly caused by the reduction in the Angstrom exponent. The correction factor for aerosol samples with submicron absorbing particles such as soot is, thus, subject to a greater error. In contrast, the refractive index of sampled dry coarse particles, dust or sea-salt, should be close to that of PSL and glass beads (1.54 - 1.59). However, the non-spherical shape of these coarse particles may result in a considerable error in OPC sizing and the derived nephelometer angular truncation correction factor.

The DC8 flew over both Mexico and the northeastern Pacific Ocean, and observed a contrast in the nephelometer truncation correction factor between dust and sea salt, consistent with the C130 observation over these two regions. The data are bounded by different slopes reflecting differences in location and ambient RH (Figure 3.9c and d). The dust dependency was observed only during the first half of experiment (over Mexico in March 2006) under dry conditions, whereas the sea-salt dependency was observed during both halves (Mexico and northeastern Pacific Ocean). Accordingly, we apply the dust angular correction factor for the INTEX-B data taken during the first part of experiment under 80% RH or lower (Figure 3.9c), and the sea-salt correction for all other INTEX-B data (Figure 3.9d).

The imperfect separation between the two aerosol species compromise the accuracy of the resulting correction factor: The root mean square of the DC8 nephelometer truncation correction factor varies by 10 – 21%, compared with the variability of 5 – 10% associated with the C130 observations. A majority of the DC8 data is classified properly as dust or sea-salt and suffers smaller relative errors than 10
- 21\%, while the rest of data is misclassified and subject to systematic biases owing to the use of inappropriate correction factors (i.e., the dust correction factor applied to sea-salt data, and the sea-salt correction factor applied to dust data). The error may be larger for non-spherical or strongly absorbing particles, as mentioned above. Also note that the DC8 dust and sea-salt dependencies (Figure 3.9c and d, respectively) are found near the C130 MIRAGE (Figure 3.9a) and IMPEX (Figure 3.9b) fit, respectively. The small systematic shift to the smaller angular correction factor for given Angstrom exponent may be explained by subtle bias in OPC sizing in the coarse mode, marginally lower inlet transmission efficiency compared to the C130, or both. The inter-aircraft difference in the correction factor at 550 nm is 4 - 11\% at an Angstrom exponent of 1, less for the more common, larger Angstrom values. Note also that the correction for disabled channels up to 130 nm (section 3.1) makes little difference. The INTEX-A data likely suffer a small degree of error similar to IMPEX, because of the lack of dust.

### 3.4 Hygroscopicity and Ambient Scattering Coefficient

Because light scattering due to most aerosols responds to changes in relative humidity, the dry scattering coefficient over 0 - 180° needs to be increased based on our f(RH) measurement made on the DC8 aircraft to yield the ambient scattering coefficient. As demonstrated in section 2.2 and Figure 2.2, the relative error of f(RH) may be 20\% at high (90\% RH) for moderately hygroscopic pollution particles whose $\gamma$ exceeds 0.3. The overall relative error in the derived ambient scattering coefficient
is at most 29%, which is the square root of sum of the squares of this \( f(RH) \) error and the truncation correction error (up to 21%). To estimate the lower boundary of the relative error, consider an occasionally encountered set of conditions where the ambient RH was as low as 50%, typical over Mexico City. Here many particles were less hygroscopic with \( \gamma \) near 0.4, resulting in a smaller relative error of \( f(RH) \) (~5%), and the truncation error may be better estimated (estimated as 5% in the previous section). The overall error in the ambient scattering coefficient for this aerosol would be about 7%. Many aerosols observed over and near Mexico were more hygroscopic and absorbing, and therefore the typical relative error may be nearer 20%.

One way to check the data validity and the uncertainty estimates above is to compare with ambient optical measurements made from other platforms. Two other aircraft flew around 21°N, 94°W over the Gulf of Mexico on 16:43 - 17:01 UTC March 10, 2006 while our C130 was making a spiral descent. The NASA Ames Airborne Tracking Sun photometer (AATS-14) directly measured aerosol optical depth from the J31 aircraft. The ambient extinction coefficients are derived as vertical derivatives of smoothed AOD vertical profiles. The measurements at 519 nm and 604 nm were interpolated, on a log scale of wavelength, to the wavelength of 550 nm. The airborne High Spectral Resolution Lidar (HSRL) measured the backscattering of aerosols at 532 nm. As Figure 3.11 shows, our corrected ambient extinction agrees well with these two ambient measurements. For calculating the C130 extinction coefficient, the humidity response of particle scattering, \( \gamma \), was assumed to be 0.49 for altitudes of 2 km and above, and 0.61 below. These were average values measured aboard the DC8 over and near Mexico. The differences at most altitudes are within
the 7 – 29% relative error of the C130 extinction coefficient. The vertical integral between 270 m and 4300 m of the C130 extinction coefficient only differs by 21% from the J31 and by 18% from the BE200. The difference is partly due to the spatial inhomogeneity of aerosols, as well as the error associated with our extinction coefficient derivation and the AATS-14 and HSRL errors in taking the vertical derivatives and translating the measured backscattering into the extinction. This supports our error estimates above of about 20%.

Unfortunately there were virtually no vertical profiles flown during MIRAGE and INTEX-B suitable for comparison with ground AOD measurements, due to the focus on low altitudes, air traffic restrictions and unfavorable weather. However, there were during INTEX-A. It was not only for the assessment of the ambient extinction but also for data consistency check against AERONET ground measurements. The agreement is mostly within 30%, all within 0.1 AOD, for the three vertical profiles. Appendix A (section 5.3 and Figure 4) discusses these closure studies in greater detail. The uncertainties estimated in this Chapter are summarized in Table 3.3.
Table 3.1  Slope, intercept and correlation coefficient of the regression line for the scattering comparison between the OPC and nephelometer.

<table>
<thead>
<tr>
<th>( \lambda ) (nm)</th>
<th>Slope</th>
<th>Intercept</th>
<th>R2</th>
</tr>
</thead>
<tbody>
<tr>
<td>450</td>
<td>1.08</td>
<td>-1.61</td>
<td>0.86</td>
</tr>
<tr>
<td>550</td>
<td>1.11</td>
<td>-1.14</td>
<td>0.85</td>
</tr>
<tr>
<td>700</td>
<td>1.15</td>
<td>-1.29</td>
<td>0.84</td>
</tr>
<tr>
<td>550 (submicron)</td>
<td>1.01</td>
<td>-0.77</td>
<td>0.78</td>
</tr>
</tbody>
</table>

MIRAGE

IMPEX

<table>
<thead>
<tr>
<th>( \lambda ) (nm)</th>
<th>Slope</th>
<th>Intercept</th>
<th>R2</th>
</tr>
</thead>
<tbody>
<tr>
<td>450</td>
<td>0.94</td>
<td>0.37</td>
<td>0.89</td>
</tr>
<tr>
<td>550</td>
<td>0.96</td>
<td>0.16</td>
<td>0.86</td>
</tr>
<tr>
<td>700</td>
<td>0.97</td>
<td>0.03</td>
<td>0.83</td>
</tr>
<tr>
<td>550 (submicron)</td>
<td>0.80</td>
<td>-0.02</td>
<td>0.78</td>
</tr>
</tbody>
</table>

The intercept is in Mm\(^{-1}\). R2 is the correlation coefficient.
Table 3.2  Slope, intercept and the root mean square (RMS) of the linear regression for the calculated nephelometer angular truncation correction factor as functions of the scattering Angstrom exponent.

<table>
<thead>
<tr>
<th>λ (nm)</th>
<th>Slope</th>
<th>Intercept</th>
<th>RMS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>MIRAGE</td>
<td></td>
</tr>
<tr>
<td>450</td>
<td>-0.26</td>
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<tr>
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<td>1.86</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td></td>
<td>IMPEX</td>
<td></td>
</tr>
<tr>
<td>450</td>
<td>-0.16</td>
<td>1.33</td>
<td>0.09</td>
</tr>
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</tr>
<tr>
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<tr>
<td>700</td>
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The RMS is of the correction factor difference between the regression line and the data with the scattering coefficient greater than 1 Mm⁻¹.
Table 3.3  Relative and absolute errors estimated for the number and optical measurements.

<table>
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<tr>
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<td>5 - 20%</td>
<td></td>
<td>3.3</td>
</tr>
<tr>
<td>Ambient Extinction Coefficient*</td>
<td>5 - 30%</td>
<td></td>
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<tr>
<td>Ambient Extinction Angstrom Exponent</td>
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<td>0.2</td>
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</table>

(*) The errors in dry scattering coefficient and ambient extinction coefficient are estimated for non-absorbing spherical particles.
Figure 3.1 Examples of number (solid curve) and volume (dashed) size distributions measured with the DMA (up to 0.2 μm) and the OPC (from 0.1 μm). (top) Ionic pollutants over the northeast Mexico observed on 12:00 - 14:00 UTC, March 28, 2006. (middle) Fresh pollution caught right over Mexico City on 19:30 - 21:00, March 22, 2006. (bottom) Dust over northern Mexico on 16:00 - 20:00, March 18, 2006.
Figure 3.2  Comparison of the aerosol number between 100 - 200 nm measured with the DMA and the OPC on the C130 aircraft during MIRAGE and IMPEX. The markers are color-coded with (top) the single scattering albedo at 530 nm and (bottom) the organic mass fraction measured with the AMS. The 1:1 line (thin solid line), linear regressions (thick dashed lines) and the geometric mean regression (thick solid line) are given in the first panel.
Figure 3.3  Comparison of the number concentrations of particles larger than 100 nm measured during MIRAGE and IMPEX. The vertical axis represents the OPC number integral, and the horizontal axis, the difference of the CN counts above 10 nm and DMA number integral between 10 and 100 nm.
Figure 3.4 The number ratio of OPC number integral between 100 - 130 nm \((N_{100-130\text{nm}})\) and that between 130 - 300 nm \((N_{130-300\text{nm}})\) observed during MIRAGE and IMPEX, as a function of the concurrent measurement of the Angstrom exponent of dry scattering coefficient. The OPC data were averaged over 30 seconds. The data with \(N_{130-300\text{nm}}\) smaller than 100 cm\(^3\) were excluded. The average within each 0.1 Angstrom exponent bin between 1.3 and 2.2 is given with a black square.
Figure 3.5  The total OPC counts compared between the two aircraft during the 3 sets of intercomparison flights. Circles indicate the March 19 data, triangles, April 17, and squares, May 15. The red markers are for the DC8 OPC corrected for the loss at the disabled channels, and the blue, uncorrected. The dashed lines indicate 20% deviation from the 1:1 agreement (solid line).
Figure 3.6  Comparison of the scattering coefficient at 550 nm between the OPC and the nephelometer over 7 - 170°, averaged over 30 seconds, for MIRAGE (left panel) and IMPEX (right). The dashed lines represent the linear regression: $y = 1.11x - 1.14$, $R^2 = 0.85$ for MIRAGE, $y = 0.96x + 0.16$, $R^2 = 0.86$ for MIRAGE, where $R^2$ is the correlation coefficient.
Figure 3.7 The scattering Angstrom exponent derived from the OPC size distribution and the nephelometer during MIRAGE. The marker size is set proportional to the dry extinction coefficient at 530 nm to highlight the data with high signal to noise ratio. Their difference does not show a clear trend with single scattering albedo.
Figure 3.8 (top) The scattering efficiency integrated over the nephelometer (7 - 170°) and the full (0 - 180°) angle ranges plotted against the particle diameter. The thick red curve indicates their ratio which is the nephelometer truncation correction factor. (bottom) The scattering Angstrom exponent for the two angle ranges.
Figure 3.9  The TSI nephelometer angular truncation correction factor calculated from the concurrent OPC measurements of the aerosol size distribution for MIRAGE, IMPEX and the first and second halves of INTEX-B. The data are plotted against the OPC-derived Angstrom exponent of the scattering integrated over 7 - 170°. The black curves represent the regression lines for the correction factor averaged over 0.1 Angstrom exponent bins, as explained in the text. The grey dashed and solid curves indicate the correction factors provided by Anderson and Ogren [1998] for total and submicron particles, respectively.
Figure 3.10  Example volume distribution of dust particles observed over the northern Mexico on 17:07 - 17:30, March 18, 2006 (red curve) and sea salt particles over the ocean near Hawaii at 500 m above sea level or lower throughout the flight on May 1, 2006 (blue). The smaller and larger bounds of model size distributions used in Anderson and Ogren [1998] are shown with dotted (the fine mode) and dashed (the coarse mode) curves.
Figure 3.11  The extinction coefficient profiles measured from the 3 aircraft (C130, J31 and BE200) around 21 °N, 94 °W over the Gulf of Mexico in 16:43 - 17:01 UTC on March 10, 2006. The optical depth between 270 m and 4300 m is given for each profile in the legend.
4 CCN, Size Distribution and Chemical Composition

A common method of deriving CCN concentration is to integrate dry particle number size distribution from a specified dry critical diameter, \(D_{dc}\). It is often a challenge to identify or parameterize this diameter because of its dependence on composition. The mass, molecular weight, degree of dissociation and effect on the surface tension need to be known of each component of a given particle of known size given supersaturation, in order to exactly solve Kohler equation for \(D_{dc}\). As in-situ aerosol mass spectrometry is just beginning to identify some of these required parameters, it is inconceivable that aerosol models or satellites be able to acquire them in a near future.

One step toward such parameterization is based on direct measurements of CCN concentration and particle hygroscopicity. These properties can constrain the critical diameter without the need for detailed information on the aerosol chemical properties [Petters and Kreidenweis, 2007]. \(D_{dc}\) was derived by applying these methods to the in-situ observations (section 4.1 and 4.2) and was evaluated against an independent measurement of bulk aerosol chemistry (section 4.3). These exercises reveal how dependent the water activity of aerosols is on the chemistry and to what degree bulk chemistry alone can constrain \(D_{dc}\), questions relevant to potential remote sensing of CCN.
4.1 Critical diameter estimated using the direct CCN measurement

Here $D_{dc}$ is estimated from the simultaneous measurements of the CCN concentration and the dry aerosol size distribution. To illustrate this approach, Figure 4.1 compares the CCN concentration and the OPC number integrated from 100 nm, both measured on the C130 aircraft over Mexico. The 30-second average of CCN concentration measured with the CCN chamber at 0.17 – 0.20% supersaturation is on the horizontal axis. The $D_{dc}$ is regarded to be 100 nm for the data points exactly on the 1:1 line where the number integral from 100 nm agrees with the CCN concentration. This is equivalent to assuming that the diameter cut is "sharp" such that all particles above it, and none below, are activated. Because the actual cut off is not perfectly sharp, the $D_{dc}$ derived in this manner should be considered as an approximation. The data points above the 1:1 line nominally indicate the cases where some particles larger than 100 nm were not activated as CCN (i.e., $D_{dc} > 100$ nm). Likewise, those below this line correspond to $D_{dc} < 100$ nm. (The marker color in Figure 4.1 will be discussed in section 4.3.) Similarly to the exercise above, the measured CCN number can be compared with the size distribution integrated from different diameters than 100 nm. In each comparison, the initial integral diameter is assigned as $D_{dc}$ for the data points on the 1:1 line.

After being determined this way for all valid data, $D_{dc}$ was adjusted to 0.20% supersaturation using the linear relationship, with a slope of $-3/2$, between the critical diameter and supersaturation both on logarithmic scales (see the derivation of this
relationship from Kohler theory in section 1.2). For example, the $D_{dc}$ estimated from a measurement at 0.17% supersaturation was decreased by 10%, reflecting the fact that the aerosols of identical chemical properties would activate at this smaller diameter if brought to 0.20% supersaturation.

Figure 4.2 exhibits the histogram of the $D_{dc}$ derived for Mexico. Because the DMA measurements up to 100 nm need to be combined with the OPC, the averaging time was extended to 60 seconds for this derivation in order to increase the number of samples available with both instruments. A lognormal fit to the distributions of $D_{dc}$ values exhibits the peak at 88 nm, with a standard deviation of 1.5. This means that most values fall between 60 and 128 nm, which corresponds to a ±40% difference in the integral number. This could imply that, if CCN concentrations are to be estimated by integrating aerosol number distributions from the dry critical diameter, the estimate will be no more accurate than ±40% unless $D_{dc}$ is independently constrained. However, this apparent variation in $D_{dc}$, though comparable with the variation in the previously observed values (section 4.3), is likely exaggerated by the measurement errors.

The uncertainty in $D_{dc}$ is expected to arise largely from the error in the supersaturation of the CCN chamber and that in the dry particle sizing. The CCN supersaturation is calibrated to an absolute error no better than 0.015 percentage points [Lance et al., 2006] (i.e., 0.185% and 0.215% could be recorded as 0.20%). This would lead to a relative error in critical diameter by ~5%, based on the -3/2 linear relationship mentioned above. The actual error in supersaturation is larger due to the complexity in deriving the inner temperature gradient of the CCN chamber.
If a 0.05 percentage point difference between the actual and nominal supersaturation is common as in the study by Ervens et al. [2007], the resulting relative error in \( D_{dc} \) is about 20%. The relative error in CCN proxy due to sizing error of OPC and DMA, on the other hand, is identified to be equivalent to about 25% (section 3.1). The resulting relative error in \( D_{dc} \) was estimated by adding/subtracting an excursion of 25% of the CCN number, and turned out to be mostly smaller than 20%. Because these errors due to the two instruments are independent of each other, the overall relative error in the derived \( D_{dc} \) can be identified as the square root of sum of the squares of them, which turned out to be \(-30\%\). This measurement error is not much less than the apparent variation in the derived \( D_{dc} \) \((-40\%)\), and therefore is difficult to separate to yield the natural variability in the critical diameter. More precise measurements are desirable for future experiments.

4.2 Critical diameter estimated using the hygroscopicity measurement

The critical diameter \( D_{dc} \) can be estimated from measurements made below saturation as well, because the particle hygroscopicity is generally in close relationship with the CCN activity of the particles above saturation. The hygroscopicity measurement does not require as strict humidity control as does the CCN measurement: While an absolute error of 1 percentage point near 0.2% supersaturation results in a 20 - 60\% relative error in \( D_{dc} \), a 1 percentage point error in the relative humidity near 84\% results in an 8\% relative error in \( D_{dc} \). Hence, the
hygroscopicity approach complements the more direct CCN measurements in estimating $D_{dc}$.

The hygroscopicity was measured with the tandem differential mobility analyzer (TDMA) on the C130 [Tomlinson et al., 2007]. As mentioned in section 2.2, particles in 50, 100, 200 or 300 nm were selected at the first DMA scan under a dry condition, were subsequently humidified to about 84% RH, and were sized. The humidified diameter divided by the dry diameter is termed growth factor, and is plotted over the vertical axis of Figure 4.3. The particle number fraction relative to the total selected particle concentration is indicated by color. (The horizontal axis will be discussed in sections 4.3 and 5.2.) The growth factor typically ranges from 1 (low hygroscopicity) to 3 (high). A TDMA scan can take more than one value of growth factor when an inhomogeneous mix of particles was sampled.

To derive $D_{dc}$ for each TDMA scan, an equation from Petters and Kreidenweis [2007]:

$$S(D) = \frac{D^3 - D_d^3}{D^3 - D_d^3(1 - \kappa)} \exp \left[ \frac{4\sigma M_w}{RT \rho_w D} \right]$$

was solved for $\kappa$, the hygroscopicity parameter. $D$ and $D_d$ are the humidified and dry diameters, respectively, $\sigma$ the surface tension at an air/water interface (0.072 Jm$^{-2}$), $M_w$ the molecular weight of pure water, $R$ the gas constant, $T$ the temperature (298K), and $\rho_w$ the density of water. The hygroscopicity parameter is linked to $D_{dc}$ by:

$$\kappa = \frac{4A^3}{27D_{dc}^3 \ln^2 S_c}$$

$$A = \frac{4\sigma M_w}{RT \rho_w}$$
where \( S_c \) is the saturation ratio (~0.84). Substituting numbers to these two equations, the relationship between \( \kappa \) and \( D_{dc} \) under 0.2% supersaturation is

\[
D_{dc} = \kappa^{(-1/3)} \times 70 \text{ nm}
\]

such that \( \kappa \) takes 1 and 0.1 for \( D_{dc} \) of 70 nm and 151 nm, respectively. The relative error in \( D_{dc} \) arises from the error in the TDMA relative humidity (the absolute error assumed to be 3 percentage points) and the random sizing error (a relative error of 5%), and is estimated to be ~25%.

Compared with the \( D_{dc} \) derived from the CCN measurements (section 4.1), the \( D_{dc} \) derived from the tandem DMA hygroscopicity measurements is generally larger and less variable. The median diameters are 114, 122, 118 and 111 nm for dry diameters of 50, 100, 200 and 300 nm, respectively (not shown). These diameters are all distinctively higher than the CCN-based median diameter of 88 nm for the identical region (Mexico). The difference translates into that of \( \kappa \) by about 0.2. A difference between the two derivation methods is seen among previous studies, but is typically smaller (\( \Delta \kappa = 0.1 \) or less). The assumption that the surface tension is constant at 0.072 Jm\(^{-2}\) regardless of chemical species may explain a part of the difference, but this hypothesis is to be verified. The histogram of the hygroscopicity-based \( D_{dc} \) is fitted to a lognormal distribution, and its width (sigma) is 1.2, 1.2, 1.2 and 1.1 for the 4 dry diameters, respectively (not shown). The smaller variability than the CCN-based \( D_{dc} \) may be a result of smaller measurement error.

The same analysis applied to the US west coast and the northeastern Pacific Ocean flown during IMPEX results in the median diameter of 114, 107, 91 and 96 nm and the sigma of 1.2, 1.2, 1.1 and 1.1 for the 4 dry diameters, respectively. The
particles in 200 and 300 nm show smaller critical diameters (higher hygroscopicity), possibly due to the influence of marine aerosols. The smaller diameters (91 and 96 nm) appear to be dominantly urban and forest fire pollution, probably with high organic content and therefore low hygroscopicity. The variation in $D_{dc}$ with bulk aerosol chemical properties is one target of our analysis, and is discussed in the subsequent section.

4.3 CCN activity and aerosol organic mass fraction

The in-situ observations over and near Mexico and the US west coast analyzed above confirmed that the dry critical diameter for CCN activation, $D_{dc}$, varies widely, though a considerable part of the variation is attributable to the measurement random errors. Constraining $D_{dc}$ would significantly improve estimation of CCN concentration. Kohler theory says that $D_{dc}$ depends on the aerosol chemistry given supersaturation. However, it is almost impossible to acquire detailed chemical properties as inputs to the Kohler equation (see the discussion at the beginning of this chapter). A more realistic prospect is that the chemical properties of the collection of aerosols in a given air mass, such as the organic/inorganic mass ratio of submicron volatile component, will be available from models in a near future. Satellites may also become capable of retrieving such information on bulk aerosol chemistry, albeit under limited conditions, as discussed in Chapter 5. With this outlook, it is useful to determine how and how well the organic mass fraction constrains $D_{dc}$. 
The organic fraction of volatile mass of submicron particles, denoted OMF, was derived from the AMS measurements of organic and ionic (sulfate, nitrate, ammonium and chloride) compounds. Because the coarse particles are not detected by this AMS, the OMF applies to the accumulation mode where the chemical properties are most relevant to CCN activation.

As indicated by the marker color of Figure 4.1, the CCN concentration tends to exceed the OPC integral under low OMF (high sulfate and nitrate) over Mexico for CCN concentration larger than ~500 cm\(^{-3}\). This observation suggests that organic particles were not as effectively activated as sulfate and nitrate particles near 100 nm. Similarly, the particle growth factor tends to be high under low OMF (the horizontal axis of Figure 4.3b) after the air masses with large concentrations of dust particles, also least hygroscopic, are separated by low (<1.3) Angstrom exponent (Figure 4.3a).

For the purpose of examining the CCN activity of particles, the derived critical diameter is a more direct and convenient point of reference than the number concentration and the growth factor. Squares in Figure 4.4 illustrate the relationship between \(D_{dc}\) and OMF observed with the TDMA, with the measurement errors indicated by grey vertical lines. Petters and Kreidenweis’s [2007] hygroscopicity parameter, \(\kappa\), is also represented in the left vertical axis to facilitate adjustment of \(D_{dc}\) to different supersaturations (see section 4.2 for the definition of \(\kappa\)).

In spite of the indicated error, the mean critical diameter increases, and \(\kappa\) decreases, as the OMF increases. This is consistent with the fact that the ionic compounds are generally more soluble than the organics. Circles in Figure 4.4 shows \(D_{dc}\) averaged on a logarithmic scale over each 0.2 OMF bin. The average \(D_{dc}\) is 111
nm over 0.2 – 0.4 OMF, and 133 nm over 0.6 – 0.8 OMF, for particles with a dry diameter of 100 nm sampled over Mexico. The difference in $D_{dc}$ is equivalent to 26% in the CCN concentration. Dusek et al. [2006] argue that size matters more than chemistry based on their observation around Europe of the CCN activities of 4 aerosol types, all with relatively high (0.58 – 0.82) organic mass fraction of particles up to 130 nm. The MIRAGE data presented here demonstrate that their argument does not hold for Mexico’s atmosphere where the OMF varies more widely. An approximation of the $\log_{10} \kappa$-OMF relationship is given by the linear regression through the bin average $\kappa$, depicted in Figure 4.4, and parameterized in Table 4.1.

As emphasized in Chapter 3, the measurement error associated with the number count is random and not biased by aerosol chemistry. The measurement errors in the CCN concentration and TDMA growth factor are likely random as well. The lack of systematic biases means that, while the accuracy of individual data certainly leaves room for improvement, the average $D_{dc}$ is neither overestimated nor underestimated substantially.

The variability of the critical diameter within each OMF bin is just as important as the average values. A part of the apparent variability is expected to arise from the natural variability. Hygroscopicity varies among ionic species and among organic species. State of mixing can also affect the overall hygroscopicity for an identical overall chemical mass mix. For example, a 50:50 external mixture of completely ionic and completely organic particles does not generally exhibit the same overall hygroscopicity as a collection of particles each internally mixed by 50:50. It is
useful to differentiate the measurement error to yield the natural variability which sets the maximum limit of accuracy if $D_{dc}$ is to be estimated from OMF in aerosol models.

The root mean square (RMS) of the $\log_{10}\kappa$ difference is mostly between 11% and 24% of a logarithmic decade (indicated in the right most column of Table 4.1). This corresponds to $D_{dc}$ differences by $8 - 20\%$ on the linear scale. This is similar, as expected, to the variability in $\kappa$ within each OMF bin represented by the vertical colored bars in Figure 4.4. This apparent variability is comparable with, or even smaller than, the $\sim 25\%$ relative measurement error identified in section 4.2, which could indicate that the natural variability is much smaller than $\sim 25\%$. It is promising that $D_{dc}$ for a collection of aerosols of unknown detailed chemical properties and state of mixing can be constrained to such a small range of values when the OMF is known.

However, caution is advised in evaluating the natural variability of the critical diameter. The particles at 50 and 100 nm dry diameters sampled over and off the US west coast flown during IMPEX saw larger apparent variability: the RMS of the $\log_{10}\kappa$ were 0.73 and 2.33, respectively. A close look at Figure 4.4b reveals that $D_{dc}$ varies most under high OMF. The small particles may contain a wider variety of organic compounds with a wider range of hygroscopicity than do the larger particles.

Also, the $D_{dc}$ derived from the CCN chamber measurement is more variable, as shown in Figure 4.5, than that based on the TDMA measurement. The derived $D_{dc}$ is particularly small when the CCN concentration exceeds 1000 cm$^{-3}$ over Mexico (Figure 4.5a). This happened when the OMF took moderate values between 0.4 and 0.6, not the low values for which $D_{dc}$ is expected to be small. The observed $D_{dc}$ is in fact higher for smaller OMF values. As the vertical black bars indicate, the apparent
variability of $D_{dc}$ approaches half a logarithmic decade, significantly larger than that for the TDMA-based measurements (Figure 4.4). The large apparent variability is probably due to the large measurement errors associated with the CCN concentration, particularly when it is less than $\sim 500 \text{ cm}^{-3}$. If so, these data do not positively reject the hypothesis that $D_{dc}$ and OMF are related in the ambient atmosphere. The difference in the results from these two methods makes the conclusion here somewhat unreliable. More measurements with higher instrument precision are needed to determine the natural variability of the CCN activity.

Experiments by dozens of research groups identified CCN activities for aerosols of various chemical species. From these studies, Petters and Kreidenweis [2007] derived the hygroscopicity parameter for ionic compounds (ammonium sulfate, ammonium nitrate, sodium chloride, sulfuric acid, sodium nitrate, sodium bisulfate, sodium sulfate and triammonium hydrogen disulphate) and organic compounds (malonic acid, glutaric acid, glutamic acid, succinic acid, adipic acid, levoglucoesan, phthalic acid, homophthalic acid, leucine, pinic acid, pinonic acid, norpinic acid, polyacrylic acid, Suwanee River fulvic acid, $\alpha$-pinene/O3/dark secondary organic aerosol, $\beta$-pinene/O3/dark secondary organic aerosol, oxidized diethylhexyl sebacate). These data are represented by black dots in Figure 4.4a and b (same data). The general range of values of $\kappa$ derived from the MIRAGE and IMPEX overlap them. If anything, the ionic compounds were observed to be less hygroscopic than previously found. However, the compounds studied previously do not necessarily represent the aerosols observed during the aircraft experiments analyzed in the present study. The archived data should be treated as no more than a crude reference. The previous data
for an almost identical set of chemical species obtained by means of CCN-based approach, also archived by Petters and Kreidenweis [2007], are shown with black dots on the vertical axes (i.e., OMF = 0 and 1) in Figure 4.5. The large variability of the MIRAGE and IMPEX data inhibits any useful comparison.

One might suspect that the insoluble aerosol component affects the CCN activity. For particles with an insoluble refractory core (e.g., soot) coated by volatile soluble material, the OMF of the volatile component is relevant to the solubility near the air/particle interface, whereas the fraction of the refractory volume may be more relevant to the solubility of entire particles. Figure 4.6 shows the CCN number comparison similar to Figure 4.1 but color-coded with the refractory volume ratio of submicron aerosols. The refractory aerosol volume refers to the volume integral of size distribution of particles heated to 300 °C, and is used as an indicator of the insoluble component. Its ratio to the volume of unheated particles does not show a clear trend (no segregation by color) with the CCN/OPC number ratio. Thus, unlike the OMF, the inclusion of insoluble core does not appear to affect the particle water activity significantly.
Table 4.1  Linear fit to the aerosol hygroscopicity / chemistry relationships

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<th>$\kappa$ at OMF =1</th>
<th>RMS</th>
</tr>
</thead>
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<td>MIRAGE</td>
<td></td>
<td></td>
<td></td>
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<tr>
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</tr>
<tr>
<td>200</td>
<td>0.39</td>
<td>0.15</td>
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<tr>
<td>300</td>
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<td>0.11</td>
</tr>
<tr>
<td>IMPEX</td>
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<td></td>
</tr>
<tr>
<td>50</td>
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</tr>
<tr>
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<td>0.08</td>
<td>2.33</td>
</tr>
<tr>
<td>200</td>
<td>0.49</td>
<td>0.19</td>
<td>0.16</td>
</tr>
<tr>
<td>300</td>
<td>0.49</td>
<td>0.23</td>
<td>0.14</td>
</tr>
</tbody>
</table>

$D_d$ is the dry diameters selected in TDMA, OMF is the organic mass fraction of volatile component of submicron aerosols, $\kappa$ is the hygroscopicity parameter. RMS is the root mean square of the differences in $\log_{10}\kappa$ between the fit and the individual data.
Figure 4.1  Comparison of the OPC number integral and the CCN concentration measured during MIRAGE and averaged over 30 seconds. The OPC number is the integral of size distribution between 100 nm and 20 μm. The CCN concentration shown here was measured under supersaturation of 0.17 - 0.20%. The AMS organic fraction of submicron volatile aerosol mass is indicated by marker color where the data is available.
The frequency of the dry critical diameter derived from the data shown in Figure 4.1 for an supersaturation of 0.20%. The lognormal fit represented with the dashed curve peaks at 88 nm and takes a geometric standard deviation of 1.5.
Figure 4.3  Growth factor measured with the tandem differential mobility analyzer aboard the C130 aircraft during MIRAGE for the particles with a dry diameter of 100 nm, plotted against the extinction Angstrom exponent (a) and the AMS organic mass fraction (b). The higher relative humidity was set to about 84%. The red and blue colors indicate relatively high and low number fractions, respectively, of the selected dry particles that exhibited the particle hygroscopicity. The marker size is set proportional to the dry extinction coefficient at 530 nm.
Figure 4.4 Comparison of the hygroscopicity parameter, $\kappa$, derived from the tandem DMA measurements and the AMS organic mass fraction for MIRAGE (a) and IMPEX (b). The size of square markers is made proportional to the OPC number integral (CCN proxy). The color represents the dry particle diameter, as indicated by the legend. The grey vertical lines indicate estimated measurement error. The dots represent the geometric mean and standard deviation within 0.2 organic mass fraction bins.
Figure 4.5 Comparison of the hygroscopicity parameter, $\kappa$, derived from the CCN chamber measurements and the AMS organic mass fraction for MIRAGE (a) and IMPEX (b). The size of square markers is made proportional to the CCN concentration. The grey vertical lines indicate estimated measurement error. The dots represent the geometric mean and standard deviation within 0.2 organic mass fraction bins.
Figure 4.6  Same as Figure 4.1 except that the submicron refractory volume ratio derived from the OPC size distributions is indicated by marker color where the data is available.
5 Chemical Composition, Hygroscopicity and Optical Properties

5.1 Chemical Composition and Optical Properties

The minimum dry diameter required for particles to become CCN at a given supersaturation, \( D_{dc} \), is determined by chemical properties of the aerosol components (section 1.2). Consistent with Kohler theory, \( D_{dc} \) derived from the in-situ TDMA measurements during MIRAGE and IMPEX aircraft experiments tended to increase with the organic fraction of volatile mass of submicron particles (OMF), as described in section 4.3. This relationship, once better constrained with more precise measurements of CCN concentration or particle hygroscopicity, could potentially facilitate model calculations of CCN concentration from pre-determined bulk aerosol chemical properties.

Inference of OMF from satellite observations would be useful, but requires links between aerosol optical and chemical properties. Such links do not generally exist. For example, both ionic and volatile organic compounds usually reside in the accumulation mode and take similar values of refractive index, resulting in similar light scattering efficiency and wavelength dependence between them. The aircraft data were explored to seek useful links under specific conditions where the aerosol optical properties resolve the chemical properties particularly well.
5.1.1 Extinction wavelength dependence

Numerous satellites are capable of retrieving the Angstrom exponent of extinction (see section 1.5 for the definition and typical values) on column integral basis. The recently-launched Cloud-Aerosol Lidar and Infrared Pathfinder Satellite Observation (CALIPSO) satellite is able to resolve this parameter, representing the wavelength dependence of extinction, for the altitudes. If related to the Angstrom exponent, aerosol chemical properties such as the OMF can be estimated from satellites.

The Angstrom exponent of extinction due to dry particles shows a linear relationship with the OMF (Figure 5.1a). The outliers, circled in the figure, were identified not only by the optical properties (the extinction Angstrom exponent and the single scattering albedo, SSA) but also by air mass location and relative humidity (not shown). The most prominent outlier is the dust, characterized by the extinction Angstrom exponent smaller than 1.3 and SSA greater than 0.98. The extinction Angstrom exponent is anti-correlated with the coarse/submicron volume ratio, as expected for its large dependence on particle size. The coarse/submicron volume was derived from the OPC size distribution with the coarse/submicron size threshold at 750 nm, assuming that the particles were spheres. The volume ratio (not shown) generally exceeds 20 for the Angstrom exponent less than 1.3.

The marine aerosols sampled over Gulf of Mexico over 0 - 2 km above sea level also had low extinction Angstrom exponent, indicative of coarse sea salt particles. The oceanic sulfate kept the organic fraction of submicron marine aerosols
low. The air masses sampled near and over the Yucatan peninsula to the east of 94°W, on the other hand, had high Angstrom exponent and generally high OMF, as expected for the biomass burning plumes observed there. Satellite algorithms are expected to be able to identify these outliers by the geographical location and the wavelength dependence, as well as ancillary model or satellite information of surface wind speed, humidity, existence of elevated plumes and other environmental parameters.

After excluding these air mass types, our Mexico pollution data shows a tight anti-correlation with the extinction Angstrom exponent. A fit to the median values in OMF bins with a width of 0.1 is

\[ \text{OMF} = -1.43 \times \text{Angstrom exponent} + 2.86 \]

If this linear regression is extrapolated, the Angstrom exponent takes 2.0 for completely ionic aerosols with an OMF of 0, and 1.3 for completely organic aerosols with an OMF of 1. For known Angstrom exponent the fit predicts the organic mass fraction to an absolute error of 0.3 (the root mean square of the difference between the observed data and the estimated values). As a minor note, although the Angstrom exponent retrieved for ambient atmosphere can be different from that under dry conditions, the difference is predicted to be subtle. Unless the RH is higher than 95%, water uptake upon humidity change does not affect the wavelength dependence significantly, because the scattering coefficients at all wavelengths change by similar ratios. More specifically, the absolute error is 0.2 or even smaller, unless both the humidity response and the dry Angstrom exponent exceed ~2, according to our simulation of diameter growth factor using the size distributions over North America.
It is hypothesized that the anti-correlation between the organic mass fraction and the extinction Angstrom exponent is explained by the chemical interaction where cations such as calcium contained in dust efficiently fix nitrate and sulfate present in the aerosol mix. These anions are supplied in abundance to the submicron particles over Mexico [DeCarlo et al., 2008]. Previous studies in Asia [Zhang et al., 2000; Kline et al., 2004] found that coarse dust particles take up nitrate according to the alkalinity, and sulfate according to the aerosol surface area. The observation over Mexico presented here is consistent with such chemical interactions. The resulting decrease in the anion supply to the submicron particles will enhance relative mass of organic compounds (OMF). This chemical interaction can occur in the presence of any, not necessarily predominant, dust surface area relative to the ionic compounds. Moderate dust surface area can exist even when the extinction Angstrom exponent is greater than 1.3 (the coarse/submicron volume ratio greater than 20), though such cases are not labeled specifically as dust in Figure 5.1.

To verify the hypothesis above, dust and pollution air masses both before and after mixing should be examined. Unfortunately, the aircraft did not encounter a situation where such an elaborate observation was possible.

However, two air masses adjacent to each other with distinctively different dust concentrations were observed over Mexico City, and provide evidence that is consistent with the hypothesis. During the horizontal leg between 21:45 – 22:00 UTC on March 10, 2006 (Figure 5.2) dust decreased, as indicated by the increase in the
Angstrom exponent plotted over the horizontal axis. Compared to the dusty air mass sampled first, the second one had 3 – 4 times as much nitrate in the accumulation mode but almost the same amounts of organic compounds and sulfate, thereby reducing the OMF from 0.85 to below 0.70. This observation can be explained by the nitrate uptake by dust described above. However, it is unknown why sulfate was less responsive to dust than was nitrate in this individual case. This feature is not evident persistently throughout the experiment. The individual case examined above observation may simply reflect the presence of enhanced nitrate in pollution particles relative to dust air masses, whether or not the two air masses mixed with each other. In any event, I am not aware of any reasonable explanation, other than the anion uptake by dust, for the OMF-Angstrom relationship observed repeatedly over Mexico.

One might speculate that the anti-correlation between OMF and extinction Angstrom exponent is explained by different sizes between the organic and ionic species within the submicron size range and that the coarse mode is irrelevant. Comparison of scattering Angstrom exponent for the submicron particles negates these speculations. This parameter is calculated from the OPC size distribution for optical effective diameters between 100 and 750 nm. The upper size, 750 nm, is considered to correspond to about 1 μm aerodynamic diameter, the conventional cut-off size for submicron particles. The calculated submicron Angstrom exponent takes a narrow range of values, mostly between 2.3 and 2.5, as represented by squares in Figure 5.3. The black line is the fit for the wavelength dependence observed with the nephelometer, copied from Figure 5.1 as a reference. The variation in the calculated submicron Angstrom exponent and, therefore, the size differences within the
accumulation mode do not explain the observed variation in the Angstrom exponent for total particles. By contrast, the Angstrom exponent calculated for the total size range (circles in Figure 5.3) matches the nephelometer-based Angstrom exponent within 0.2. With dust (Angstrom < 1.3) excluded, the OPC-derived Angstrom exponent varies almost as widely as the nephelometer-based values. These features are consistent with what we found during the data validation (section 3.2, Figure 3.7).

If the accumulation mode does not account for the observed relationship between the total Angstrom exponent and OMP, the coarse mode has to. This is implied by the difference in the calculated Angstrom exponent between the submicron and total (squares and circles, respectively in Figure 5.3) size ranges, which increases with the OMP. The coexistence of high coarse aerosol loading and high OMP is also confirmed by the OPC size distribution averaged for different OMP values (0.2 – 0.4, 0.4 – 0.6, 0.6 – 0.8) shown in Figure 5.4. To yield the distributions presented in this figure, size distribution of extinction was computed with Mie theory with a constant refractive index of 1.59, was divided (normalized) by the simultaneously measured nephelometer total scattering coefficient and was averaged. Enhanced particle loading above 5 μm is most pronounced in the highest OMP bin. This is indicative of dust, the only coarse particles observed during MIRAGE away from the Gulf of Mexico.

There is little reason to believe that the apparent connection between the OMF and dust arises at the emission of the particles. Organic compounds of atmospheric particles are generated at a wide variety of strong sources including industry, transport, households, agriculture, forest fire and sea surface. It is difficult to imagine
that deserts are comparably strong a source of organic compounds. The observed coexistence of high OMF and high dust loading must occur during transport, if not at the sources of the organic, inorganic and dust particles. I believe the dust uptake of nitrate and sulfate mentioned above is the most likely explanation for the anticorrelation between OMF and extinction Angstrom exponent.

The abundant anions and dust are likely the prerequisite for the observed chemical effect over Mexico. Air masses elsewhere with these constituents may exhibit similar effects, but the precise relationship between OMF and Angstrom exponent may vary with their relative mass to other aerosol components.

Dust is usually inactive and unimportant as CCN due to its weakly hydrophilic nature and relatively low number concentration. The observation and discussion above imply that dust particles can also impede CCN activation of other particles by removing highly soluble aerosol component (nitrate and sulfate) from the size range with most CCN (fine and accumulation modes). For example, if dust raises the OMF from 0.3 to 0.7, the dry critical diameter at 0.2% supersaturation is estimated to increase from 111 nm to 133 nm, based on the hygroscopicity of 100-nm dry particles measured over Mexico (section 4.2, Figure 4.4a). This corresponds to a ~20% decrease in the CCN concentration derived from the OPC size distribution. Thus dust can impose significant influence on the aerosol indirect effect on clouds not only due to their own physicochemical properties but also through chemical action.
5.1.2 Absorption wavelength dependence

One more link was found between the aerosol chemical and optical properties. The wavelength dependence of absorption reveals enhanced shortwave absorption for dust and some organic components relative to soot due to the variations in refractive index over wavelength and size. The absorption wavelength dependence is not retrieved from current satellites, but has been relatively easily and quickly observed on ground and in aircraft with such instruments as PSAP [Bergstrom et al., 2002; Kirchstetter et al., 2004; Clarke et al., 2007]. The relationship presented below between the wavelength dependence of absorption represented by Angstrom exponent, single scattering albedo (the scattering divided by the extinction) and OMF over Mexico may provide a tool to estimate the aerosol chemical composition from optical measurements when chemical instruments are not available. More importantly, knowledge of the variation in the absorption with the aerosol chemical species refines the model calculation of aerosol direct and semi-direct effects.

Figure 5.5 illustrates the relationship among the absorption Angstrom exponent derived from the 3-wavelength PSAP absorption measurement (plotted over the horizontal axis), single scattering albedo at 530 nm (SSA, indicated by the marker color) and OMF (vertical axis) over Mexico. When the SSA is lower than 0.92, the absorption wavelength dependence mostly takes values between 1.3 and 1.7, characteristic of low dust conditions. The wavelength dependence of absorption generally decreases with decreasing OMF, and can be extrapolated to the absorption Angstrom exponent of 1.1 at an OMF of 0. This is consistent with the fact that black
carbon absorbs all wavelengths, taking an absorption Angstrom exponent near 1.0 [Bergstrom et al., 2002; Kirchstetter et al., 2004] unless accompanied by some organic compounds such as humic like substances (HULIS) and dust which raise both the wavelength dependence and the OMF. As SSA increases, the absorption Angstrom exponent increases, particularly under high OMF. This can be a result of the soot becoming a less dominant absorber relative to the organic compounds, dust or both. The Angstrom exponent extrapolated to zero OMF takes 1.0 – 1.1, near the black carbon value, at the higher SSA too, as expected for black carbon.

The aerosols characterized by high SSA generally exhibits the largest (3 or larger) wavelength dependence. The browning effects between dust and organic compounds cannot easily be separated because these two aerosol components coexist (discussed in section 5.1.1). Also, because high SSA is generally associated with low absorption coefficient, the filter-based measurement of absorption suffers large relative errors for this class of aerosols.

Nonetheless, the relationship described here helps identify the aerosol types when the absorption wavelength dependence is available on suborbital platforms and, perhaps, on satellites in the future. Owing to the complex mix of various components (i.e., industry/urban pollution, biomass burning, and dust), Mexico will serve as a test domain for absorption-based satellite algorithms.
5.2 Hygroscopicity and Optical Properties

The CCN activity may be extrapolated from the humidity response of aerosol size below saturation, as discussed in section 4.2. Consequently, remote sensing of aerosol hygroscopicity would be of value in refining remote sensing of CCN. Unfortunately, only a weak relationship was evident between the TDMA hygroscopicity and the extinction Angstrom exponent (Figure 4.3a, mentioned in section 4.2). For the air masses with high dust loading indicated by the extinction Angstrom exponent smaller than 1.3, the growth factor is near 1, as expected for its hydrophobic nature. For the pollution particles, the growth factor shows a weak trend with the extinction Angstrom exponent. To look into this hygroscopicity variation within the pollution samples, the hygroscopicity measured under Angstrom exponent greater than 1.3 was plotted against the simultaneously measured organic mass fraction (Figure 4.3b). Though weak, the anti-correlation is consistent with the hygroscopic nature of ionic compounds relative to the organic.
Figure 5.1 The relationship between the organic mass fraction (OMF) and the nephelometer extinction Angstrom exponent observed during MIRAGE over and near Mexico and averaged over 60 seconds. Marker size is proportional to the dry extinction coefficient (Mm⁻¹) at 530 nm. The linear regression (black line) is made for the means values (black circles) over 0.1 OMF bins for the Mexico pollution data excluding the other types of air mass (red circles).
Figure 5.2  Chemical mass observed with the AMS during 21:45 - 22:00 UTC on March 10, 2006 over Mexico City. The progress of time corresponds approximately to the shift from the small to the large values of the extinction Angstrom exponent plotted over the horizontal axis. The green, red and blue dots are for organic compounds (µg/m³), sulfate (10 µg/m³) and nitrate (10 µg/m³). The circles represent the organic mass fraction (%).
Figure 5.3 The Angstrom exponent of dry scattering coefficient calculated from the 30-second average OPC size distribution, for the total size range up to 20 μm (pink circles) and the submicron size range up to 750 nm (light blue squares), compared with the concurrent measurement of the AMS organic mass fraction (OMF). The air masses with biomass burning particles, marine aerosols and substantial dust concentration are excluded. Marker size is proportional to the dry extinction coefficient (Mm⁻¹) at 530 nm. The horizontal bars indicate the mean and one standard deviation over 0.1 OMF bins for these two calculated values (red and blue, respectively) as well as those for the nephelometer total extinction Angstrom exponent (black, the same as Figure 5.1).
Figure 5.4  The normalized extinction size distribution averaged for the three classes of organic mass fraction (OMF) indicated in the legend. The solid and dashed curves are for the unheated and heated (to 300 °C) particles, respectively, such that the difference between them represents the contribution by volatile aerosol component.
Figure 5.5   The Angstrom exponent of absorption measured during MIRAGE, plotted with the AMS organic mass fraction (vertical axis) and the single scattering albedo (SSA, color). Marker size is proportional to the dry extinction coefficient (Mm$^{-1}$) at 530 nm. The yellow, red, purple, blue and cyan lines represent the data for the SSA bins of 0.90 - 0.92, 0.92 - 0.94, 0.94 - 0.96, 0.96 - 0.98 and 0.98 - 1.00, respectively. The linear regression to the absorption Angstrom exponent averaged over each 0.1 OMF bin (squares) are 0.9 * OMF + 1.1, 1.1 * OMF + 1.1, 1.4 * OMF + 1.1, 2.3 * OMF + 1.0 and 7.7 * OMF + 0.9, respectively, with the root mean square of the difference between the observation and the fit being 0.4, 0.3, 0.9 and 4.3, respectively.
6 Size Distribution and Optical Parameters

The cloud-nucleating ability of particles has been examined with regard to their chemical properties. It has also been shown that some piece of information on bulk aerosol chemistry over Mexico can be inferred through optical measurements. This chapter discusses whether the other key determinant of the concentration of CCN – aerosol size distribution – can be estimated optically.

Remote sensing of size distribution serves many scientific (e.g., study of aerosol evolution) and social (e.g., monitoring for public health) interests. Retrievals of the size distribution and integral number have been extensively studied [Higurashi and Nakajima, 1999; Dubovik and King, 2000b]. However, retrieving the concentration of CCN is particularly challenging because not all particles are optically active, as mentioned in the introduction (section 1.5). Fortunately, the study of CCN requires not a complete size distribution but the number of particles larger than the dry critical diameter, \(D_{dc}\). The exact sizes of soluble particles above this diameter matter little, because virtually all of them are activated.

This chapter discusses how well the number of dry particles 100 nm or larger, \(N_{\text{OPC}, \geq 100\text{nm}}\), can be constrained with the aerosol optical parameters that can be remotely sensed. It will be shown that \(N_{\text{OPC}, \geq 100\text{nm}}\) is related to the ambient extinction coefficient, its wavelength dependence and the single scattering albedo when certain conditions are met. Similar analyses on the column integral basis are presented as well.
In order to focus on the microphysical assessment, \( N_{\text{OPC, } \geq 100\text{nm}} \) is considered a CCN proxy here, regardless of the aerosol chemical composition. Approximating the collective \( D_d \) to be 100 nm is justified by the C130 observations: on average, the CCN concentration at 0.2% supersaturation and the number integral from diameters near 100 nm (90 – 122 nm to be more precise) compare favorably, as demonstrated in Chapter 4.

6.1 Local Relations of CCN proxy Concentration and Extinction Spectra

The primary method employed in this analysis is the comparison between the concentration of CCN proxy and the extinction coefficient, both measured from aircraft. The relationships between these two properties can help remote sensing of the CCN concentration, because satellites can directly observe optical properties but not the CCN concentration. Nakajima et al. [2001] suggest that the number to extinction ratio can be constrained with the wavelength dependence of extinction. In this section this idea is tested with the aircraft data.

Satellites currently report not the extinction coefficient but its vertical integral, the aerosol optical depth (AOD). As mentioned in section 5.1.1, CALIPSO was recently launched with a lidar instrument on it designed to retrieve the back scattering as a function of altitude. It is assumed that this or subsequent lidar satellites will resolve the AOD into different altitudes with sufficiently high accuracy for our purpose here, though this assumption is to be validated. As far as this assumption is
correct, the local air masses, to which the aircraft data are registered, are the more
natural choice of domain for our analyses than the vertical columns. (Nonetheless, the
aircraft data integrated over the column will also be discussed in section 6.4.) In
addition to the vertical resolution, particle growth due to humidity changes influences
the satellite and aircraft measurements [Shinozuka et al., 2007] (Appendix A). The
humidity effect will be addressed in section 6.3.

Figure 6.1a compares the extinction coefficient and the CCN proxy
volume, both averaged over 30 seconds, observed during the first half of
INTEX-B over Mexico and the Gulf of Mexico. The geometric standard deviation, $\sigma_g$,
of the CCN proxy-to-extinction ratio (slope of the relation) is 1.9. This means that
most data exist between -47% and +88% (represented with the thin dashed lines) of
the geometric mean value ($17 \text{ cm}^{-3}/\text{Mm}^{-1}$, represented with the thin solid line).
Similarly, the number-to-extinction ratio observed during MIRAGE over and near
Mexico (Figure 6.1b), during IMPEX over and off the US west coast (Figure 6.1c)
and during INTEX-A over the mainland US (Figure 6.1d) have geometric mean of 23,
17 and 28 cm$^{-3}$/Mm$^{-1}$, respectively, and geometric standard deviation of 1.8, 2.0 and
2.1, respectively.

The geometric mean and standard deviation, instead of the arithmetic, are
used throughout this chapter in order to consider cloud susceptibility. The inverse
relationship between the CCN concentration and the susceptibility (section 1.1)
means that cloud reflectivity is equally uncertain between CCN estimates of $100 \pm 90$
$\text{cm}^{-3}$ and $1000 \pm 900 \text{ cm}^{-3}$. In other words, not the absolute variability in $CCN_{pr}$ in cm$^{-3}$/Mm$^{-1}$ but the relative variability expressed as a percentage of the center value.
reflects the potential ability of satellites to estimate the indirect effect on clouds, hence the use of logarithmic scales.

The variability represented by these $\sigma_g$ values is generally larger than the instrument relative error (~25% in number, 10 – 21% in dry extinction), and, therefore, mostly reflects the natural variability in the number-extinction relationship. If satellite retrievals were to rely only on the extinction coefficient at 530 nm, the CCN cannot be constrained better than this natural variability. It does not help that the CCN proxy is least constrained at particle concentrations below 500 cm$^{-3}$ where cloud properties such as reflectivity are most sensitive to CCN changes (i.e., high susceptibility). These relationships between the particle concentration and the extinction coefficient need to be better constrained for accurate remote sensing of CCN.

The Angstrom exponent of extinction separates the relationships into different slopes. Blue markers of Figure 6.1a represent the samples with large particles such as dust. They scatter light efficiently per particle number (hence their positions relatively close to the bottom right corner of the graph), regardless of wavelength (hence the small Angstrom exponent, indicated by the color). Conversely, the scattering efficiency of smaller particles is much less (data points closer to the top left corner) and more sensitive to wavelength (large Angstrom exponent indicated by the reddish marker color). Thus, the INTEX-B data (Figure 6.1a), as well as the MIRAGE and IMPEX data (Figure 6.1b and c, respectively), provide empirical evidence that the wavelength dependence of extinction, for its sensitivity to the aerosol size, can
constrain the CCN concentration given the extinction coefficient. The INTEX-A data (Figure 6.1d) is an exception, and this will be discussed later.

To quantitatively assess the effectiveness of extinction Angstrom exponent as a constraint, it is plotted against the CCN-proxy-to-extinction ratio \((\text{cm}^3/\text{Mm}^{-1})\), \(CCN_{pr}\) in Figure 6.2. The symbol size is made proportional to the dry extinction coefficient such that remote sensing of the air masses marked with small symbols would represent low aerosol burdens and small contributions to AOD. The extinction Angstrom exponent \((A, \text{horizontal axis})\) generally increases with \(CCN_{pr}\) (vertical axis), and is approximated as:

\[
\log_{10} CCN_{pr} (\text{cm}^3/\text{Mm}^{-1}) = 0.3 \times A + 0.9
\]

for the INTEX-B Mexico data for \(A = 1.0 - 1.8\) (Figure 6.2a). This regression was made over the geometric mean \(CCN_{pr}\) for the 0.2-wide Angstrom exponent bins with at least 100 data points. Cases with an extinction coefficient smaller than 1 \(\text{Mm}^{-1}\) were excluded to reduce noise. For example, the square at an Angstrom exponent of 1.5 in Figure 6.2a indicates that the geometric mean \(CCN_{pr}\) for the INTEX-B data with the Angstrom exponent between 1.4 and 1.6 is 21 \(\text{cm}^3/\text{Mm}^{-1}\). The associated vertical bar spans one geometric standard deviation, 16 – 28 \(\text{cm}^3/\text{Mm}^{-1}\). These statistics correspond to the center value and boundary shown in Figure 6.1a with thick lines.

The geometric standard deviation of \(CCN_{pr}\) within each bin is visualized by the vertical bars. Any reduction in the variance implies a more robust potential retrieval of CCN for a given extinction Angstrom exponent. The vertical bars encompass factors of 1.3 – 1.4 of the geometric mean \(CCN_{pr}\) for the typical pollution
particles with the Angstrom exponent between 1.3 and 2.0, an improvement from the factor of 1.9 projected without the use of Angstrom exponent.

Note that these variances include the random relative errors of our aircraft measurements. They were estimated to be 25 - 26% for the CCN proxy (section 3.1) and 5 - 21% for the dry scattering, the dominant part of the dry extinction (section 3.3). These independent measurement uncertainties determine the combined relative error in $CCN_{pr}$ to be 26 - 33%. This needs to be differentiated from the apparent variability of $CCN_{pr}$ to yield the natural variability. The natural variability alone, the square root of the difference of the squares of the apparent variability and the measurement error, turns out to be between 20 – 30%.

For example, if a satellite reports the extinction coefficient and the extinction Angstrom exponent to be 20 Mm$^{-1}$ and 1.5, respectively, for a dry air mass, the center value of $CCN_{pr}$ is 22. This is evident if one substitutes $A$ with 1.5 in the equation above. The geometric standard deviation is 1.17 at $A = 1.5$, which means one standard deviation of $CCN_{pr}$ lie between -15% and +17% of the center value, i.e., 19 - 26 cm$^3$/Mm$^{-1}$. The CCN proxy concentration is given as the derived $CCN_{pr}$ times 20 Mm$^{-1}$, and is estimated to be 440 cm$^3$ with one standard deviation spanning between 380 and 520 cm$^3$.

The variability derived above from the 30-second average data should be considered as the data smoothed over a flight path of ~4 km long, because the ground speed of aircraft was usually near 130 m/s. The variability estimate is not applicable as it is to satellite data which are smoothed over a volume, not a line. For example, the variability among aerosol properties smoothed over columns above 4 x 4 km$^2$.
satellite grids generally appears smaller than that over 4-km-long lines. Thus, the variation in spatial variability with spatial scale needs to be known in order to determine the potential accuracy of CCN retrieval. I leave this issue as a task for separate studies.

During MIRAGE the C130 aircraft covered generally the same region as the DC8 did during the first half of INTEX-B, but it spent more time near Mexico City (less over the Gulf of Mexico). Both aircraft observed a similar number-extinction relationship. The data obtained during the 12 MIRAGE flights (Figure 6.2b) appear over a similar area of the graph as those for the 7 DC8 flights (Figure 6.2a). A similar regression line for $CCN_{pr}$ against the dry extinction Angstrom exponent

$$\log_{10}CCN_{pr} \text{ (cm}^3/\text{Mm}^{-1}) = 0.3 \times A + 1.0 \text{ for } A = -0.4 - 2.2$$

is obtained even for the mix of Asian pollution, North American biomass burning particles, US urban pollution and marine aerosols sampled during IMPEX over and off the US west coast (Figure 6.2c). To highlight the similarity, the fit line for IMPEX is superimposed on the other panels.

Importantly, the vertical bars become long as the Angstrom exponent decreases in the IMPEX data (Figure 6.2c). For aerosol distributions associated with Angstrom exponent values near 0, large fractions of extinction are contributed by coarse particles (dust and sea salt). These particles and the majority of CCN proxy (the particles near 100 nm) arise from different sources (wind-induced physical processes at deserts and ocean surface vs. fuel combustion). As a result, the aerosol concentrations in these two separate size ranges are only weakly related with each other. Therefore, the light extinction is poorly related to the particle concentration.
The weak linkage between extinction coefficient and CCN proxy leads to anti-correlation between the extinction and the $CCN_{pr}$. Larger markers indicative of large extinction coefficient consistently appear close to the bottom of the graph (small $CCN_{pr}$) only for small $A$.

The number concentration of CCN proxy can be constrained to a relatively narrow range in presence of coarse particles, though the extinction coefficient is insensitive to it. This is because with the presence of coarse particles offering the sites for coagulation, the number concentration over Mexico rarely exceeds $200 \text{ cm}^{-3}$. When the extinction Angstrom exponent is lower than 0.5, the CCN proxy concentrations are lower than $200 \text{ cm}^{-3}$ for 90% the INTEX-B Mexico dust samples and 96% of the IMPEX dust and sea-salt samples. However, this is not good news. As discussed earlier, the relative error in CCN concentration is more important than the absolute error for the study of the aerosol indirect effect on clouds, because the cloud susceptibility is inversely proportional to the CCN number concentration. The relative variance in $CCN_{pr}$, indicated by the vertical bars in Figure 6.2, is larger near the Angstrom exponent of 0 than it is near the Angstrom exponent of 1.5, the typical value for the Mexican pollution.

The INTEX-B (Figure 6.2a) and MIRAGE (Figure 6.2b) data exhibit less variability in $CCN_{pr}$ for the small Angstrom exponent. Because of the ubiquitous presence of submicron pollution particles, the wavelength dependence of extinction can be low only with relatively large scattering by coarse particles. Implications of this feature are two-folds. First, $CCN_{pr}$ are mostly lower and less variable than for IMPEX. The relatively small variation in $CCN_{pr}$ for a given Angstrom exponent
facilitates the potential remote sensing of CCN over Mexico. Second, samples with low Angstrom exponent are harder to find over Mexico than over the ocean within the IMPEX domain. The relatively small sample number with low Angstrom exponent seems to exaggerate the variability in $CCN_{pr}$ (not shown) derived from our aircraft measurements.

The INTEX-A data show a different picture. The average $CCN_{pr}$ is more variable than the other experiments (Figure 6.2d). Recognized instrument issues, such as random contamination by particles generated upon OPC heater switching observed during INTEX-A, might give rise to an insensitivity of extinction to the number. To check this possibility, the same plot was generated using the CN counter and DMA measurements instead of the OPC (Figure 6.3). Unlike the OPC, the DMA used our traditional heating system which is proven free of valve switch contamination. Here the difference between the CN count and DMA integral number up to 100 nm is used as a CCN proxy. Cases with relatively abundant (exceeding 1.5 times the >10-nm CN count) ultrafine (>3 nm) particles were removed in order to reduce the error due to the difference in the lower detection size limit between the CN and the DMA. The resulting $CCN_{pr}$ is free of possible OPC instrument problems, but spans over a similar range of values to the OPC based data, albeit with the smaller sample number.

These consistent results from both approaches imply that the larger range of $CCN_{pr}$ values for INTEX-A evident in Figure 6.2d is attributable to the properties of the aerosols. It is hypothesized that the pollution particles over the mainland US are enhanced in fine particle sizes, as indicated by the high Angstrom exponent, that their CCN proxy concentration can fluctuate without significantly affecting the extinction.
A picture consistent with this hypothesis is depicted in Figure 6.4a (and in Figure 6.4b in logarithmic scales to reveal the details) where the black markers represent the subset of INTEX-A data with the Angstrom between 2.0 and 2.2. This US pollution data encompass wider CCN proxy ranges at given extinction coefficients than do the INTEX-B data (red) with the Angstrom exponent between 1.4 – 1.6, an example of typical Mexican pollution. The Mexican pollution in general exhibits a well defined number-to-extinction relationship when stratified with the extinction Angstrom exponent, as we saw in Figure 6.1a. The blue circles in Figure 6.4a represent the data for IMPEX coarse particles (sea salt and dust; a subset of data shown in Figure 6.1c) which take the Angstrom between 0 and 0.2. Besides the smaller average extinction than the Mexican pollution, a less steep slope is evident. This difference reflects the separate sources of coarse and fine modes mentioned above.

In order to visualize this point in a different manner, Figure 6.4c shows the number size distributions corresponding to the data in Figure 6.4a, divided by the extinction coefficient and averaged. The vertical bars for each of the normalized distribution indicate one standard deviation of the logarithm of the number distribution per extinction. The INTEX-B Mexico (red lines) saw a narrow range of number distribution per extinction, whereas the long vertical bars associated with the INTEX-A data (black) indicate how variable the number concentration of fine particles can be without affecting the extinction even for sizes larger than 100 nm. Even the US pollution data with the wavelength dependence as low as typical Mexican pollution suffer a large variation in $CCN_{pr}$. This is presumably due to the same reason, i.e., the concentration of optically active particles (near 300 nm) is not
well related to that of the fine particles (near 100 nm). Thus, the CCN proxy is better constrained for Mexico pollution than for US pollution. As a minor note, the number distribution is equally variable among the locations at about 20 nm and smaller. The accumulation-mode aerosol loading can suppress such small, newly-formed particles. The negative correlation in the aerosol concentration between these two size ranges can lead to the apparent large variation in the number divided by extinction.

Possible reasons for this difference between regions include the regulations on the emission of particle mass from industry and transport as well as the sophisticated combustion technology in the US. Either of these can result in smaller pollution particles over the US than over Mexico. The data presented here suggest that such regulations and technology keep the extinction low, but may not reduce the number of particles. This implies that such regulations and technology are imperfect: They may improve the visibility and reduce the aerosol direct effect, but fail to mitigate the aerosol indirect effect on clouds and, possibly, related health hazards.

Ageing can also help explain the wide variety of the fine particle concentration over and around the mainland US. Figure 6.4d illustrates the degree of ageing for the subset of the INTEX-A data with which sulfur dioxide and sulfate mass were simultaneously measured. As sulfur dioxide get converted to sulfate the indicated age index approaches 1. The reddish symbols correspond to the most aged aerosols, including biomass burning particles. They are associated with relatively small CCN concentrations, because, as particles are transported, the number of fine particles is reduced due to condensation and coagulation while mean particle size increases. This suggests relationships of CCN to extinction may be parameterized
differently near sources compared to further away. The effects of ageing are discussed more in the subsequent section.

In summary, as the extinction Angstrom exponent deviates from 1.3 to smaller values, $CCN_{pr}$ becomes less constrained. Coarse particles (low Angstrom exponent) suppress the number concentration by offering the sites of coagulation, resulting in relatively small changes in the CCN number concentration while the extinction can vary broadly, hence the reduced sensitivity of the extinction to the CCN proxy. In the other extreme, the US pollution particles (high Angstrom exponent) tend to be too small to significantly affect the extinction, but are highly variable in their concentration, again leading to the reduced sensitivity of the extinction to the CCN proxy. If particle age is known, the CCN concentration in the US pollution may be constrained better. Otherwise, the Angstrom exponent can most effectively constrain $CCN_{pr}$ for cases with the Angstrom exponent near 1.3 - 1.5, like the pollution particles observed over and near Mexico. The remote sensing of the CCN proxy concentration can be accurate to factors of 1.2 – 1.3.

6.2 SSA Effects on Number-Extinction Relations

In the previous section we demonstrated that the extinction Angstrom exponent can effectively separate pollution from coarse particles (dust and sea salt). However, the CCN proxy concentration is only resolved to 20 – 40% of the median value within the pollution, less effectively for coarse particles and the US fine pollution. We looked for additional constraints, and found that the single scattering albedo (SSA, the ratio of scattering to the extinction) can be used for a majority of the
pollution air masses observed over Mexico. This optical parameter can be estimated from satellite observations, though not as readily as the AOD and extinction Angstrom exponent. This section illustrates how the remotely sensed SSA can constrain the CCN concentration, and why. This will be followed by the discussion of capabilities required by satellites to use SSA in number retrievals.

Similarly to the analysis in the previous section, the CCN proxy concentration and the light extinction coefficient, both measured from aircraft, are compared in Figure 6.5. Any feature that separates the data into distinct relationships improves a potential satellite retrieval of the CCN concentration based on the extinction coefficient. The SSA represented by the marker color does just that. The color gradient for a given extinction coefficient is partly explained by the fact that coarse particles such as dust and sea salt, with their relatively small CCN proxy-to-extinction ratio \( CCN_{pr} \), section 6.1), are less absorbing than pollution particles. If this were the only underlying reason for the SSA gradient, i.e., if the SSA differentiated the coarse particles from the pollution without effectively stratifying the data within the pollution, its role as a constraint would be redundant with the extinction Angstrom exponent.

In fact, the SSA does characterize the pollution data in a fundamentally different manner from the extinction Angstrom exponent. As explained in the previous section, the extinction Angstrom exponent removes excess extinction due to large particles and weights the extinction to that contributed by the particles nearly as small as the CCN. On the other hand, the use of SSA together with the extinction coefficient reveals a relation to the absorption. Unlike extinction, absorption in
pollution air masses is often dominated by light-absorbing soot particles that are in
the same size range as most CCN (ca. 100 nm). A limitation is that not all CCN
absorb light, but in the air masses over Mexico and in other regions influenced by
combustion aerosol most CCN do. Therefore, a positive correlation between the
absorption and the CCN concentration is expected in the first half of INTEX-B and
MIRAGE data. The differences in slopes for more absorbing aerosol (blue-green and
low SSA) in different regions evident in Figure 6.5 suggest regional characterization
could be used to develop relations between CCN proxy and extinction.

Because the extinction Angstrom exponent and the SSA work as constraints
due to the fundamentally different causes, together they constrain $CCN_{pr}$ more
effectively than the use of either one. To demonstrate this point, $CCN_{pr}$ is color-coded
with the SSA in Figure 6.6. The data with low SSA tend to take higher $CCN_{pr}$ at any
given Angstrom exponent between 1.3 and 2.0. The geometric average and standard
deviation of $CCN_{pr}$ is given for two single scattering albedo bins (0.90 – 0.95 and
0.95 – 1.00) for the 0.2-wide Angstrom exponent bins for at least 20 samples for each
experiment. The data with extinction smaller than 5 Mm$^{-1}$ was excluded from the
calculation in order to reduce the error arising from the PSAP filter-based
measurement. This stratification by SSA ranges results in a standard deviation smaller
than that for the Angstrom-based approach (Figure 6.2) by 0 – 13 percentage points
(absolute difference). The $CCN_{pr}$ for Mexico’s pollution particles can be constrained
down to a factor of 1.2 or less (numbers after differentiating the ~30% measurement
relative error), an improvement from the errors of 20 – 30% without using the SSA.
Soot particles and associated emissions are a key to understanding this behavior as many are too small to scatter effectively, but absorb strongly. Soot particles are often coated with volatile material (e.g., sulfate and organics) [Andreae and Gelencsér, 2006; Clarke et al., 2007] and have sizes near 100 nm that makes them constitute a considerable fraction of CCN proxy. Therefore, the abundance of coated soot particles near 100 nm are linked to both enhanced CCN and a low SSA. These particles are fresh near sources, but as they age, they gain more volume due to deposition of soluble mass, and therefore scatter more, while their number concentration will remain constant or decrease due to coagulation (after accounting for air dilution). As a result, the SSA increases, and the number-to-extinction ratio decreases (due to the increased scattering and possibly decreased number), compared to values closer to the sources.

To further clarify the role of soot in relating SSA to $CCN_{pr}$, the DMA and OPC size distributions measured during MIRAGE over Mexico were sorted with the SSA. The data associated with the Angstrom exponent between 1.6 and 1.8 were selected for this analysis, so that the selected size distributions contain small and similar dust concentrations. We know polluted air masses have high extinction and high number concentration, but what matters in the potential remote sensing of CCN is their ratio. Therefore the distributions were divided by the extinction before being averaged. To reduce the uncertainty associated with the PSAP absorption measurement, the data with the nephelometer scattering less than 5 Mm$^{-1}$ were removed. Solid curves in Figure 6.7a and Figure 6.7b show that the resulting unheated number distribution near 100 nm averaged for the most absorbing SSA bin
(0.92 - 0.94) is about twice as high as that in the least absorbing bin (0.96 - 0.98). This demonstrates that the extra number of particles (potential CCN) under low SSA does not contribute to the extinction. Most of the refractory and absorbing particle mass resides near the optically effective size of 300 nm (Figure 6.7c). The SSA difference is driven by the relative number difference near this diameter in the heated (to 300 °C) particles, a proxy for soot: it is about twice as high in the smallest SSA bin as in the highest (see the dashed curves in Figure 6.7b). Scattering, also peaking near 300 nm, is enhanced under low SSA too, but just by 30%, too low to counteract the 100% absorption enhancement.

These complicated figures may invite several questions. Why is the scattering near 300 nm enhanced by 30% despite the fact that the size distribution was normalized by extinction, most of which is scattering. This is because the extinction Angstrom exponent near 300 nm is dampened by absorption (Figure 6.7d) unless compensated for by marginally higher aerosol scattering in the wavelength-sensitive accumulation mode. The variation in coarse dust concentration also explains the deviation of the normalized extinction from the unity. Note also in Figure 6.7a that the heated aerosol size distributions (dashed) do not match between the DMA and the OPC by a factor of about 3 while the differences between the unheated distributions (solid) are much smaller. This indicates that the OPC overestimates the refractory soot size. This is consistent with our simulation of OPC response to absorbing particles. The side scattering over 35 - 145° that the OPC detects is higher for soot particles due to its high (both in real and imaginary) refractive index (up to 1.85 - 0.71i [Bond and Bergstrom, 2006]) than for the calibration PSL particles (n = 1.59)
for fine particles up to about 300 nm, according to our Mie calculation after Pinnick et al. [Pinnick et al., 2000]. This simulation is an approximation for qualitative assessment, and is not suitable for accurately quantifying the sizing error: Black carbon is not single spheres but often clusters of smaller spherules so that Mie theory is not strictly applicable.

The unheated size distributions have better agreement between the DMA and OPC, well within the 25% relative error in the OPC number (section 3.1). We also note that the observed refractory mass includes organic compounds not volatile at 300 °C such that the most soot mass is probably at the OPC diameters between 100 nm and 200 nm, rather than 300 nm. These facts only strengthen our point that the light absorption is more sensitive to particles in the CCN size range than is the scattering.

One might suspect that the SSA gradient apparent in Figure 6.6a is induced by the presence of organic compounds, rather than the absorbing soot. This is not the case. Our MIRAGE dry aerosol data taken over Mexico exhibits no trend along the vertical axis with organic fraction (Figure 6.8). The extinction Angstrom exponent is underestimated by about 0.1 for this subset of data due to the lack of multiwavelength f(RH) measurement (section 5.1.1). This is too small to explain the SSA stratification. Also, RH variation does not play a role in this data set measured under dry instrument conditions. Apart from submicron volatile aerosol composition and RH, we are not aware of any factor but absorption that influences the observed Angstrom-number relationship (Figure 6.6). Hence, the direct relationship between low SSA and enhanced soot particle number is expected for near source emissions. The rapid observed accumulation of soluble material on these soot particles will enhance their
effectiveness as CCN in the size range consistent with the observed link between SSA and CCN proxy.

This relationship between SSA and $CCN_{pr}$ serves as a constraint on a remote sensing retrieval of CCN, when SSA is available from satellite observations. MODIS relies on the spectral dependence of reflectance to select the right combinations of fine and coarse aerosol models. The preset models include the SSA and size information together. As such, one single source of information (spectral dependence) is used to derive two parameters (SSA and the Angstrom exponent). This retrieval method is not ideal for our method of estimating CCN proxy which requires SSA and Angstrom exponent as two independent input variables. Multi-angle and polarization-sensitive remote sensing techniques may provide these two optical properties independently from each other, allowing improved retrievals.

The SSA argument described above implies that absorbing particles are significant contributors to the CCN concentration. Mexican pollution, excluding the low-Angstrom dust and sea-salt, is dominated by aerosol with an absorbing soot component. To find out whether less absorbing particles exhibit the SSA trend, we examine the US pollution data. The INTEX-A data (Figure 6.5d and Figure 6.6d) includes much higher ratios of $CCN_{pr}$ but has generally higher SSA values. Less clear trend exists between the $CCN_{pr}$ and SSA, compared with the other pollution data. The extinction Angstrom exponent and SSA together only constrain the number-to-extinction ratio to 50 - 100%, as the vertical bars indicate. However, the lower SSA data do stand out as having the highest CCN proxy. Also, the influence of ageing,
Figure 6.4d, complicates the issue. Hence, a more complex procedure for identifying airmasses appropriate for remote sensing would need to be developed.

### 6.3 RH Effects on Number-Extinction Relations

So far the measurements of dry aerosols have been examined, but remote sensing of CCN is made at ambient RH. Most particles become smaller as the relative humidity of the sampled air decreases during the transport to the instruments. The measurements under the dry conditions do not capture the aerosol properties, the light extinction in particular, in the ambient conditions unless corrected for the humidity difference. The f(RH), the humidity response of the light scattering, measured aboard the DC8 aircraft enables us to make such a correction as well as to simulate the extinction coefficients at arbitrarily selected RH. The correction and simulation are vital in assessing the resolution of potential CCN remote sensing, and are detailed here.

As for the dry data, the Angstrom exponent stratifies the number and extinction comparison under ambient conditions (Figure 6.9a). The figure shows fewer data points than the dry data (Figure 6.1a) because our f(RH) measurement operated reliably only during the last 3 of the 9 INTEX-B flights over Mexico after fixing leak, as mentioned in section 2.2. To view the same data in a different format, \( CCN_{pr} \) and the extinction Angstrom exponent are compared for the fraction of INTEX-B data for which f(RH) data is available, for three RH conditions. They are dry (grey circles in Figure 6.9b), at ambient RH (squares in Figure 6.9b) and in Figure 6.9c the collection of data simulated for RH values between 10 and 90% with an
increment of 10%. Higher RH results in lower $CCN_{pr}$ because of the increased extinction, the denominator of $CCN_{pr}$.

In the atmosphere the ambient RH varies over a wide range. As a result, the number-to-extinction ratio ($CCN_{pr}$) adjusted to the measured ambient RH (Figure 6.9b) encompasses a wide range. The wide variation in $CCN_{pr}$ with RH shown in this figure and Figure 6.9c means that if the ambient RH is not known, the $CCN_{pr}$ suffers relative errors of 60 – 80%. This confirms the conclusion of our previous study [Kapustin et al., 2006] that the microphysical properties of dry aerosols, such as CCN proxy, are only loosely identified without knowing the ambient RH.

If the ambient RH is known, $CCN_{pr}$ for pollution particles over Mexico can be constrained to a similar degree as for the dry conditions, even without precise knowledge of particle hygroscopicity. The average of the $\gamma$ values obtained for urban pollution at altitudes higher than 2 km during INTEX-B was $0.48 \pm 0.09$ (the mean and one standard deviation; Figure 6.10). This value of $\gamma$ translates into a mean $f(RH)$ of 1.25 and one standard deviation ranging between 1.20 and 1.31 for 50% ambient RH, for the pollution particles sampled over Mexico. The variation in the relationship between aerosol number and dry extinction (20 - 30%) is much larger than the 5 - 6% relative error posed by neglecting the variation in aerosol hygroscopicity. Therefore, the use of 0.5 as a bulk $\gamma$ value does not significantly deteriorate the CCN proxy estimate for Mexico’s pollution.

While the air over Mexico City is rarely more humid than 70% RH, the pollution air mass from the city can mix with humid air over the Gulf of Mexico. At higher ambient RH, the $CCN_{pr}$ can take a wider range of values at given Angstrom
exponent as depicted in Figure 6.9c. If the variation in γ, represented by the standard deviation of 0.09 for MIRAGE, is not considered, the estimated humidity response will suffer a relative error of 20 – 30% at 80% ambient RH, and that of about 50% at 90% ambient RH. This is also the case over the US where the pollution particles take roughly the same range of γ and the ambient humidity takes a wide range of values [Clarke et al., 2007; Shinozuka et al., 2007].

Also, knowing γ is important for coarse particles over and near the Gulf of Mexico. Sea salt and dust take similarly low Angstrom exponent, but very different hygroscopicity. For marine aerosols observed in the lowest 2 km layer over the Gulf of Mexico γ was increased by hygroscopic marine aerosols to 0.63 ± 0.09. For air masses dominated with dust particles, γ was between 0.2 and 0.3. The large difference in γ means that the f(RH) for these two aerosol types are different by a factor of about 2 under 80% ambient RH. In remote sensing, differentiating these species based on properties established for a location, altitude and other conditions can reduce this error and ensure the best possible CCN estimate.

If satellites algorithms are to derive CCN_{pr}, the overall error will depend on the precision of Angstrom exponent and ambient RH measurements for given ambient RH and aerosol hygroscopicity [Kapustin et al., 2006]. If satellites are capable of estimating the Angstrom exponent to about an absolute error of 0.2 [Abdou et al., 2005; Redemann et al., 2005; Russell et al., 2007], the ratio is estimated within a factor of ~1.2 of the center value given the RH response. Furthermore, if the ambient RH is known to 10 percentage points for a γ of 0.5 at 80% ambient RH, the humidity response will be accurate to -18% and +41%. The different degrees of errors
between higher and lower bounds are due to the fact that $\gamma$ is an exponent. As a result, the upper/lower bounds of overall $CCN_{pr}$ relative error will be $\pm 27\%$/$\pm 46\%$ under these assumptions, and smaller for less hygroscopic particles and drier conditions.

Comparison among Figures 6.9b and 6.9c reveal that, unlike the large changes in CCN proxy, the Angstrom exponent does not dramatically decrease upon humidification despite the greater diameters. The ambient Angstrom exponent is overestimated, because the $f(RH)$ measured near 550 nm is assumed the same for the other wavelengths. Based upon our simulation of diameter growth factor using the size distributions over North America [Shinozuka et al., 2007] (Appendix A) and another similar simulation [Anderson et al., 2005], the absolute error in this parameter caused by ignoring the $f(RH)$ wavelength-dependence is 0.2 or even smaller, unless both the humidity response and the dry Angstrom exponent exceed $-2$. The low RH sensitivity makes the Angstrom exponent useful in estimating the dry particle size but useless in estimating the RH effect. A small reduction in Angstrom exponent at higher RH is evident at a closer look at the transition from dry to ambient conditions (Figure 6.9b), owing to the increased fractions of scattering relative to absorption.

Note also that for Figure 6.9 the lower diameter limit (100 nm) for the number integral is set for dry particles regardless of the RH for which the extinction is calculated. This treatment is in accordance with the Kohler curves, each of which is drawn for a dry diameter, and consistent with our OPC data obtained under dry conditions.
6.4 Column Integral

Most existing satellites observe the column integral properties. The objective here is to evaluate the potential to translate them into CCN number concentration. To this end, we calculate the AOD of selected vertical air columns flown during the experiments and link it to the CCN proxy. Details and examples of this procedure are discussed in length in [Shinozuka et al., 2007] (appendix A).

Figure 6.11a shows the column integral CCN proxy concentration and the dry aerosol optical depth for MIRAGE, IMPEX, INTEX-B and INTEX-A. INTEX-A data shows a large variation. Fine industrial particles tend to exhibit high number/extinction ratio as discussed in section 6.1. As is the case with the local air mass analysis, the Angstrom exponent separates the number-to-AOD relationship over Mexico (Figure 6.11b) and, more clearly, over the northeastern Pacific Ocean and the US West Coast (Figure 6.11c, note the different scales from Figure 6.11b). Another representation of the same data set given in Figure 6.11d reveals the positive correlation between the CCN per AOD and the Angstrom exponent, consistent with the relationships evident in the local air masses in terms of the slope of the relationships and the variance in $CCN_{pr}$ (section 6.1).

The data analyses for these column integral data are more limited than the local air mass data. This is because the smaller number of available data points impedes statistical treatment (section 6.1), and the lack of absorption measurement at many altitudes inhibits SSA stratification (section 6.2). Nonetheless, the consistency with the local air mass analysis suggests that the use of Angstrom exponent and,
perhaps, the use of SSA can improve the estimate of CCN concentration on the column integral basis.
Figure 6.1 The OPC number integral as CCN proxy and the dry extinction coefficient, both averaged over 30 seconds, observed during (a) INTEX-B over Mexico, (b) MIRAGE over Mexico, (c) IMPEX over the northeastern Pacific Ocean and (d) INTEX-A over the mainland US. The symbol color indicates the extinction Angstrom exponent. The scales are identical for all panels except for the color scale for (d). The thin solid and dashed lines in panel (a) indicate the geometric mean (17 cm\(^{-3}\)/Mm\(^{-1}\)) and standard deviation (1.9), respectively, of the slope such that most data reside between the boundaries. The thick lines show the statistics (geometric mean 21 cm\(^{-3}\)/Mm\(^{-1}\), geometric standard deviation 1.3) for the subset of data with the Angstrom exponent between 1.4 and 1.6 as an example.
Figure 6.2 The CCN proxy-to-extinction ratio \((CCN_{pr})\), or the slope of the data shown in Figure 6.1, plotted against the extinction Angstrom exponent \((A)\). The vertical bars encompass one geometric standard deviation of \(CCN_{pr}\) within each 0.2-wide Angstrom bin with at least 100 data points. The 4 panels correspond to the experiments noted in the caption for Figure 6.1. The regression line for IMPEX, \(\log_{10}CCN_{pr} (\text{cm}^3/\text{Mm}^2) = 0.3 + 1.0\), is superimposed on all panels as a reference. Note that the horizontal scale for the bottom right panel is different from the rest.
Figure 6.3  Same as Figure 6.2d except the difference between the CN and DMA particle counts is used as CCN proxy.
Figure 6.4 (a) Subsets of the data shown in Figure 6.1, to highlight the different tightness of the number-to-extinction relationship among the coarse particles (blue), Mexican pollution (red) and US pollution (black). (b) Same as (a) but in logarithmic scales to expand the area for small concentration and extinction. (c) The mean and standard deviation (taken on a logarithmic scale) of the size distribution divided by the extinction and averaged for the aerosol types. The DMA and OPC distributions were combined at 150 nm and smoothed. (d) The subset of INTEX-A data shown in (a) colorcoded with the ageing indicator.
Figure 6.5  Same as Figure 6.1 except that the symbol color indicates the single scattering albedo for dry conditions. The scales are identical for all panels.
Figure 6.6  Same as Figure 6.2 except that the symbol color indicates the single scattering albedo for dry conditions. The vertical bars encompass one standard deviation of $CCN_{pr}$ within each 0.2-wide Angstrom bin within each of the SSA bins (blue lines for 0.90 - 0.95, red for 0.95 - 1.00).
Figure 6.7  
(a) The DMA and OPC size distributions of unheated (solid curves) and heated (to 300 °C; dashed curves) particles, divided by the extinction coefficient and averaged for the SSA bins of 0.92 - 0.94, 0.94 - 0.96 and 0.96 - 0.98.  
(b) The ratio of the size distributions of the lowest and highest SSA bins.  
(c) The scattering (thick curves) and absorption (thin) distributions calculated with a hypothetical refractive index of 1.51 - 0.02i for the size distributions shown in (a).  
(d) Extinction Angstrom exponent calculated for two refractive indices, 1.5 and 1.5 - 0.02i.
Figure 6.8  Same as Figure 6.2b except that the symbol color indicates the organic mass fraction of submicron nonrefractory particles and that the scales are different.
Figure 6.9  (a) The CCN proxy and the ambient extinction coefficient, both averaged over 60 seconds, observed during INTEX-B over Mexico. The humidity response of aerosol scattering measured with the f(RH) system was used to adjust the dry scattering coefficient to the ambient conditions. The symbol color indicates the extinction Angstrom exponent. (b) The CCNproxy-to-extinction ratio (CCN$_{pr}$), or the slope of the data shown in Figure 6.9a, plotted against the extinction Angstrom exponent (A), colorcoded with the ambient RH. The grey circles indicate the CCN$_{pr}$ under the dry instrument condition. (c) The CCNproxy-to-extinction ratio simulated for 10 - 90% RH.
Figure 6.10  The exponent, $\gamma$, for the humidity response of aerosol scattering observed during INTEX-B over Mexico.
Figure 6.11  (a) Column integral number of particles larger than 100 nm compared with the dry aerosol optical depth (AOD) for the vertical profiles flown during the MIRAGE, IMPEX, INTEX-B and INTEX-A experiments. (b) The column number and AOD comparison over Mexico. The marker color indicates the Angstrom exponent of dry AOD. (c) Same as (b) but for the US West Coast and northeastern Pacific Ocean. Note the different scales. (d) The column integral number divided by the dry AOD, compared with the AOD Angstrom exponent.
7 Conclusions

Aerosol size distributions, chemical composition and multi-wavelength scattering/absorption as well as the response of size and scattering to changes in humidity were measured over Mexico, the mainland US and the northeastern Pacific Ocean from aircraft. The relationships between these aerosol properties were examined to assess whether the optical signals that satellites detect can be translated into the CCN concentration. The CCN remote sensing strategy employed in this study is to retrieve the aerosol chemical composition, to derive the dry critical diameter under 0.2% supersaturation and to retrieve the concentration of particles larger than this diameter. This supersaturation is characteristic of extensive low and weakly convective clouds expected to exert a significant climate impact. The findings were:

- The organic fraction of submicron volatile aerosol mass over Mexico may be estimated to an absolute error of about ±0.3 from the satellite observation. Dust particles probably play an important role. While their large sizes lower the extinction Angstrom exponent, they take up nitrate and sulfate ions to the coarse mode, increasing the mass of organic compounds relative to the ionic in the submicron aerosols. (Chapter 5)

- Attempts to associate the dry critical diameter with the aerosol chemical composition were hampered, apparently by low accuracy of the CCN concentration measurement. More field and laboratory studies are needed so that the aerosol chemical composition is translated to the minimum dry
diameter from which the aerosol size distribution is integrated to yield the CCN concentration. (Chapter 4)

- The retrieval of the CCN number concentration appears feasible for Mexican and Asian pollution. Considerable fractions of the particle number reside in the optically active accumulation mode, and are well related with the concentration of finer (~100 nm) yet CCN-active particles, thus linking the light extinction and number concentration. As a result, the wavelength dependence of extinction, an aerosol-size-dependent satellite product, can be used to approximate the number fraction to constrain the CCN concentration to a relative error of 20 - 30%. This error arises from the natural variation in the relationship between aerosol number and extinction, not from measurement error. The number-extinction linkage is, however, uncertain for air masses dominated by dust and sea-salt particles (coarse particles to which aerosol number is insensitive) or by US pollution (fine particles to which aerosol extinction is insensitive). (Chapter 6)

- The remote sensing of the aerosol number concentration over Mexico can be improved further by the use of single scattering albedo (SSA). This is because coated fine soot particles contribute significantly to the aerosol CCN number such that the visible light absorption fluctuates with the number concentration. Higher numbers and lower SSA near sources associated with fresh aerosols transition to lower concentrations and higher SSA during ageing. Such relations may exist in other regions but are likely to be regionally specific. (Chapter 6)
• The humidity response of aerosol light scattering can be estimated to a relative error of about 5% over Mexico, because of generally low ambient RH. This makes the estimate of CCN concentration easier for the pollution there than over the Gulf of Mexico and the US where an inappropriate estimate of the humidity response could lead to a 50% relative error in CCN estimate due to high humidity. (Chapter 6)

• Higher CCN proxy number and lower SSA near sources associated with fresh aerosols transition to lower CCN proxy concentrations and higher SSA during ageing. This suggests stratification for airmass age might improve potential retrieval of CCN. (Chapter 6)

• The number-extinction relationship over vertical columns is consistent with that for local air masses. (Chapter 6)

These observations provide an improved context for understanding the capabilities and limitations for inferring CCN from spectral remote sensing. They also highlight how refinements in measurements of SSA and the vertical profiles of humidity could improve this analysis. Moreover, regional characteristics that link spectral properties to physical chemistry suggest potential for tailoring retrievals to specific regions. An example was given over Mexico where coarse particle dust revealed in the scattering Angstrom exponent was related to the organic mass fraction of the accumulation mode. This was shown to be related to the critical activation diameter of this aerosol arising through loss of soluble ionic compounds from the accumulation mode to the coarse dust aerosol. Different couplings between aerosol
physicochemistry and optics may exist over other extensive regions. Implementing retrieval schemes for such regional properties will probably be essential to the objective of inferring CCN from satellite.
APPENDIX A  Shinozuka et al., [JGR 2007]

Aircraft profiles of aerosol microphysics and optical properties over North America: aerosol optical depth and its association with PM2.5 and water uptake

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Abstract

Aerosol column optical depth (AOD) is related to the aerosol direct radiative effect and readily available as a satellite product. The mass of dry aerosol up to 2.5 μm aerodynamic, or PM2.5, is a common measure of surface aerosol pollution at selected regional sites. A link between these two parameters would provide a way to infer PM 2.5 and its change over extensive regions observed by satellites. This requires determination of the response of aerosol dry mass to the widely variable influence of ambient humidity and its optical contribution to column AOD. During the INTEX-North America aircraft campaign, we obtained 72 profiles of visible aerosol light scattering up to 10 km and its response to water uptake. The ambient AODs determined from these measurements, and confirmed for 3 profiles near surface AERONET, were generally below 0.4 except in the presence of a humid boundary layer with high aerosol loading. The fraction of ambient AOD due to water uptake, Wf, was found to be 37 ± 15% (average and standard deviation). Boundary layer PM2.5 was estimated (PM2.5_proxy) from low altitude size distributions measured from the aircraft. Despite the large variety of vertical aerosol structure, the ambient AOD was found correlated with the PM2.5_proxy with R^2 = 0.77, after 4% of data with AOD > 0.8 for >90% RH were removed. Our results support the application of remote sensing to retrievals of surface PM 2.5 mass. The wavelength dependence of ambient AOD was found to be less effective in stratifying the mass vs. extinction relationship on the column integral basis than on a layer by layer basis.
1 Introduction

Aerosols affect Earth's radiative balance, hydrological and biogeochemical cycles, visibility and human health. Emissions, whether from urban/industrial sources such as cars and factories or from natural sources such as forest fires, desert and ocean surface, are typically reported as mass under dry conditions. The mass of aerosols up to an aerodynamic diameter of 2.5 μm, or PM2.5, is widely monitored on ground (e.g., AIRNow, a US government agency, http://www.airnow.gov/) and used to assess and regulate pollution.

Aerosol optical depth (AOD) is a measure of the extinction of light passing throughout the atmosphere and is relevant to the direct radiative effect. Unlike PM2.5, AOD is defined over the entire air column and readily available from radiance measurements with satellite and ground sensors at multiple wavelengths [Tanre et al., 1997; Chu et al., 1998; Holben et al., 1998; Kahn et al., 1998].

If surface PM2.5 measurements are shown to relate strongly to radiance or AOD, there is potential for using satellites to infer PM2.5 with high resolution over regions not monitored with ground PM2.5 networks. Liu et al. [2004] and Liu et al. [2005] parameterized surface PM2.5 using satellite and model products and achieved moderate correlations with surface measurements on a seasonal average (not concurrent measurement) basis. Dubovik and King [2000a] and Kaufman et al. [1997] translate radiance and its wavelength dependence measured with sun
photometers and the Moderate Resolution Imaging Spectroradiometer (MODIS) satellite into aerosol size distribution. Gasso and Hegg [2003] link the satellite products to column-integral (not near-surface) aerosol mass, and compared with measurements made with sizing instruments aboard aircraft. While various closure experiments in the past decade focused on validating surface AOD vs. satellite AOD measurements [Chu et al., 2002; Remer et al., 2002; Chu et al., 2003; Ichoku et al., 2003], limited in-situ data is available for comparison of surface PM 2.5 with satellite radiances [Wang and Christopher, 2003].

In translating remotely sensed column optical properties into dry aerosol mass, relative humidity (RH) needs to be considered. Hygroscopic aerosol components respond to increasing RH by growing in size and scattering more light [Tang and Munkelwitz, 1991; Malm, 1994; Howell et al., 2006]. Both aerosol models and remote sensing attempt to account for these humidification effects though using different input variables and methods. In-situ observations can provide means to identify how well models compute ambient AOD given dry aerosol size distributions, water uptake and ambient RH and, as demonstrated by Gasso and Hegg [2003], how accurately remotely sensed ambient AOD can be translated into dry AOD and mass.

The goal of this paper is to examine AOD response to water uptake and its relationship to PM2.5 by taking advantage of aircraft profiles over extensive regions of North America. The AOD is calculated at the ambient RH conditions for 72 profiles made during descents and ascents, using scattering coefficients measured
under both low and near-ambient RH. Results are compared with independent
ground measurements when possible. A PM2.5_proxy for dry aerosols is calculated
from size distributions measured at 500 ± 200 m. To stratify the resulting AOD vs.
PM2.5_proxy relationship, we also calculate the relative contributions from different
altitudes and those from the aqueous component to the AOD.
2 Measurements and Instrumentation

We collected data during the Intercontinental Chemical Transport Experiment -- North America (INTEX-NA) experiment, a major NASA science campaign to understand the transport and transformation of gases and aerosols on transcontinental and intercontinental scales and their impact on air quality and climate. The NASA DC-8 research aircraft was deployed mostly over the eastern half of the continental US and the Atlantic Ocean off the US East Coast from July 1 to August 15, 2004 as described in Singh et al., [2006].

Aerosols were conveyed to the aerosol instrumentation aboard the DC-8 aircraft using the University of Hawaii solid diffuser inlet. This inlet and sample plumbing has recently been shown to pass aerosol with dry aerodynamic diameter of 4.8 μm with better than 50% efficiency [McNaughton et al., 2007].

Total and submicrometer aerosol scattering coefficients were measured using two TSI model 3563 3-wavelength integrating nephelometers [Anderson et al., 1996b; Heintzenberg and Charlson, 1996]. The submicrometer TSI nephelometer employed a 1-μm aerodynamic impactor maintained at 30 lpm by an Alicat Scientific volumetric flow controller. Sample air residence time inside the nephelometers was about 10 seconds, and the instrument relative humidity (RH) usually lower than 30%.
Two single-wavelength (near 540 nm) Radiance Research model M903 nephelometers were operated in parallel, one at 80% (RH1) and the other at <40% (RH2) to provide RH sensitivity of aerosol scattering [Howell et al., 2006]. The wet to dry scattering ratio, f(RH), was averaged for 60 seconds and used to calculate γ based on Eqn. 1.

\[
\text{Eqn. 1: } f(\text{RH}) = \frac{(1-\text{RH}_1/100)}{(1-\text{RH}_2/100)}^\gamma
\]

γ characterizes scattering response that is determined by the aerosol chemistry, mixing state, sizes and refractive index. These are primarily determined by source type and location as well as transport and scavenging processes, and not directly related to ambient RH. Using the calculated γ, we can calculate f(RH) for the ambient RH, or f(ambRH), by replacing RH1 and RH2 with the measured ambient RH and the TSI nephelometer (<40%) RH, respectively. The resulting f(ambRH), when multiplied to the total dry scattering coefficient measured with the TSI nephelometer at 550 nm, gives the scattering coefficient under the ambient RH.

A prototype 3-wavelength Radiance Research particle soot absorption photometer was provided by Dr. David Covert (University of Washington) to measure aerosol light absorption at 470, 530, 660 nm. The absorption coefficients are based upon calibration for this new instrument reported elsewhere [Virkkula et al., 2005], but some recent indications suggest result may differ from the true absorption by about 20%. In the present study the absorption at 530 nm is used to relate the scattering coefficient to extinction. Because the absorption rarely exceeded 10% of extinction
integrated over vertical profiles, the measurement uncertainty results in a 2% or less error in estimated aerosol optical depth.

An optical particle counter (OPC, a modified LAS-X, Particle Measurement Systems, Boulder, Colorado) measured the dry (RH < 30%) aerosol size distribution between 0.1 μm and about 10 μm [Clarke, 1991]. The particle size was calibrated with polystyrene latex spheres whose refractive index is 1.59. The data was obtained every 3 seconds, but averaged over 30 – 60 seconds to reduce error due to low counting statistics at about 1 μm or larger. The He-Ne laser operates at 633 nm detecting light scattered by individual particles over 35 – 145 degrees. Since the OPC measures optically, it is well suited to modeling aerosol optical properties.
3 OPC Validation

In this study the dry size distribution measured with the OPC is used to model the ambient response of scattering to water uptake as well as to estimate the dry aerosol mass. It is evaluated here against the concurrent dry nephelometer measurements. The uncertainty in the derived volume is also considered.

Scattering coefficient at 550 nm was calculated using Mie theory from the OPC distribution for the TSI nephelometer detection angle (7° - 170°). For comparison with the submicron scattering coefficient, we used the size distribution up to 750 nm [McMurry et al., 2002]. Figure 1 shows 30-45 second averages of derived scattering coefficients for all horizontal flight legs during INTEX-NA. The calculated scattering coefficients over both size ranges are within 10% of the measured scattering values with correlation coefficients of 0.95. The submicron agreement is better than the total that suffers poorer coarse particle counting statistics. The intercept of 0.39 Mm⁻¹ is reasonable, because it is comparable to TSI nephelometer noise level for a 30-second average (~0.3 Mm⁻¹) [Anderson et al., 1996a].

Uncertainties in sample flow rate (~3%) and refractive index may contribute to the non-ideality too.

OPC particle sizing is sensitive to the refractive index, n, of the sampled particles [Pinnick et al., 2000]. Silica test particles (n = 1.45 - 1.46) with diameters 730 nm and 1.58 μm appear at sizes 630 nm and 1.25 μm, respectively for the PSL-calibrated
(n = 1.59) OPC, showing similar degrees of sensitivity to that demonstrated in a previous study with oleic acid (n = 1.46) particles [Hand and Kreidenweis, 2002].

The 13 – 20% diameter underestimate, or 35 – 50% volume underestimate for the silica spheres constitutes an upper bound of error estimate. The DC-8 sampled a wide variety of natural and anthropogenic aerosol types including urban/industrial pollution and biomass burning from Alaskan/Canadian forest fires during INTEX-NA. The mass was generally dominated by sulfates and organic carbon [Clarke et al., Submitted] such that the real part of refractive index is likely to lie between the PSL and silica. Therefore, the OPC derived volume may underestimate the actual by about 20%. Apart from this possible bias in estimated mass, the high correlation with the independent direct measurement demonstrates the OPC’s consistent performance throughout the experiment. This assures that our data set captures variation in the aerosol mass to extinction ratio with aerosol properties and meteorological conditions.
Figure 1. Scattering coefficient derived from the OPC size distribution compared to the nephelometer direct measurement under dry conditions. The particle size ranges are 0.1 – 20 μm (dot) and 0.1 – 1 μm (square).
4 Wavelength Dependence of Ambient Scattering Coefficient

Aerosol number and size, from which mass may be derived, cannot be uniquely determined by light reflectance measured at one wavelength alone. Most satellites detect at multiple wavelengths in order to provide additional constraints. We wish to establish the ambient aerosol multi-wavelength optical properties from the aircraft data in order to assess the satellite capability in estimating the aerosol mass from spectral radiances. The first step is to estimate the wavelength dependence of ambient scattering coefficient at various altitudes. The wavelength dependence is usually expressed as Ångström exponent ($\hat{A} = \frac{-d\log(\sigma)}{d\log(\lambda)}$, where $\sigma$ is the scattering, and $\lambda$, the wavelength). $\hat{A}$ is often near 1-2 for small particles (e.g. fresh pollution under dry conditions) and near 0 for large particles (e.g. mineral dust or sea salt).

Although dry scattering was measured at three wavelengths aboard the aircraft, the scattering at higher RH was measured at a single wavelength (near 540 nm) to get $f(\text{ambRH})$. The ambient Ångström exponent, $\hat{A}_{\text{amb}}$, was not measured. Instead, we modeled this wavelength dependence using the measured dry size distribution and $f(\text{ambRH})$, as described below. The result helps to reconstruct the column AOD at multiple wavelengths (Section 5.2) and is evaluated against independent ground measurements (Section 5.3).
In order to model humidity growth, aerosol diameters were increased by the aerosol growth factor, \( g(RH) \), that ranges from 1 to 2 with an increment of 0.01.

Subsequently, we used Mie theory and a volume-weighted average of the dry aerosol refractive index (1.59) and the refractive index of water (1.33) to compute ambient aerosol optical properties at three wavelengths for each OPC distribution. These were averaged for 30 - 45 seconds during the horizontal flight legs. The ratio of the scattering coefficients calculated from each OPC distribution to the dry value yielded \( f(RH) \).

Figure 2 compares the Ångström exponent between the humidified (i.e., simulated) and dry (i.e., measured) aerosols. As expected, data points lie near the 1:1 line for low \( f(RH) \) values. Larger \( f(RH) \) values reduce \( A \) from the dry conditions. This reduction in \( A \) is most pronounced when \( A_{\text{dry}} \) takes large values. The dependency of scattering upon wavelength and size is consistent with Mie theory. An undesirable consequence is that \( A_{\text{amb}} \) is less sensitive than \( A_{\text{dry}} \) to the dry aerosol size distribution, weakening satellite's ability to employ wavelength dependencies to derive dry aerosol mass. Here we simulate \( A_{\text{amb}} \) calculated from our measured \( f(\text{ambRH}) \) (adjusted to the ambient RH using Eqn. 1) and \( A_{\text{dry}} \). A regression line for any simulated \( f(RH) \) value passes through the dry and ambient Ångström exponent coordinates of (0.4, 0.4). As a result, the simulation result was approximated with a polynomial fit.

\[
A_{\text{amb}} = (-0.022 \times f(RH)^3 + 0.16 \times f(RH)^2 - 0.47 \times f(RH) + 1.3) \times (A_{\text{dry}} - 0.4) + 0.4
\]
The $\tilde{A}_{\text{amb}}$ calculated with this equation is correlated with the simulated $\tilde{A}_{\text{amb}}$ with a slope of 0.99 and an $R^2 > 0.99$. This result is not sensitive to the choice of refractive index. For distributions with small or large Ångström exponents, reducing the refractive index from 1.59 to 1.51 – 0.01i results in just a 1% larger $\tilde{A}_{\text{amb}}$ even for $f(RH)$ as large as 3.
Figure 2. Ambient Angstrom exponent simulated with the measured aerosol size distribution and sorted with scattering ratio, f(RH). When scattering coefficients are converted from dry conditions to ambient, the wavelength dependence is generally reduced, particularly for large f(RH) and dry Angstrom exponent values.
5 Vertical Profiles and Aerosol Optical Depth

Our goal is to examine the variation of column integral optical properties over the continental US, the influence of water uptake upon them and their relationship to the effective dry aerosol mass concentration (PM$_{2.5\text{proxy}}$) measured in the boundary layer. We will relate these to two satellite products, column AOD and its wavelength dependence. The latter are established below using the ambient scattering coefficients derived on a layer basis in the previous section. Where available the results are compared to ground-based observations to check the overall consistency of this approach.

5.1 Vertical profiles

For the column AOD calculation we selected 72 aircraft ascending and descending profiles that spanned at least between 500 and 5000 m, some including portions of horizontal in-progress flight legs. We exclude several profiles where 1) more than 20% of the optical depth is due to aerosols at altitudes above the aircraft altitude according to the LIDAR data or 2) when profiles included data more than 200 km away from the lowest altitude. Shown in Figure 3 are four examples of the profiles. The ambient scattering coefficient at 550 nm is given as the product of dry scattering coefficient and $f(\text{ambRH})$ adjusted with the Eqn. 1 for the ambient RH.
a) July 1, 23:02 – 23:43 UTC (Figure 3a) over the Central Valley of California, the winds were northwesterly up to 2 km and southerly 3 – 5 km. The ambient RH varied between 40 – 60%. Back trajectory analysis [Fuelberg et al., 2006] indicates that the air above 5 km had traveled in the free troposphere over the Pacific Ocean for one week, keeping the aerosol concentration low.

b) July 20, 18:09 – 18:37 UTC (Figure 3b) over Illinois, the boundary layer and free troposphere were separated by a strong inversion. A trough over the East Coast and a strong ridge over the Rocky Mountains produced northwesterly winds in the free troposphere. The back trajectories show that the air had traveled over the Pacific Ocean and Canada without nearing the surface for a week prior. The aged boundary layer air up to 2900 m trapped local pollutants, and the very high RH (75 - 98%) grew them to scatter effectively. The measured aerosol number counts did not rise, confirming that possible droplet shatter of clouds at the inlet did not increase the scattering coefficient.

c) July 20, 21:59 – 22:13 UTC (Figure 3c) over New Hampshire, the planetary boundary layer was not distinct from the free troposphere. Westerly/northwesterly winds from Pacific Ocean through Canada and Great Lakes prevailed over the free troposphere. A humid shallow boundary layer below 200 m embedded in southerly winds from the US East Coast accounts for moderate aerosol scattering near the surface.
d) Figure 3d shows a special case where a thick plume of biomass burning aerosol resided in the upper troposphere (7 - 10 km) on July 18, 18:10 – 19:09. The mid-troposphere and boundary layer were influenced by westerly winds traveled over Great Lakes and slow flow from Northwest Canada, respectively. This air mass experienced limited dilution due to swift transport from its origin at the surface over Alaska several days prior.

Most of the observed profiles had similar structures to either one of the first three cases where local pollution is trapped in the boundary layer while the free troposphere contains aerosols transported long-range from other sources. The enhanced upper troposphere plume shown in the last panel is not representative of profiles observed on other days during the experiment.

5.2 AOD estimate and uncertainty

Most satellites generate column aerosol products such as AOD. Consequently, the first step in the analysis was to characterize the column AOD for the 72 INTEX-A profiles. The AOD at 550 nm is dominated by the vertical integral of the ambient scattering coefficient derived from the nephelometer measurements, such as those shown in Figure 3. The scattering coefficients at 440 and 675 nm were simulated using the ambient Ångström exponent calculation in Section 4. The final AOD profiles account for light attenuation due to absorption based on the assumption that the measured absorption coefficient applies to ambient conditions [Nessler et al.,
Occasionally, we interpolated over layers without aircraft measurements. For the altitudes with no absorption measurement, we assumed the experiment-wide average single scattering albedo (SSA), which decreased from 0.96 near the surface to 0.88 at 6 km at 550 nm.

The AOD contributed by the altitudes lower than the lowest aircraft altitude (500 m or lower) was assumed to be equal to that of the layer of the same thickness immediately above it multiplied by a pressure adjustment factor. The factor accounts for the atmospheric pressure gradient with altitude and ranged between 1 and 1.06. Because pollution sources are at the surface, the scattering coefficient can be higher than this well mixed assumption as you approach the surface (see Figure 3c for example). Hence in a poorly mixed near-surface layer, this assumption may bias the estimated AOD toward low values.

The extinction coefficient due to the aerosols in the troposphere above the highest altitude flown by the DC-8 (>5 km to 10 km) was assumed to be the experiment-wide mean of 2.7, 2.0, 1.6 Mm$^{-1}$ at 450, 550 and 700 nm, respectively. We also assume here that the lowest 5% of AOD values measured by the J31 between 5 and 7.5 km reflect a clean upper troposphere and are representative of stratospheric AOD. This stratospheric AOD was identified to be 0.014, 0.0077 and 0.0053 at 440, 550 and 675 nm, respectively. These values were estimated using differential AOD measured from the J31 aircraft [Russell et al., 2006] during the INTEX-A over the US East
Coast. This stratospheric AOD accounts for 20% or less of the total ambient AOD for most profiles.

Unusually low or high AOD values were excluded by focusing on the center two thirds of our observations. Uncertainty in the estimated ambient column AOD ranges over 16 – 46% for this data, with a median value of 23%. It originates primarily from the f(RH) measurement and the contribution from near-surface layer. The scattering increase from the dry to ambient RH conditions is subject to the errors in γ and ambient RH measurements. Assuming a 4% uncertainty in the RH measurement and 5% in the Radiance Research nephelometer scattering measurement, Eqn 1 provides γ to an accuracy of <14% for this data. This translates into <15% uncertainty in f(RH). Doubling and halving the estimated extinction in the near-surface layer below the minimum aircraft altitude results in median ambient AOD changes by +12% and -6%, respectively.

Minor sources of error include the dry scattering measurement noise (<1 Mm⁻¹), compensated for when integrated over the altitudes), the truncation correction (~4% for no-impactor-cut samples, less for submicron [Anderson and Ogren, 1998]), absorption (2%, discussed in Section 2) and the aerosol AOD in the upper troposphere (in the order of 0.01).
5.3 AERONET comparison

Profiles over AERONET sites [Holben et al., 1998] provided an opportunity to evaluate our calculated column AOD. The estimated AOD is compared here with AERONET level 2.0 data that has been pre and post field calibrated, automatically cloud cleared and manually inspected. Three of the INTEX-NA vertical profiles met our selection criteria that the aircraft at its lowest altitude was located within 100 km of the AERONET site and that the AERONET site was under clear sky within 4 hours (equivalent to 100 km at a wind speed of 7 m/s) of the aircraft/AERONET measurements being compared. These large spatial and temporal differences make the comparison less precise than coordinated aircraft spiral ascents/descents over the ground sites. However, the comparison is valuable in demonstrating the general consistency in our estimate of AOD and its wavelength dependency.

The ambient AOD shows reasonable agreement with AERONET AOD data for the 3 vertical profiles (Figure 4). The horizontal bars indicate one standard deviation of the AERONET 15-minute-average AOD within ± 4 hours of the aircraft overpass. In order to assign a measure of variance to the aircraft AOD profile, we assume the variance in AOD is similar to that evident in the vertical integral of the lidar backscatter taken within 100 km of the AERONET site. The product of this coefficient of variance and the AOD from the profile provides an estimate of aircraft
AOD variance for all wavelengths. The vertical bars in Figure 4 indicate this spatial and temporal variance as well as the measurement uncertainty.

The poorest agreement between calculated and observed ambient AOD occurs for the lowest AOD values which were measured at the Fresno California AERONET site (36.8 °N, 119.8 °W) on July 1, 23:02 – 23:43 UTC (Figure 3a). Cirrus clouds may have been present near 10700 m in the vicinity of the ground site. The aircraft data shows that, while the scattering coefficient at this altitude remained below the detection limit, the ambient RH exceeded 95%. The highest AOD was measured at the Bondville, Illinois AERONET site at (40.1 °N, 88.4 °W) on July 20, 18:09 – 18:37 UTC (Figure 3b). The lidar found a high spatial variability of aerosol scattering, resulting in the long vertical error bar. The variance estimates from the AERONET data (horizontal bars) indicate that clouds did not affect the measurements or were effectively removed. This profile with the highest f(ambRH) value highlights the application of our Ångström exponent modeling. If we ignore the wavelength dependence of f(ambRH) for this high humidity case, the calculated AOD deviates from the best estimate by +0.03 (+5%) at 440 nm and -0.02 (-7%) at 675 nm (triangles in Figure 4). Incorporating the wavelength dependence of f(ambRH) into the ambient AOD calculation results in only marginally better agreement with the AERONET direct measurements.

These comparisons do not represent “closure” studies. However, the agreement demonstrates the general validity of our approach for obtaining ambient AOD and its
wavelength dependency. Where concurrent airborne and ground based measurements of column AOD can be more effectively compared over appropriate spatial and temporal scales, we expect that differences would be smaller than those presented here and mainly reflect non-ideal instrument behavior and uncertainties in the aerosol properties such as size distribution, refractive index, and hygroscopicity. We note that even deliberate in-situ closure profiles for AOD evaluations are expected to yield calculated AOD uncertainties on the order of 15-20% [Redemann et al., 2003].
Figure 3. Selected vertical profiles of dry (thin solid curve) and ambient (thick solid curve) scattering coefficients along with the measured ambient RH (dashed curve). Plus signs on the vertical axes indicate the altitude of 80% ambient AOD contribution. A map of the flight track is inserted for each profile.
Figure 4. Ambient AOD derived from the aircraft measurements of scattering and f(RH) compared with the AERONET measurements at 440 nm (blue circles), 550 nm (green circles) and 675 nm (red circles) for the first three profiles of Figure 3. The triangles indicate the result of ignoring wavelength dependence of scattering increase. The bars indicate temporal and spatial variances observed by AERONET and aircraft LIDAR, respectively, in addition to the measurement uncertainty.
6 Mass estimate and local mass scattering efficiency

Here we estimate aerosol density and PM2.5 mass in the boundary layer. The aerosol mass and extinction is linked in the local domain, before extending our scope to the vertical column in next section.

Aerosols in the boundary layer were predominantly of urban origin. Biomass burning events identified using measured gas concentrations were mostly found in the free troposphere [Clarke et al., submitted to JGR], with limited influence on the mass-scattering relationship in the boundary layer. Also, we do not find any air mass where aerosol sizes up to 2.5 μm were dominated by dust.

The limited contribution of biomass burning and dust plumes relative to regional pollution justifies the use of a single density value for the size distributions in the boundary layer in our selected vertical profiles. Previous DMA measurements made for urban aerosols in Atlanta resulted in a density range of 1.54 – 1.77 g/cm³ [McMurry et al., 2002]. The variability of this density estimate is less than ±10%. We use a value of 1.7 g/cm³ and estimate an uncertainty associated with the choice of density at 15% considering that Atlanta may not represent the US nation-wide urban pollution. Clarke et al., [submitted to JGR] estimated mass of ions, organic compounds and black carbon using chemical mass and size distribution...
measurements during INTEX-NA. Their density for most of the urban pollution samples falls in 1.5 – 1.7 g/cm$^3$, to further support our choice of density in the present paper. We do not estimate the aerosol mass of biomass burning or dust in the troposphere, or column integral mass.

PM2.5 mass was approximated by this density times the integral between 100 nm and 1.9 $\mu$m of OPC volume distribution taken at 500 ± 200 m above sea level (PM2.5$_{\text{proxy}}$). This upper size cut roughly corresponds to an aerodynamic diameter upper limit to 2.5 $\mu$m for the assumed particle density. The volume integral is weakly sensitive to the upper cut size unless there is a large relative volume in the coarse mode. Cut at 2.4 $\mu$m instead, the volume is higher only by a maximum of 3% for 95% of the samples. The largest particles can also suffer from inertial collision into the inner wall of inlet, resulting in undercounting. However, the loss is considered negligible for aerodynamic sizes of 2.5 $\mu$m and below [McNaughton et al., in press, Aerosol Science and Technology, 2006]. The particle size measured with the OPC is sensitive to the refractive index, which may result in a mass underestimate of about 20% (Section 3). The 15% uncertainty in density discussed above brings the overall PM2.5$_{\text{proxy}}$ uncertain range to -15% and +25% (lower and upper limits). Furthermore, we emphasize that size distributions measured at our lowest altitudes of 500 ± 200 m may not reflect surface concentrations when strong near surface gradients exist. Despite these limitations, the estimated PM2.5$_{\text{proxy}}$ remains useful in estimating correlation between the dry aerosol mass and the column optical properties as well as
in sorting their relationship with relative humidity and wavelength dependence of light extinction.

The regression between the measured aerosol volume and scattering at an altitude of 500 m yielded the expression Dry Volume ($\mu m^3/cm^3$) = 0.076 * Ambient Scattering Coefficient ($Mm^{-1}$) + 1.8, and gives a root square mean volume difference of 1.8 $\mu m^3/cm^3$ while the volume ranged between 0 and 20 $\mu m^3/cm^3$. The $R^2$ is 0.86 for all cases under ambient RH of 90% or lower. This robust relationship is consistent with the observation that aerosols in the boundary layer were predominantly of urban origin.

The ambient scattering coefficient per dry PM2.5 mass is 5.0 ± 2.2 m$^2$/g (mean and one standard deviation), and the ambient extinction per dry PM2.5 mass centers at 5.3 m$^2$/g. The dry scattering per dry PM2.5 is 3.6 ± 1.3 m$^2$/g. Mass scattering and extinction efficiencies (MSE and MEE, respectively) for total aerosols (not truncated at 2.5 $\mu m$ aerodynamic) are expected to be slightly lower than these values, but are not available owing to the lack of a reliable measurement of coarse mode size distribution and total mass.

Our submicron MEE estimated at 55% RH for our dry OPC volume is 4.6 ± 1.4 m$^2$/g in the boundary layer, and close to previous ship measurement for North America’s boundary layer aerosol of about 3.7 ± 1.3 m$^2$/g at 55% RH [Quinn and Bates, 2005]. Even closer agreement was found for this parameter between our optical techniques.
and the latter for the INDOEX data [Clarke et al., 2002]. The possible volume underestimate of about 20% mentioned earlier in Section 3 would only improve the overlap between these values. The submicron MEE is the scattering coefficient measured behind an impactor with a 50% cut size of 1 μm aerodynamic, adjusted to an RH of 55% using the measured total f(RH), increased by the dry submicron absorption coefficient and divided by the dry OPC aerosol volume integral up to 750 nm (equivalent to 1 μm aerodynamic) and a density of 1.7 g/cm³. And this falls into the range of submicron MEE for non-sea-salt sulfate aerosols (2.9 - 5.3 m²/g) and particulate organic matter (4.4 - 7.6 m²/g), observed over Indian and Atlantic Oceans by Quinn et al. [2002].

A similar variance is associated with the dry submicron MEE computed for a refractive index of 1.59 from our OPC size distribution instead of the nephelometer measurement: 4.1 ± 1.3 m²/g. This is a result of moderate variation in the shape of size distribution. The effective diameter (volume/area*6) of the total distribution (including coarse mode) varied between 260 and 570 nm for the center two thirds of our data.
7 Discussions

7.1 Altitude of 80% AOD Contribution

Because both water vapor and aerosols originate at the planetary surface we expect higher ambient scattering coefficient at the surface and within the planetary boundary layer than in the free troposphere. This has been shown to be the case in clean marine conditions [Shinozuka et al., 2004]. However, wet and dry convective events can inject both gas phase secondary aerosol precursors (e.g., SO$_2$) and primary aerosols (e.g., soot, biomass smoke) into the free troposphere especially during summer in North America. These high scattering layers are often only hundreds of meters thick but are hundreds of kilometers in horizontal extent, and difficult to observe from satellites or to predict using chemical transport models.

In order to evaluate the range of altitudes that dominate AOD over North America we identify the altitude below which column extinction accounts for 80% of the total column AOD. This is plotted as a histogram in Figure 5a for all INTEX-A profiles, and is shown as plus signs on the vertical axis of the profiles in Figure 3. Its uncertainty is mostly driven by the f(RH) error (discussed in section 5.2) and has a median of -24% and +48% for positive and negative f(RH) excursion, respectively. A smaller (~5%) uncertainty results from the lack of measurements below 500 m. Of the 72 profiles, 38 (53%) have more than 80% of the total column AOD below 3000
m, and 53 (74%) below 5000 m. This is usually due to natural and anthropogenic aerosols generated and trapped within the boundary layer as shown in Figures 3b and 3c. We note that in a few cases, pollution from remote sources may have subsided into boundary layer after being transported in the free troposphere [Clarke et al, submitted]. Figure 3a is a variant of this type. In this case, pollution in the boundary layer (<2.0 km) led to moderate scattering coefficients, but relative humidity was low. Air transported from the south in the free troposphere below 5 km was also influenced by anthropogenic aerosols at moderate (50%) relative humidity. This led to an 80% AOD altitude of 3.6 km illustrating the importance not only of high aerosol loading but the influence of relative humidity on AOD. AOD larger than 0.4 were generally associated with high scattering near the surface up to 2.5 km (Figure 5b) primarily due to high aerosol loading and RH.

There are three exceptions to these general features, all of which occurred on July 22. During this flight total aerosol scattering reached values as high as 300 Mm$^{-1}$ in biomass burning plumes near 4 km. Even in these cases, the boundary layer contributed most of the AOD. These biomass burning plumes were dry (~20% RH) and contributed little more than 20% of the total column ambient AOD. The dry scattering values were near 100 Mm$^{-1}$ in the boundary layer, but due to high RH the ambient scattering exceeded ~200 Mm$^{-1}$ accounting for almost 80% of the total column AOD.
Layers with elevated scattering values were observed occasionally at high altitudes on other days but did not result in a large column AOD enhancement. On July 18 (Figure 3d), the biomass plume from Alaskan/Canadian forest fires traveled across the continent to the northeastern Canada, and exhibited a fractional AOD of 0.26 between 7 and 10 km over an otherwise clean marine column (AOD up to 7 km was 0.06). The water uptake was negligible in the dry (ambient RH near 30%) layer thus the column AOD was driven solely by the high aerosol loading aloft. The July 18 and 22 profiles are exceptional but forest fire plumes were not randomly sampled as flights were directed to their location in order to study them.

### 7.2 AOD and its water fraction over the continental US

Here we describe general features of AOD observed over the US mainland, and discuss its variation in terms of the two most important factors, hygroscopicity (related to chemical components) and ambient RH (driven by meteorology) for the given dry aerosol concentration (related to PM 2.5). This assessment is expected to provide input to regional aerosol models that compute the optical properties such as ambient AOD, and to assess remote sensing capability in estimating dry AOD and PM 2.5. The AOD variation is discussed again in Section 7.4 in relation with the boundary layer aerosol mass.

Ambient AOD estimated for the vertical profiles (Section 5.2) are plotted over the continental US map for all times during the experiment in the summer of 2004.
(Figure 6a). Red bars illustrate the dry aerosol scattering integrated over the altitudes (dry AOD) without applying humidity growth rate. The difference (blue bars) indicates the AOD attributed to water uptake. We define the water fraction of AOD, \( W_f \), as

\[
\text{Eqn. 3: } W_f = 1 - \left( \frac{\text{dry AOD}}{\text{ambient AOD}} \right)
\]

The frequency of dry and ambient AOD and \( W_f \) are shown in Figure 6b. Note that individual profiles in the figure are not statistically representative of a specific area, season, meteorology or any other conditions. Local weather alone exposes aerosols to a variety of mixing, transport and humidity conditions that may result in higher variance in AOD and \( W_f \) than what the experiment experienced.

AOD is 0.3 or lower for most cases, and are generally lower over the ocean than over the land, primarily due to airmass type and proximity to sources. However, the air over the ocean off the northeastern Canada and further east was affected by some pollutants which were brought by southwesterly winds from New England and other areas. In contrast, south of about 40°N and away from the land we only encountered small AOD. Two of these profiles sampled outflow that had passed over Pennsylvania. The ambient scattering coefficient was moderate near 50 Mm\(^{-1}\) in 1 - 2 km, but dropped to ~20 Mm\(^{-1}\) at lower altitudes. This suggests that pollutants from the land had been scavenged in the boundary layer or lifted up over cleaner and cooler air. In the other two profiles, the air had circulated over the ocean for at least a week prior to the measurement at all levels, and carried few pollutants.
The AOD over land does not show a clear trend with reference to location, because aerosol sources are closer and transport patterns are more complex than over the ocean (Section 5.1). In one profile (the tallest bar in Figure 6a; omitted in Figure 6b) the ambient AOD was 1.4 due in part to high ambient RH (>90%). Under different wind and humidity patterns the AOD is often lower than 0.1 in this vicinity.

The water fraction varied widely. The high elevation fire aerosols over northeast Canada (Figure 3d), for example, were weakly hygroscopic with little water contribution to AOD (12%), as is indicated by the almost completely red bar located at the far right. The estimated Wf is a function of γ and ambient RH. These two parameters could positively correlate with each other, if, for example, aerosols had been dominated by sea-salt (hygroscopic particles often found in humid air) or dust (hydrophobic particles often found in dry air). For an analysis later it is important to realize that these two factors were found independent for the INTEX-NA data.

One way to demonstrate the relative importance of ambient RH vs. physiochemistry (γ) to the ambient AOD is to simulate the ambient AOD with a fixed ambient RH (say at 80%). The result (Figure 7a) illustrates how much AOD variation is driven by that of γ independent of ambient RH variation. The unusually high ambient AOD case in Figure 6 shows a reduced but still large percentage due to water. Wf (Figure 7b) takes a narrower range of values, 0.46 ± 0.11 (mean and one standard deviation) at 80% RH, than the same parameter simulated with the observed RH (Wf = 0.37 ± 0.15, Figure 6b). Wf simulated for other fixed ambient RH values shows similarly
narrower distributions (Figure 8). These express the degree by which knowing ambient RH can improve estimates of dry-ambient AOD. There are differences in Wf among the profiles for a given RH. Realistic values of hygroscopicity (determined primarily by chemistry and size distribution) are essential in modeling the ambient AOD and in retrieving dry AOD to 10% or better.

### 7.3 Model and satellite retrieval accuracies

So far we have used the measured aerosol dry scattering, its humidity response and the ambient RH to establish ambient AOD. Below, the ambient AOD is recalculated with reasonable uncertainties in the input variables. We claim that the ambient AOD sensitivity revealed from this test can be scaled with error associated with input of $\gamma$ in regional aerosol models. Satellite retrieval of aerosol water fraction and PM2.5 may suffer a similar limitation.

Values of $\gamma$ are rarely available, particularly due to the poorly known influences from organic carbon (OC) fractions [Quinn et al., 2005]. Clarke et al. [submitted] found $\gamma$ to vary by $\pm 0.1$ or less for a given OC fraction. We assume here, for the sake of a sensitivity test, that the regional aerosol models can generate $\gamma$ values to $\pm 0.1$ provided they resolve the OC fraction. An increase in $\gamma (\Delta \gamma)$ by 0.1 in Eqn. 1 results in a 3 - 21% (median 9%) increase in the ambient AOD ($\Delta$AOD) depending on the vertical profile considered and the associated ambient RH (dots in Figure 9). If $\Delta \gamma$
remains near or within ± 0.1, Δ γ and Δ AOD are almost linearly correlated with each other. Similarly, an increase from the observed ambient RH by 5 and 10 percentage points (without any variation in γ imposed) results in an increase in the median ambient AOD of 11% (not shown) and 26% (circles), respectively.

The error in the ambient RH and γ need to be minimized for a model to maintain an uncertainty in the ambient AOD similar to that claimed in the MODIS AOD observation over land (± 0.05 ± 0.15 * AOD [Remer et al., 2005]). Using a simulation with ambient RH increased by 10 percentage points for the measured γ, about two thirds of the 72 profiles lie within the uncertainty in the MODIS best estimate of AOD over land. If the model γ is overestimated by 0.1, then the column effective ambient RH has to be known to ~6 percentage points (squares in Figure 9) in order to maintain similar uncertainties. Downward bias in the input variables is less critical: Even if γ and RH are underestimated by 0.3 and 20%, respectively, most data, those with small AOD in particular, remains within the MODIS uncertainty.

For remote sensing, the length of the vertical bars in Figure 8 provides the expected ranges of uncertainty in translating ambient AOD into dry AOD without using a spectral dependence: These are 15% of the ambient AOD, or 6 – 13% when the RH is known. Using multiple wavelength remote sensing does not help to constrain either γ or water fraction. Figure 10 compares column γ with the Ångström exponent of the ambient AOD. The marker size is proportional to the ambient AOD at 550 nm to better identify measurements with a high signal to noise ratio. The July 18 data
partially affected by the biomass burning plume (squares), for example, show a weakly positive correlation expected for the mixture of biomass burning and urban pollution (low to high change in Ångström exponent and hygroscopicity). However, the relationship between these two parameters is not well defined for the entire experiment. This holds true for a comparison between the water fraction and Ångström exponent (not shown) as well. The Ångström exponent takes a rather narrow range of values, while the various mixture of organic (not hygroscopic) and inorganic (many species of them being hygroscopic) material results in a wide variation in hygroscopicity.

7.4 PM$_{2.5}$$_{proxy}$ vs. AOD

As mentioned earlier, a relation demonstrated between column AOD and near surface integral dry mass, estimated from our integrated distributions (PM$_{2.5}$$_{proxy}$), would support use of remote sensing to assess PM$_{2.5}$ remotely. Our boundary layer PM$_{2.5}$$_{proxy}$ and column AOD show a linear trend (Figure 11). The geometric mean regression is expressed as AOD = 0.019*PM$_{2.5}$$_{proxy}$ (μg/m$^3$) + 0.0022, with R$^2$ of 0.77 (R$^2$ = 0.60 including the outliers). The root mean square of AOD and mass differences from the regression line is 0.076 and 3.3 μg/m$^3$, respectively. The R$^2$ is lowered from that for the actual mass-AOD correlation by the limited precision of the OPC measurement, evident in the scattering comparison with the nephelometer (see Section 3 and Figure 1). Also note that a part of the intercept reflects light attenuation due to particles that do not contribute to the boundary layer mass, such as the stratosphere’s AOD (0.008). The error bars reflect the estimates made in Section
6 for PM2.5proxy and in Section 5.2 for the ambient AOD. In particular, the possible 20% mass underestimate discussed in section 3 may lower the slope to 0.016. We emphasize that this regression is only applicable for summertime US. Application for different seasons or other regions remains to be demonstrated. This figure was made after removing three outliers where ambient AOD > 0.8. These outliers were observed near or above clouds. The air was stagnated in two of them, and flowing rapidly eastward in the other. The ambient RH was high (>90%), and the aerosols were hygroscopic, making these distinct from the other data points.

RH variability alone does not explain all of the remaining outliers. The high elevation biomass burning plume (Figure 3d) manifests itself as a low PM2.5proxy (1.7 µg/m³) high AOD (0.33) case. Since most contribution to AOD was made at 7 km or higher, the AOD is least influenced by the boundary layer aerosol mass. Other profiles with high altitudes of 80% contribution are indicated with small dots in Figure 11, and lie among the normal cases with low or moderate AOD. In practice, chemical transport models or satellites with vertical resolution (e.g., CALIPSO) could identify or exclude cases with high elevation plumes, and increase the predictability of the boundary layer PM2.5 mass.

Although there is a tendency for higher Ångström exponents to lie below the line in Figure 11, this parameter helps to constrain the mass PM2.5 proxy to AOD ratio only to a limited extent. A smaller (< 1.5) ambient Ångström exponent is generally associated with a larger mass per AOD. Due to generally diverse aerosol types at
different altitudes, this relationship is less evident over the column than on a layer by layer basis (not shown). Also, the humidification of aerosols makes the Ångström exponent less sensitive to changes in the size distribution, as was found in Section 4 and Figure 2. Once expanded to a larger number of samples, this approach will give a guideline of the degree to which the use of spectral dependence differentiates the near-surface mass. It remains possible that, in combination with other observable parameters, the wavelength dependence may help improve the remote sensing resolution. However, this investigation using ambient RH, fine mode fraction and location failed to demonstrate this.

Our AOD-PM2.5 relationship overlaps, albeit with a greater slope of regression line, with that found by Wang and Christopher [2003]. They did the comparison on a daily basis with MODIS and ground PM2.5 data in Jefferson County, AL to find a slope of 0.014. Their results show considerably more scatter. This is expected because of their longer sampling time and because the present study compares the nephelometer derived optical depth with OPC derived volume, whereas their relationship is made with spatially averaged satellite and surface data. Our study also explicitly addresses the role of f(RH), as they suggested was needed. The inferred mass is better correlated with the optical properties in our data than it is in the real atmosphere, because we neglect the case by case variations in refractive index and density. The similar trends found by these two independent studies for different locations, timing, measurement techniques and averaging methods provide
confidence in the results, and encourages the use of these approaches for inferring PM2.5.
Figure 5.  
(a) Frequency of height up to which 80% of ambient column AOD exist.  
(b) The 80% AOD height and ambient AOD. A data point with AOD and altitude of 1.4 and 1.6 km is omitted.
Figure 6.  (a) Dry (red) and ambient (blue) AOD pictured over the measurement locations. Each bar represents a vertical profile flown in the summer of 2004. Grey bars indicate the estimated fraction of AOD contributed from the altitudes above DC-8 coverage (upper free troposphere and stratosphere). The tick has a 0.1 increment. (b) Frequency of dry (red) and ambient (blue) AOD. The light extinction for altitudes above DC-8 coverage is not included. One data point, an ambient AOD of 1.4, is not shown. The black bars indicate one minus their ratio, or the water fraction.
Figure 7. Same as Figure 6 except that the ambient AOD is simulated for a constant RH of 80%.
Figure 8. Mean and standard deviation of water fraction simulated for the 72 INTEX-A vertical profiles with the measured and fixed RH. Knowing the ambient RH reduces the error in translating remotely sensed single-wavelength ambient AOD into dry AOD, particularly under low RH associated with shorter bars.
Figure 9. Ambient AOD simulated with positive excursion in $\gamma$ and ambient RH for sensitivity test. The dashed curves indicate the nominal uncertainty in MODIS AOD observations over land.
Figure 10. Column average $\gamma$ compared to the Angstrom exponent of ambient AOD. Dot size is proportional to the ambient AOD. Squares indicate the July 18 data.
Figure 11. The ambient AOD and boundary layer aerosol mass (PM2.5proxy) for the 72 vertical profiles. The regression line for all but 3 outliers (AOD > 0.8) is AOD = 0.019*PM2.5proxy (µg/m³) + 0.022, $R^2 = 0.77$ ($R^2 = 0.60$ including the outliers). Small dots indicate profiles with high altitude of 80% AOD contribution, and the color, ambient Angstrom exponent.
8 Summary

During the INTEX-North America aircraft campaign, we generated vertical profiles of visible light scattering by dry aerosols and its response to water uptake, \( f(\text{ambRH}) \), over the troposphere. Urban/industrial pollutants and forest fire plumes were found at various altitudes depending on the air stability, winds and scavenging processes prior to the measurements. The \( f(\text{RH}) \) was measured at 550nm and its wavelength dependence simulated using the measured size distribution. Applying \( f(\text{ambRH}) \) values defined at 550 nm to other wavelengths could cause a 5 - 7% error at 440 and 675 nm. The ambient AOD was estimated based on these measurements and simulation, and found consistent with the sunphotometer measurements from ground.

About 80% of the total column AOD was found to be below 3 km for 53% of the vertical profiles and below 5 km for 74%. Ambient AOD larger than 0.4 required both high aerosol loading and high RH, and were always found with high contribution from the surface layer up to 2.5 km. Over the US mainland, both the ambient RH and \( \gamma \) are important for determining the water contribution to AOD. Modeling the ambient AOD from dry aerosol size distributions to accuracy comparable to the MODIS AOD determination over land requires input of column effective ambient RH to be known within about 6 percentage points when \( \gamma \) is known to 0.1. Dry AOD inferred from remote sensing without knowledge of column effective RH has a typical error equivalent to 15% of the ambient AOD. This uncertainty is reduced to 6
- 13% when the column effective ambient RH is known. The column Ångström exponent exhibited a relatively narrow range (mostly 1.3 – 1.9), and did not show a trend with the hygroscopicity or the water fraction of ambient AOD, perhaps due to the wide variety of mixing between organic and inorganic material and the negligible concentrations of dust and sea salt. Hence, the wavelength dependence of radiances did not help us constrain evaluation of the dry AOD and mass over the continental US.

Our measured size distribution provided an estimate of boundary layer PM2.5 dry mass (PM2.5\textsubscript{proxy}) to a ~25% accuracy. Representative values of PM2.5\textsubscript{proxy} were compared with column AOD for different aerosol profiles and column effective ambient RH. Ambient AOD correlated well with the boundary layer PM2.5\textsubscript{proxy} (AOD = 0.019*PM2.5\textsubscript{proxy} (\(\mu g/m^3\)) +0.0022, R\(^2\) = 0.77) for 96% of the data in spite of the large variations in vertical aerosol structure. This supports the potential application of satellite derived AOD for the inference of near surface PM2.5. Removing high-ambient-RH (>90%) high-AOD (>0.8) cases appears more effective than use of the wavelength dependence of radiances to remotely sense PM2.5.
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