Constraining climate model simulations of aerosol size distributions over the North Pacific and North America using *in-situ* airborne measurements

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Dedication

This work is dedicated to my mother and father, Barbara and Ian M'Naughton, who supported me emotionally and financially throughout my education. From my mother, I learned creativity and compassion; from my father, integrity and a prairie work ethic. Without their steadfast belief in my abilities, I doubt I would have obtained my Environmental Engineering degree much less my PhD in Oceanography.

I would also like to dedicate this work to my wife Lianne M'Naughton and our son Ezekiel. Lianne is my inspiration and the source of all my self confidence. She is a creative and enthusiastic mother, a brilliant sea turtle and pelagic fisheries researcher, a lovely free-diver and surfer. Throughout this eight year journey of continual self doubt, she has constantly reminded me that I not only could, but that I would complete this work. Ezekiel Makani-keoe is my reminder that family play time is the most important thing in my life. His laughter is motivation at a time when humanity itself is endangering all life on Earth.

Aloha mai, welina mai, aia ka 'ōlelo o ka hana kilo lani
[Aloha and welcome, here is the telling of the study of the sky]

Cameron Stuart M'Naughton, PhD
May 18th 2008, Honolulu, Hawai'i
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Abstract

The effect of aerosols on climate is poorly understood compared to greenhouse gases. Aerosols can scatter and/or absorb solar radiation (the “direct effect”) and modify cloud properties (the “indirect effect”), affecting Earth’s radiation balance and hydrological cycle. Aerosol lifetimes vary from minutes to weeks in the Earth’s atmosphere, so they are heterogeneously distributed in both time and space. Over longer time scales, aerosols can influence climate through sulfur (e.g. CLAW Hypothesis) and iron (e.g. Iron Hypothesis) biogeochemical cycling.

Determination of natural and anthropogenic aerosol effects on past and future climate can only be achieved using global climate models (GCM’s). Satellites allow global measurements of the present-day atmosphere, but require calibration/validation by observations in-situ. Ground- and ship-based observations are confined to the surface boundary layer which can be decoupled from overlying layers and the free troposphere. Here I use in-situ aircraft measurements from five NASA and NSF airborne field campaigns conducted over the North Pacific and North America between 2001 and 2006 to establish a reduced set of airmass types that are stratified vertically, by source region and according to processes governing their characteristics. For each airmass type the aerosol size distribution, mixing state, optical properties and chemical composition are summarized and discussed.

In this study I found, i) parameterizations of background free troposphere aerosol overestimate extinction by ~50%, minimizing the differences between pre-industrial versus contemporary radiative forcing, ii) meteorological model errors in water vapour mixing
ratio can overwhelm the influence of composition-dependent aerosol hygroscopicity on radiating forcing, iii) aerosol number in convective cloud outflow over North America in summer were reduced by $1/e$ after ~2 days with no detectable increase in aerosol mass or decrease in SO$_2$, illustrating the need to simulate both mass and number distributions in order to predict aerosol indirect effects, iv) in April 2006 the deposition of Asian pollution and dust to the subtropical Eastern North Pacific could result in a 25% increase in surface ocean nitrogen and a 10-30% increase in iron, SeaWiFS/MODIS satellite retrievals indicate an 8-9% increase in chlorophyll in the same region two weeks after the event.
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1 Available from http://ipcc-wg1.ucar.edu/wg1/wg1-figures.html
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Figure 5.2 – Assessment of number closure between the lognormal fits to the unheated and refractory aerosol distribution and to their ratio (RCN ratio) compared to the 1-Hz CN counter data.

Figure 5.3 – Same as figure 5.1 but for data collected in the FT near Alaska.

Figure 5.4 – Same as figure 5.2 but for data collected in the FT near Alaska.

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indicates a fetch of ~3000 km over a 4-5 day period. For the INTEX-B average wind speed, 8.0 m s⁻¹, 3000 km represents a BL residence time of ~4.3 days. The "polluted" MBL back trajectories (bottom) might represent aged pollution entraining into the MBL after being transported slowly across the ENP in the LT.

**Figure 5.7** - Mean aerosol volume distribution for the FT near Hawai‘i (top-left). Regressions of CaCO₃ vs. size distribution integral volume multiplied by a Chinese Loess bulk density of 2.06 g cm⁻³ results in an 11 wt% estimate of the calcite content (top-right). Volatile and refractory accumulation-mode chemistry is summarized in the pie chart and is dominated by ammonium sulfate (bottom-left). Aerosol nitrate is highly correlated with calcium (bottom-right).

**Figure 5.8** - Same as figure 5.7 but for FT Asian aerosol measured near Alaska.

**Figure 5.9** - Regression of molar equivalents of total supermicrometer sulfate aerosol (top-left) and Sₗₗₒ (top-right) versus calcium in the FT near Hawai‘i. Regression of molar equivalents of aerosol nitrate (bottom-left) and Nₗₗₒ (bottom-right) versus calcium.

**Figure 5.10** - Same as figure 5.9 but for FT Asian aerosol measured near Alaska.

**Figure 5.11** - Sulfate (top-left) and sulfate plus nitrate (top-right) neutralization versus molar equivalents of calcium in the FT near Hawai‘i. Regressions of excess sulfate (bottom-left) and excess sulfate plus nitrate (bottom-right) versus molar equivalents of calcium.

**Figure 5.12** - Same as figure 5.11 but for FT Asian aerosol measured near Alaska.

**Figure 5.13** - Geochemistry ratios for major cations in Asian Dust (top row) measured near Hawai‘i. Anion-cation imbalances (bottom-left) can largely be attributed to the missing CO₃⁻ ion from calcite or dolomite (bottom-center and right).

**Figure 5.14** - Same as figure 5.13 but for FT Asian aerosol measured near Alaska.

**Figure 5.15** - DIAL LIDAR profile of aerosol depolarization during the May 4th INTEX-B flight.
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Figure 5.17 – DIAL LIDAR Ozone along the DC-8 flightpath on May 4th, 2006. Barely discernable through the central peak in O₃ (0:00 UTC) is the in-situ measurements of Avery et al., mapped to the local field in real time via the ICATS data system.

Figure 5.18 – Excess sulfate and sulfate plus nitrate for FT aerosol measured in upper troposphere airmasses rich (> 800 fCi std m⁻³) stratospheric airmass tracer ⁷Be.

Figure 5.19 – Excess (SO₄²⁻ + NO₃⁻) versus ⁷Be shows no clear trend indicating that higher excess nitrate values are a result of higher emissions of nitrate precursors at the source and not re-exposure to stratospheric sulfuric and/or nitric acid.

Figure 5.20 - Same as figure 5.9 but for CBL aerosol measured in Central Highlands of Mexico.

Figure 5.21 - Same as figure 5.11 but for CBL aerosol measured in Central Highlands of Mexico.

Figure 5.22 - Same as figure 5.13 but for CBL aerosol measured in Central Highlands of Mexico.

Figure 5.23 – Dust lifting off former lakebeds on the outskirts of Mexico City on March 19th, 2006. Note the burn scars in the lower left portion of the image and the intense light extinction in this unprocessed image of the Mexico City boundary layer.

Figure 5.24 – Dust devil with a vertical extent of ~>1 km over agricultural land southwest of Mexico City during the March 12th, 2006 INTEX-B flight. This image has been colour and contrast enhanced.

Figure 5.25 – Principle component 2 versus PC-3 for the eleven-year MLO record. When shaded by major ion mass fractions airmasses of unique character can be identified as labelled. Independent confirmation of the aerosol character is assessed using TSI nephelometer angstrom exponent. Volcanic and pollution dominated aerosol are are found in the central PC-2 values while
supercmicrometer dust and nitrate are found in the more negative PC-2 values.

**Figure 5.26** – Principle component 2 versus PC-3 and shaded by ammonium neutralization of sulphate and nitrate. The INTEX-B data are mapped into the parameter space and labelled along with other significant events from the 11-year record.

**Figure 5.27** – Degree of sulphate neutralization by ammonium as a function of aerosol calcium (left). Degree of sulphate plus nitrate neutralization by ammonium as a function of aerosol calcium (right). Both plots are shaded by scattering Angstrom exponent. High values indicate scattering dominate by accumulation mode aerosol, low values indicate scattering dominated by supermicrometer dust.

**Figure 5.28** – Excess sulphate aerosol as a function of aerosol calcium (left). Excess sulphate plus nitrate as a function of aerosol calcium (right). Both plots are shaded by scattering Angstrom exponent. High values indicate scattering dominate by accumulation mode aerosol, low values indicate scattering dominated by supermicrometer dust.

**Figure 5.29** – Ratio of aerosol nitrate to total nitrate as a function of aerosol calcium. Data are shaded by scattering Angstrom exponent. High values (red-shading) indicate scattering dominate by accumulation mode aerosol, low values (blue-shading) indicate scattering dominated by supermicrometer dust.

**Figure 5.30** – STEM2K3 predictions of dust mass (μg std m⁻³) in the 5.4 km layer (top); 3 km layer (middle); and 1 km layer (bottom).

**Figure 5.31** – Aerosol scattering ratio measured by the DIAL LIDAR during the April 23rd 2006 INTEX-B Flight. Anthropogenic pollution and Asian Dust are entraining into the MBL (~1-1.5 km) from the FT. Note the “ultraclean” layer above the dust. In the clean layer refractory CN ~0 cm⁻³ and Ozone is ~25 ppbv indicative of the marine stratus cloud outflow “buffer layer”.

**Figure 5.32** – Aerosol depolarization ratio measured by the DIAL LIDAR during the April 23rd INTEX-B flight. High returns above the MBL are indicative of non-
spherical dust while the spherical MBL sea salt and the FT pollution aerosol do not depolarize the LIDAR return.

**Figure 5.33** – Scattering Angstrom exponent plotted along the April 23rd, 2006 DC-8 flight track. Markers are scaled by scattering intensity at 550 nm and indicate the presence of dust directly above the MBL inversion and its entrainment near 30°N, 165°W.

**Figure 5.34** – Same as figure 5.33 but shaded by fRH at 80% RH. Note the suppression of f(RH) in the MBL at 30°N, 165°W, compared to 37°N, 161°W due to the entrainment of Asian Dust.

**Figure 5.35** – April (top-left) and May (top-right) 2003-07 monthly averaged surface ocean chlorophyll retrievals from the 9 km resolution merged SeaWiFS/MODIS satellite retrievals. The bottom panels plot the same data but for the two week period of the April 2006 dust storm (bottom-left) and the two week period after the dust storm (bottom-right). Chlorophyll concentrations north of Hawai‘i, especially near 30°N, 165°W are elevated in the two weeks after the dust storm. This is the region where the NASA DC-8 measured Asian dust in the MBL after it entrained from the FT.

**Figure 5.36** – TRMM satellite retrievals of precipitation for the weeks of April 22-30 and May 1-8, 2006. Precipitation north of 30°N is associated with the passage of two frontal systems. In each case the warm sector of the front (south of 30°N) contained Asian pollution and dust which is likely being removed by wet deposition. A deeper (6-8 km) convective cell formed NE of Hawai‘i on April 30th, when both the DC-8 and the Mauna Loa Observatory were recording Asian pollution and dust in the FT near Hawai‘i.

**Figure 5.37** – Chlorophyll histograms between 20-30°N and 140-180°W for the maps shown in figure 5.35. Chlorophyll concentrations the week of the dust storm are no different than the April mean when the outliers skewing the 2003-07 April mean are ignored. Data from two weeks after the dust storm are significantly higher than the 2003-07 May average and the two weeks prior to the dust event. Using either the median or the mean the histograms
show an 8-9% increase in chlorophyll two weeks after the April 15th-30th dust storm period indicative of a biological response to the input of anthropogenic nitrogen and/or mineral dust, i.e. iron.

**Figure 5.38** – Top panel is the time series of 8-day average 2006 SeaWiFS/MODIS chlorophyll retrievals between 20-30°N and 140-180°W (red) compared to the 2003-07 monthly averages (green line, +/-1σ dashed line). Monthly averages from 1989-2006 in-situ chlorophyll measurements at Station ALOHA are shown as blue lines, the 2006 data as blue squares. Bottom panel records the night time measurements of total nitrogen (green) and calcium (black) at Mauna Loa and show that calcium measured on April 30th is the 28th largest event in the 12-year record.

**Figure 5.39** – April (top-left) and May (top-right) 1998-2007 monthly averaged surface ocean chlorophyll retrievals from the 9 km resolution SeaWiFS satellite retrieval. The bottom panels plot the same data but for the two week period of the April 1999 dust event (bottom-left) and the two week period after the dust storm (bottom-right). Chlorophyll concentrations north-east of Hawai‘i are elevated in the two weeks after the dust storm. This is the region where the NASA P3-B measured Asian dust and pollution above the trade-wind inversion during the PEM Tropics B mission [Clarke et al., 2001].

**Figure 5.40** – Chlorophyll histograms between 20-30°N and 140-180°W for the maps shown in figure 5.39. Chlorophyll concentrations the week of the dust storm are less than the April mean. Data from two weeks after the dust storm are significantly higher than the 1998-2007 May average and the two weeks prior to the dust event. Using either the median or the mean the histograms show an 8% increase in chlorophyll two weeks after the April 7th-22nd dust storm period, indicative of a biological response to the input of anthropogenic nitrogen and/or mineral dust, i.e. iron.

**Figure 5.41** – Top panel is the time series of 8-day average 1999 SeaWiFS chlorophyll retrievals between 20-30°N and 140-180°W (red) compared to the 1998-
2007 monthly averages (green line, +/-1σ dashed line). Monthly averages from 1989-2006 in-situ chlorophyll measurements at Station ALOHA are shown as blue lines, the 1999 data as blue squares. The bottom panel records the night time measurements of total nitrogen (green) and calcium (black) at Mauna Loa and show that calcium measured on April 15-18th is the largest dust transport event measured during the 12-year MLO record.
1.0 Introduction

1.1. Modeling atmospheric aerosols with global climate models

In 1979, Eric Shettle and Robert Fenn published the first comprehensive inventory of atmospheric aerosol size distributions and refractive indices. Measurements prior to the mid 1960’s were available but Shettle and Fenn were the first to include the effects of relative humidity on aerosol optical properties. Their parameterization was developed using in-situ measurements of atmospheric aerosols from ground-based and airborne platforms primarily for estimating light transmittance, angular light scattering distributions, contrast reduction, and sky radiances.

In 1985, the members of the British Antarctic Survey discovered the Antarctic “Ozone Hole”. This development lead to the 1989 signing of the Montreal Protocol and represents a paradigm shift in man’s understanding of our ability to directly affect the composition of the Earth’s atmosphere. Subsequently, the stratosphere, ozone-depleting CFC’s, and other greenhouse gases (GHG’s) received extensive study. The effects of suspended particulate matter on Earth’s radiation balance received much less attention.

By the 1980’s and early 1990’s, it became clear that not only long-lived GHG’s but also shorter-lived atmospheric aerosols, both natural and anthropogenic, had the ability to affect the Earth’s radiation balance. We learned that aerosols participate directly in the Earth’s radiative balance by scattering and absorbing incoming solar radiation [Charlson et al., 1992; Clarke and Noone, 1985]. And, that they participate indirectly via their role as cloud condensation nuclei (CCN) [Albrecht, 1989; Twomey et al., 1987].
In 1991, Guillaume d’Almeida, Peter Koepke and Eric Shettle co-authored an updated inventory of atmospheric aerosols and their radiative effects entitled, "Atmospheric Aerosols: Global Climatology and Radiative Characteristics". Their goal was to provide the emerging modeling and remote sensing communities with an inventory of aerosol size distributions and optical properties. This work is considered a milestone as it provided the scientific community with improved aerosol formulation for the investigation of the effects of atmospheric aerosols on the Earth’s radiation balance.

1.1.1. Recent advances in modeling the aerosol size distribution

Computer models used to study the general circulation of the Earth’s oceans and atmosphere have developed to include transport and interactions of atmospheric trace gases and aerosols. The first of these global climate models (GCM’s) were limited not only by computing power but also by our fundamental lack of understanding of the complexity of feedbacks between Earth’s physical, chemical and biological systems. Computing power and the use of the internet increased exponentially during the 1990’s. As computing power and software algorithms evolved, so did global climate models. GCM’s and regional scale chemical transport models (CTM’s) evolved by including increasingly complex atmospheric dynamics and chemical kinetics at higher spatial and temporal resolutions.

Hess et al. [1998], developed the Fortran-based software package, OPAC, or Optical Properties of Aerosols and Clouds with aerosol parameterizations based on Shettle and Fenn [1979], Deepak and Gerber, [1983], d’Almeida et al. [1991] and Koepke et al. [1997]. OPAC allowed GCM’s and CTM’s to incorporate aerosol optical
properties as well as the effects of relative humidity into their radiative transfer calculations by allowing the user to generate a series of aerosol "types" based on an their inventory of aerosol "components". These could be mixed in order to better represent the complex nature of the ambient atmospheric aerosol population. Table 1.1 is a reproduction of Hess et al., Table 1c which tabulates the aerosol components available in OPAC. OPAC assumes log-normally distributed size distributions and Table 1.1 shows the number median radius ($r_{\text{modN}}$), volume median radius ($r_{\text{modV}}$), geometric standard deviation of the distribution ($\sigma_g$), the minimum and maximum diameters over which the distribution is integrated, as well as the particle density ($\rho$), and the aerosol mass per cubic meter of air, integrated over the size distribution and normalized to 1 particle per cubic centimeter of air ($M^*$).

Calculations of aerosol optical properties that use Mie scattering theory require as input an aerosol number distribution. When Hess et al. developed OPAC, GCM's and CTM's did not track aerosol number but instead simulated only aerosol mass. Thus the $M^*$ parameter is a key component of OPAC which allows the models to convert their currency, aerosol mass, into aerosol number and thus aerosol optical properties. Accurately calculating aerosol number from simulations of aerosol mass became even more important as the significance of the aerosol indirect effect became more apparent. As I will demonstrate OPAC and other parameterizations of the aerosol size distribution replicate ambient aerosol number over optically significant sizes with reasonable accuracy. However, the parameterization's representation of sizes relevant to aerosol number and thus CCN are poor.
The $M^*$ parameter can be calculated for any aerosol size distribution by taking the ratio of the integral mass distribution to that of the number distribution. For any aerosol number distribution described by a 3-parameter log-normal curve the mass distribution ($p^*$volume distribution) can be efficiently computed from the number distribution (and vice versa) using equation 7.52 from Seinfeld and Pandis [1998].

\[
\ln \overline{D_{pgv}} = \ln \overline{D_{pg}} + 3 \ln^2 \sigma_g
\] (1.1)

where $D_{pgv}$ and $D_{pg}$ refer to the volumetric and number median diameters (VMD and NMD), respectively.

Aerosols rarely exist as individual components in the Earth’s atmosphere. In fact they often exist as internal and external mixtures of several components. Since generalized aerosol models were required, Hess et al. grouped the aerosol components into representative aerosol types that could be used to describe atmospheric aerosols on a global basis. Table 1.2 is a reproduction of Hess et al.’s Table 4 which includes the mass mixing ratios they determined for these aerosol types. The bellwether OPAC model is a widely accepted algorithm as evidenced by Hess et al. receiving 298 citations in the peer-reviewed literature by December, 2006.

This computationally efficient method of describing aerosol optical properties was readily incorporated into GCM’s and CTM’s through the use of lookup tables. An example of the lookup table from the University of Iowa’s regional CTM, “STEM-2K3” is shown in Table 1.3. The aerosol mass within a specific model grid-cell is first converted to aerosol number using $M^*$. Each column of the table represents a specific wavelength of light ($\lambda=0.25$, 0.3, 0.4, 0.55, 0.7, 1.5 $\mu$m) whereas each row represents an
individual value of ambient relative humidity (RH=0, 50, 70, 80, 90, 95, 98, 99%).

Aerosol extinction for a given wavelength and relative humidity is determined by multiplying the aerosol number density by the corresponding value in the look-up table.

Extinction at intermediate values of relative humidity is computed by linear interpolation.

Similar tables exist for both single scatter albedo (SSA), and asymmetry parameter (g) allowing models to compute radiative forcing due to aerosols.

Table 1.1 – Table 1c from Hess et al., [1998] listing OPAC aerosol components.

<table>
<thead>
<tr>
<th>Component</th>
<th>File name</th>
<th>$\sigma$</th>
<th>$r_{max}$ (µm)</th>
<th>$r_{med}$ (µm)</th>
<th>$r_{min}$ (µm)</th>
<th>$r_{med}$ (µm)</th>
<th>$\rho$ (g cm$^{-3}$)</th>
<th>$M^*$ (µg m$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Insoluble</td>
<td>INSO</td>
<td>2.51</td>
<td>0.471</td>
<td>6.00</td>
<td>0.005</td>
<td>20.0</td>
<td>2.0</td>
<td>2.37E1</td>
</tr>
<tr>
<td>Water-soluble</td>
<td>WASO</td>
<td>2.34</td>
<td>0.0212</td>
<td>0.15</td>
<td>0.005</td>
<td>20.0</td>
<td>1.8</td>
<td>1.34E-3</td>
</tr>
<tr>
<td>Soot</td>
<td>SOOT</td>
<td>2.00</td>
<td>0.0118</td>
<td>0.05</td>
<td>0.005</td>
<td>20.0</td>
<td>2.2</td>
<td>8.62E-1</td>
</tr>
<tr>
<td>Sea salt (acc. mode)</td>
<td>SSAM</td>
<td>2.03</td>
<td>0.209</td>
<td>0.04</td>
<td>0.005</td>
<td>20.0</td>
<td>2.2</td>
<td>2.24E2</td>
</tr>
<tr>
<td>Sea salt (con. mode)</td>
<td>SSCM</td>
<td>2.03</td>
<td>1.73</td>
<td>7.90</td>
<td>0.005</td>
<td>60.0</td>
<td>2.2</td>
<td>2.78E-2</td>
</tr>
<tr>
<td>Mineral (acc. mode)</td>
<td>MINM</td>
<td>1.95</td>
<td>0.07</td>
<td>0.27</td>
<td>0.005</td>
<td>20.0</td>
<td>2.6</td>
<td>5.53E0</td>
</tr>
<tr>
<td>Mineral (con. mode)</td>
<td>MIAM</td>
<td>2.00</td>
<td>0.39</td>
<td>1.60</td>
<td>0.005</td>
<td>20.0</td>
<td>2.6</td>
<td>5.53E0</td>
</tr>
<tr>
<td>Mineral-transported</td>
<td>MITR</td>
<td>2.20</td>
<td>0.50</td>
<td>3.00</td>
<td>0.02</td>
<td>5.0</td>
<td>2.6</td>
<td>1.59E1</td>
</tr>
<tr>
<td>Sulfate droplets</td>
<td>SUSO</td>
<td>2.03</td>
<td>0.0695</td>
<td>0.31</td>
<td>0.005</td>
<td>20.0</td>
<td>1.7</td>
<td>2.28E-2</td>
</tr>
</tbody>
</table>
Table 1.2 – Table 4 from Hess et al., [1998] listing aerosol types carried by OPAC.

<table>
<thead>
<tr>
<th>Aerosol types</th>
<th>Components</th>
<th>( N_j ) (cm(^{-3}))</th>
<th>( M_j ) (µg m(^{-3}))</th>
<th>Number mixing ratios (( n_j ))</th>
<th>Mass mixing ratios (( m_j ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Continental clean</td>
<td>total</td>
<td>2600</td>
<td>8.8</td>
<td>1.0</td>
<td>0.591</td>
</tr>
<tr>
<td></td>
<td>water soluble</td>
<td>2600</td>
<td>5.2</td>
<td>1.0</td>
<td>0.591</td>
</tr>
<tr>
<td></td>
<td>insoluble</td>
<td>0.15</td>
<td>3.6</td>
<td>0.577E-4</td>
<td>0.021</td>
</tr>
<tr>
<td>Continental average</td>
<td>total</td>
<td>15 300</td>
<td>24.0</td>
<td>0.458</td>
<td>0.583</td>
</tr>
<tr>
<td></td>
<td>water soluble</td>
<td>7000</td>
<td>14.0</td>
<td>0.261E-4</td>
<td>0.396</td>
</tr>
<tr>
<td></td>
<td>insoluble</td>
<td>0.4</td>
<td>9.5</td>
<td>0.542</td>
<td>0.021</td>
</tr>
<tr>
<td>Continental polluted</td>
<td>total</td>
<td>50 000</td>
<td>47.7</td>
<td>0.314</td>
<td>0.658</td>
</tr>
<tr>
<td></td>
<td>water soluble</td>
<td>15 700</td>
<td>31.4</td>
<td>0.12E-4</td>
<td>0.298</td>
</tr>
<tr>
<td></td>
<td>insoluble</td>
<td>0.6</td>
<td>14.2</td>
<td>0.586</td>
<td>0.044</td>
</tr>
<tr>
<td></td>
<td>soot</td>
<td>34 300</td>
<td>7.8</td>
<td>0.686</td>
<td>0.079</td>
</tr>
<tr>
<td>Urban</td>
<td>total</td>
<td>158 000</td>
<td>99.4</td>
<td>0.177</td>
<td>0.563</td>
</tr>
<tr>
<td></td>
<td>water soluble</td>
<td>28 000</td>
<td>56.0</td>
<td>0.459E-5</td>
<td>0.358</td>
</tr>
<tr>
<td></td>
<td>insoluble</td>
<td>1.5</td>
<td>35.6</td>
<td>0.949E-5</td>
<td>0.298</td>
</tr>
<tr>
<td></td>
<td>soot</td>
<td>130 000</td>
<td>7.8</td>
<td>0.823</td>
<td>0.079</td>
</tr>
<tr>
<td>Desert</td>
<td>total</td>
<td>2300</td>
<td>225.8</td>
<td>0.87</td>
<td>0.018</td>
</tr>
<tr>
<td></td>
<td>water soluble</td>
<td>2000</td>
<td>4.0</td>
<td>0.117</td>
<td>0.033</td>
</tr>
<tr>
<td></td>
<td>mineral (nuc.)</td>
<td>269.5</td>
<td>7.5</td>
<td>0.119</td>
<td>0.033</td>
</tr>
<tr>
<td></td>
<td>mineral (acc.)</td>
<td>30.5</td>
<td>168.7</td>
<td>0.133E-1</td>
<td>0.747</td>
</tr>
<tr>
<td></td>
<td>mineral (c.o.)</td>
<td>0.142</td>
<td>45.6</td>
<td>0.617E-4</td>
<td>0.202</td>
</tr>
<tr>
<td>Maritime clean</td>
<td>total</td>
<td>1520</td>
<td>42.5</td>
<td>0.987</td>
<td>0.071</td>
</tr>
<tr>
<td></td>
<td>water soluble</td>
<td>1500</td>
<td>3.0</td>
<td>0.987</td>
<td>0.071</td>
</tr>
<tr>
<td></td>
<td>sea salt (acc.)</td>
<td>20</td>
<td>38.6</td>
<td>0.132E-1</td>
<td>0.398</td>
</tr>
<tr>
<td></td>
<td>sea salt (c.o.)</td>
<td>3.2E-3</td>
<td>0.9</td>
<td>0.211E-5</td>
<td>0.021</td>
</tr>
<tr>
<td>Maritime polluted</td>
<td>total</td>
<td>9000</td>
<td>47.4</td>
<td>0.422</td>
<td>0.160</td>
</tr>
<tr>
<td></td>
<td>water soluble</td>
<td>3800</td>
<td>7.6</td>
<td>0.222E-2</td>
<td>0.814</td>
</tr>
<tr>
<td></td>
<td>sea salt (acc.)</td>
<td>20</td>
<td>38.6</td>
<td>0.222E-2</td>
<td>0.814</td>
</tr>
<tr>
<td></td>
<td>sea salt (c.o.)</td>
<td>3.2E-3</td>
<td>0.9</td>
<td>0.356E-6</td>
<td>0.019</td>
</tr>
<tr>
<td></td>
<td>soot</td>
<td>5180</td>
<td>0.3</td>
<td>0.576</td>
<td>0.006</td>
</tr>
<tr>
<td>Maritime tropical</td>
<td>total</td>
<td>6600</td>
<td>20.8</td>
<td>0.983</td>
<td>0.058</td>
</tr>
<tr>
<td></td>
<td>water soluble</td>
<td>590</td>
<td>1.2</td>
<td>0.983</td>
<td>0.058</td>
</tr>
<tr>
<td></td>
<td>sea salt (acc.)</td>
<td>10</td>
<td>19.3</td>
<td>0.167E-1</td>
<td>0.928</td>
</tr>
<tr>
<td></td>
<td>sea salt (c.o.)</td>
<td>1.3E-3</td>
<td>0.3</td>
<td>0.217E-5</td>
<td>0.014</td>
</tr>
<tr>
<td>Arctic</td>
<td>total</td>
<td>6600</td>
<td>6.8</td>
<td>0.197</td>
<td>0.382</td>
</tr>
<tr>
<td></td>
<td>water soluble</td>
<td>1300</td>
<td>2.6</td>
<td>0.197</td>
<td>0.382</td>
</tr>
<tr>
<td></td>
<td>insoluble</td>
<td>0.01</td>
<td>0.2</td>
<td>0.152E-5</td>
<td>0.029</td>
</tr>
<tr>
<td></td>
<td>sea salt (acc.)</td>
<td>1.9</td>
<td>3.7</td>
<td>0.288E-3</td>
<td>0.544</td>
</tr>
<tr>
<td></td>
<td>soot</td>
<td>5300</td>
<td>0.3</td>
<td>0.803</td>
<td>0.044</td>
</tr>
<tr>
<td>Antarctic</td>
<td>total</td>
<td>43</td>
<td>2.2</td>
<td>0.998</td>
<td>0.910</td>
</tr>
<tr>
<td></td>
<td>sulfate</td>
<td>42.9</td>
<td>2.0</td>
<td>0.109E-2</td>
<td>0.045</td>
</tr>
<tr>
<td></td>
<td>sea salt (acc.)</td>
<td>0.47E-1</td>
<td>0.1</td>
<td>0.123E-3</td>
<td>0.045</td>
</tr>
<tr>
<td></td>
<td>mineral (tra.)</td>
<td>0.53E-2</td>
<td>0.1</td>
<td>0.123E-3</td>
<td>0.045</td>
</tr>
</tbody>
</table>
Table 1.3 – University of Iowa STEM 2K3 model Mie scattering lookup table for aerosol extinction due to sea salt. Columns represent wavelength of light, rows are for differing relative humidities.

<table>
<thead>
<tr>
<th>C** sea salt</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt; 9.132E-04,9.455E-04,9.934E-04,1.037E-03</td>
</tr>
<tr>
<td>&gt; 2.255E-03,2.304E-03,2.412E-03,2.536E-03</td>
</tr>
<tr>
<td>&gt; 2.814E-03,2.880E-03,3.005E-03,3.164E-03</td>
</tr>
<tr>
<td>&gt; 3.378E-03,3.445E-03,3.593E-03,3.777E-03</td>
</tr>
<tr>
<td>&gt; 4.757E-03,4.825E-03,5.006E-03,5.252E-03</td>
</tr>
<tr>
<td>&gt; 6.929E-03,7.044E-03,7.249E-03,7.560E-03</td>
</tr>
<tr>
<td>&gt; 1.199E-02,1.214E-02,1.238E-02,1.280E-02</td>
</tr>
<tr>
<td>&gt; 1.832E-02,1.849E-02,1.878E-02,1.930E-02</td>
</tr>
</tbody>
</table>

The OPAC model allowed the global parameterization of atmospheric aerosols and their optical properties. Mass of each aerosol type was allowed to vary as a function of time through dynamic processes such as primary aerosol sources, condensation or evaporation of aerosol mass, advection, dispersion, diffusion, wet/dry deposition and to a limited extent gravitational settling. The parameterization, however, is limited in that dynamic processes that affect the aerosol component mixing ratios, mass median diameters or the distribution’s standard deviation were typically ignored. Examples of these processes include:

- nucleation (gas-to-particle conversion),
- condensational growth; evaporative loss,
- coagulation (conservation of mass but not number; a process that can create internal mixtures from external mixtures),
- particle activation and cloud scavenging/processing,
- heterogeneous chemical transformations,
• size dependent particle sources/sinks (e.g. sea salt aerosol generation as a function of wind-speed/sea-state or gravitational settling of mineral dusts during long-range transport).

In addition, the OPAC model considered only a limited number of aerosol components because the chemical composition of the atmospheric aerosol was, at the time, poorly constrained. As an example, OPAC carries the single component “Soot” to represent light absorbing carbon (LAC). Recent studies have shown that light absorbing carbonaceous species include black carbon (“soot”), “brown carbon”, and humic like substances (HULIS) which have differing spectral dependencies of absorption [Clarke et al., 2007; Graber and Rudich, 2006; Kirchstetter et al., 2004]. Also, state-of-the-art models should consider aerosol component mixtures in order to accurately model amplification of light absorption by inorganic and organic aerosol coatings [Fuller et al., 1999; Schnaiter et al., 2005a].

Finally, aerosols specified by type (e.g. urban pollution), exhibit temporal (minutes to seasons) and spatial (regional to global) variations. Contemporary examples are the urban pollution from the developing economies of India and China. China’s industrial power production is fueled by high-sulfur coal resulting in a high mass fraction of anthropogenic sulfate as well as organic aerosols [Bahreini et al., 2003]. Emissions from the Indian sub-continent are commonly referred to as the “Indian Brown Cloud” because they contain a high proportion of light-absorbing carbonaceous aerosols derived from fossil- and bio-fuel use [Guazzotti et al., 2003; Mayol-Bracero et al., 2002].

Within the existing OPAC model framework, when urban pollution from these regions are classified as, “Continental Polluted”, or “Maritime Polluted”, their extensive
aerosol properties such as total aerosol mass and extinction would be allowed to vary. However, the modeled aerosol field will have identical intensive optical characteristics such as SSA, Ångstrom exponent, and f(RH); a significant limitation.

In 2001, and again in 2007 [IPCC], aerosols were identified as one of the largest source of uncertainty when simulating the Earth’s radiative balance. Figure 1.1 is a reproduction of the IPCC Working Group I (Physical Basis of Climate Change) figure summarizing uncertainties associated with determining radiative forcing in the Earth’s climate system.

The uncertainty in aerosol radiative forcing, compared to that of GHG’s, is due to their dynamic nature, their relatively short atmospheric lifetime, and the complexity of their interaction in the Earth’s hydrological cycle [Lohmann and Lesins, 2002; Penner et al., 2004; Raes et al., 2000; Ramanathan et al., 2001]. The difficulty in modeling the global aerosol population was well known even to Shettle and Fenn, [1979] when they recognized that:

_Given the natural variability of the atmospheric aerosol almost any aerosol model is supported by some measurements and no model (or set of models) will be consistent with all measurements._

The Aerosol Model Intercomparison Initiative (AeroCom) was created in 2003 to provide a platform for detailed evaluations of aerosol simulations in global models. AeroCom’s approach is to evaluate the performance of global aerosol models through model comparisons, algorithm development for aerosol sources/sinks and dynamics and by comparisons to empirical observations. The goal is to understand model differences,
relative performance, identify uncertainties, and thereby improve simulations of aerosol properties [Kinne, 2006; Penner et al., 2006; Schulz et al., 2006; Textor et al., 2006].

AeroCom's state-of-the-art aerosol models are imbedded inside so-called "driver models" which uniquely simulate atmospheric dynamics and thermodynamics. Since the driver models simulate these processes with different mathematical formulae it is often a challenge to compare aerosol model performance. An example of this limitation is differences in the driver model simulation of water vapour and/or temperature. Even when two independent aerosol models predict a similar budget of aerosol at a particular location, differences in the relative humidity field will affect the predicted ambient aerosol optical properties. This difficulty is independent of aerosol model differences in prescribing aerosol sources and sinks; a term which is often standardized when investigating differences associated with aerosol dynamics [Textor et al., 2006].

In general, chemical transport models (CTM's) calculate aerosol size distributions "offline" based on the prescribed meteorology from the "driver-models". Global climate models (GCM's) predict aerosol size distributions "on-line" using the models' internal meteorology. Thus GCM's are considered prognostic whereas CTM's are prognostic in-so-far as the driver-model is operating prognostically.
Figure 1.1 - (A) Global mean radiative forcings (RFs), grouped by agent type. Anthropogenic RFs and the natural direct solar RF are shown. Columns indicate other characteristics of the RF; efficacies are not used to modify the RFs shown. Time scales represent the length of time that a given RF term would persist in the atmosphere after the associated emissions and changes ceased. No CO2 time scale is given, as its removal from the atmosphere involves a range of processes that can span long time scales, and thus cannot be expressed accurately with a narrow range of lifetime values. (B) Probability distribution functions (PDFs) from combining anthropogenic RFs in (A). Three cases are shown: the total of all anthropogenic RF terms (block filled red curve); LLGHGs and ozone RFs only (dashed red curve). and aerosol direct and cloud albedo RFs only (dashed blue curve). Surface albedo, contrails and stratospheric water vapour RFs are included in the total curve but not in the others. For all of the contributing forcing agents, the uncertainty is assumed to be represented by a normal distribution (and 90% confidence intervals) A one-million point Monte Carlo simulation was performed to derive the PDFs (Boucher and Haywood, 2001). Natural RFs (solar and volcanic) are not included in these three PDFs. Climate efficacies are not accounted for in forming the PDFs (from [IPCC, 2007]).

1 Available from http://ipcc-wg1.ucar.edu/wgl1/wg1-figures.html
1.1.2. Model representations of the aerosol size distribution

In general there are three schemes which aerosol models use in order to describe the aerosol size distribution. Each scheme has its own advantages and disadvantages and in some cases the aerosol models use different schemes simultaneously to represent different aerosol processes. The simplest scheme for representing the aerosol size distribution is the bulk scheme. Bulk aerosol algorithms use prescribed aerosol size distributions, mixing ratios and optical properties to represent the aerosol size distribution. An example of the bulk scheme is the previously discussed OPAC inventory whereby the model varies only the total aerosol mass for each component or aerosol type. Bulk schemes usually use log-normal distributions with fixed median diameters and standard deviations. The second scheme is the modal approach. The comprehensiveness of the approach increases with the number of aerosol moments treated as prognostic variables; for example, number, mass or both, and number of modes employed. In general, single-moment algorithms choose aerosol mass as the prognostic variable and do not track aerosol number. When modeling the aerosol indirect effect, tracking aerosol number is critical and can only be accurately modeled using a two-moment approach, i.e. resolving both aerosol mass and number. Most modal schemes consider log-normally distributed aerosol mass and/or number concentration but use fixed standard deviations ($\sigma_b$). The third type of scheme is the bin scheme (also called sectional or spectral models). This approach uses a series of aerosol size bins in order to model the aerosol size distribution. Accuracy of this method increases with the number of bins, but at the cost of computation
efficiency. Table 4 from Textor et al. [2006], summarizes the aerosol schemes used by the current AeroCom models.

Aerosol models participating in the AeroCom project which employ the aerosol binning scheme have between 8 and 41 total bins. In most models these bins are assigned to specific aerosol components. For example, the NASA GISS ModelE aerosol model contains 13 bins; 2 for SS, 4 for DU, 4 for DU/SO4 (used for heterogeneous reactions) but single bins only for BC, POM and SO4. A higher resolution, two-moment sectional aerosol model, TOMAS, developed by Adams and Seinfeld [2002], uses 30 evenly spaced logarithmic bins between 0.01 and 10.0 \( \mu \)m. This microphysical model tracks both aerosol number and mass, has been incorporated into the NASA GISS GCM, and has been used to study the effects of both sulfate and sea salt on CCN populations [Pierce and Adams, 2006].

From Table 4 of Textor et al. [2006] it is evident that many models employ a single bin to represent important aerosol components such as sulfate or particulate organic matter (POM). While in general a specific wavelength dependent mass extinction efficiency \( \alpha_{\text{ep,\lambda}} \) can be assigned to accumulation mode aerosols such as sulfates, observations have shown that species like POM can exist at very different median diameters depending on their source [Clarke et al., 2007]. Different median diameters lead to different extinction efficiencies [Boucher and Anderson, 1995] and absorption enhancement by coating absorbing material [Fuller et al., 1999; Schnaiter et al., 2005b] which affect direct radiative forcing.

Also of concern to is how the simulated aerosol number distribution behaves when aerosol are activated to become cloud condensation nuclei. In other words, how
well are the modal or binning schemes representing both the size and the number of potential CCN and thus the aerosol indirect effects? Because of the recognized difficulty in estimating aerosol number in the Aitken mode and because of the differing cloud microphysical schemes employed by the driver-models, only a few of the AeroCom models currently consider the effects of aerosols on clouds (ARQM, PNNL and UIO_GCM, [Textor et al., 2006]).

Finally, in order to evaluate the CLAW Hypothesis [Charlson et al., 1989], Iron Hypothesis [Martin, 1990], and human-induced climate change; GCM’s will be required to couple physical processes with biogeochemical feedbacks between the ocean and the atmosphere. As an example, future models will be required to simulate not only the radiative properties of aeolian dust over the solar spectrum but also size fractionation during long-range transport because clay and silt sized particulate differ chemically [Lafon et al., 2006; Liu, 1985].

1.1.3. Model treatments of aerosol mixtures: internal versus external mixing

Aerosols are solid or liquid particles suspended in the atmosphere. They can be emitted as particles and are labeled as primary aerosol (e.g., soot, mineral dust, sea salt), or they can be formed from gas-phase precursors (H$_2$SO$_4$, NH$_3$, volatile organic carbon) and are labeled as secondary aerosol. Some aerosol are homogeneous in composition, for example pure sulfuric acid, H$_2$SO$_4$ (l), or aerosol can be heterogeneous, (e.g. sea salt). Additionally, condensation of gaseous precursors onto primarily aerosol or coagulation between primary and secondary aerosol can produce internally mixed particles with separate phases from external mixtures.
Aerosol mixtures commonly occur whenever clean marine airmasses mix with continental airmasses perturbed by anthropogenic emissions [Quinn and Bates, 2005]. The remote marine aerosol is a mixture of sulfates and sea salt that span four orders of magnitude in particle diameter (i.e. 12 orders of magnitude in mass). Whereas half the Aitken mode ($D_p = 0.01-0.10 \mu m$) sulfate aerosol population is internally mixed with "ultrafine" sea salt particles [Clarke et al., 2006], these ultrafine seasalt particles constitute less than 10% of the total Aitken mode volume. The supermicrometer sea salt particles ($D_p > 1.0 \mu m$) exist as liquid droplets under average ambient relative humidity (80%) in the marine boundary layer. These large aerosol dominate the total volume distribution but are also internally mixed with non-sea salt aerosol sulfate (nss-SO$_4$) derived from condensation and coagulation of secondary aerosol sulfate. The accumulation mode particles ($D_p = 0.1-1.0 \mu m$) contain cloud-processed, volatile and internally mixed volatile and refractory sulfate/sea salt aerosol.

As continental emissions are blown offshore or pristine marine air is blown onshore, airmasses mix. Ignoring the contribution of secondary organic aerosols formed from natural vegetation sources, the anthropogenic aerosols begin as an external mixture of Aitken mode primary "soot" aerosol. The organic carbon (OC) and black carbon (BC), "soot" particulate becomes internally mixed with condensing inorganic ions, (sulfate, nitrate and ammonium) and semi-volatile organic compounds [Bahreini et al., 2003; Quinn et al., 2006]. Time scales of this process range from seconds to hours. Fresh anthropogenic emissions are also associated with supermicrometer anthropogenic aerosols [Seinfeld and Pandis, 1998]. These "urban dusts" are externally mixed with the accumulation mode aerosol population but can develop a coating of volatile inorganic,
OC and BC aerosols as the airmass ages. The scientific question becomes not only, how to simulate this aerosol population’s dynamics and heterogeneous chemistry; but also, how to measure it?

Approximately half the AeroCom models consider these species as external mixtures while the remainder use a combination of external and internal mixing. Empirical studies have documented the need to consider the effects of internally mixing on aerosol optical properties [Fuller et al., 1999; Schnaiter et al., 2005a]. As a result, considerable efforts are being made to improve the mixing processes in these aerosol models.

The information contained within this dissertation will aid the modeling community by documenting the extent of internal versus external mixing commonly observed in the troposphere. I also investigate the relationship between internally mixed aerosol number and internally mixed aerosol volume (i.e. mass).

1.1.4. Modeling aerosol dynamics

Steep gradients in aerosol number and mass exhibit a high degree of variability on horizontal scales of just 100’s of meters and on vertical scales of 10’s of meters [Stull, 2001]. Even while state-of-the-art global aerosol models are improving the fidelity of their aerosol representations, comparisons to ground-based and airborne in-situ measurements remains a challenge due to their inability to model sub-grid scale processes.

Less than half the AeroCom models consider the effects of nucleation, condensation and coagulation. Most global models consider the aging of black carbon (BC) and secondary organic aerosol (SOA) where the solubility of these species increases
over time due to oxidation [Kanakidou et al., 2005]. Only three of the AeroCom models consider cloud processing. As a result, though the direct effect of aerosols can be estimated from these global models, estimating the indirect effect and the broader role of aerosols in the hydrological cycle remains a challenge [Penner et al., 2006].

For this reason higher resolution, zero-dimensional (parcel) models have been developed. These models include detailed treatments of all the relevant microphysical and chemical processes that govern and maintain the aerosol size distribution in the marine boundary layer [Katoshevski et al., 1999; Raes, 1995]. The chief drawback to this approach is that the “Box Models” do not include atmospheric transport processes such as horizontal advection/dispersion.

More sophisticated 1D (Lagrangian) models have also been used to study MBL aerosol populations and to test our understanding of aerosol microphysics [Caffrey et al., 2006; Fitzgerald et al., 1998]. These models require meteorological inputs from a driver-model or employ climatological averages for the region of interest. While 0-D and 1-D models can be used to predict CCN and investigate heterogeneous chemical reactions between aerosol species (e.g. SO$_4^{2-}$ and mineral dust), they cannot be employed globally due to their computational demands.

Finally, regional scale CTM’s with spatial resolutions of 10’s of km’s have also been developed. These have been used successfully for flight planning purposes while operating prognostically during airborne field campaigns [Carmichael et al., 2003]. These models represent a compromise between GCM’s and Lagrangian models but suffer many of the same short-comings. In particular, the regional CTM’s rely on
meteorological and aerosol boundary conditions which themselves may not accurately reflect the ambient atmospheric conditions nor the aerosol population.

1.2. Aerosol in the remote marine boundary layer

In the remote marine environment there are four principle sources of natural aerosols. Sea salt aerosol production by wind and breaking waves is the dominant source of primary aerosol mass while the entrainment of aerosol from the free troposphere is expected to dominate MBL aerosol number concentrations [Katoshevski et al., 1999]. In-situ atmospheric oxidation of reduced sulfur is the third source of MBL aerosol. Once formed, these sulfur oxidation products condense on pre-existing aerosol surface area forming secondary, non-sea salt aerosol sulfate. Under favorable conditions (e.g. high RH, low pre-existing aerosol surface area), $\text{H}_2\text{SO}_4$ can homogeneously nucleate and/or nucleate heterogeneously with other compounds (e.g. $\text{NH}_3$ or halogens) to form new particle number in the marine atmosphere [Kulmala et al., 2004]. Under suitable conditions this population of newly formed secondary aerosols may grow through a combination of condensation and coagulation with the potential to become effective as CCN in the remote marine environment. The final source of aerosol number/mass in the MBL is the advection of natural continental aerosol into the MBL. This process is important in the coastal environment but is less important over the remote ocean due to the short atmospheric residence times of these aerosols [Raes et al., 2000].
1.2.1. The CLAW Hypothesis

In 1987, Charlson, Lovelock, Andreae and Warren (CLAW) published their seminal paper, *Oceanic phytoplankton, atmospheric sulfur, cloud albedo and climate* [Charlson et al., 1987]. The CLAW Hypothesis proposed that dimethylsulfide (DMS) producing phytoplankton, photo-oxidation of DMS to sulfuric acid and subsequent gas-to-particle conversion of $\text{H}_2\text{SO}_4 (g) \rightarrow \text{H}_2\text{SO}_4 \text{ (aer)}$ controlled the background number of submicrometer aerosol in the remote marine boundary layer (MBL). They proposed that these sulfate aerosols control the number of cloud condensation nuclei influencing cloud properties and therefore surface albedo over the World's Oceans. *Charlson et al.*, proposed that any climate forcing that increased (or decreased) phytoplankton production of DMS would result in a negative climate feedback that would decrease (or increase) global mean temperature through its feedback on marine stratus clouds. The link between DMS production and CCN has been well established [*Boyd and Doney*, 2003; *Denman et al.*, 1996]. The intricacy of this biogeochemical feedback mechanism is sufficiently complex that it remains an active research area for both observational scientists and climate modelers [*Ayers and Catney*, 2007].

1.2.2. Sources of sulfur in the marine boundary layer

There are four principle sources of sulfur in the marine atmospheric environment; three natural and one anthropogenic.

Both sulfuric acid ($\text{H}_2\text{SO}_4$) and sulfur dioxide ($\text{SO}_2$) are primary sulfur emissions from volcanoes [*Stoiber et al.*, 1987]. The sulfur released from these volcanoes can be either primordial sulfur locked within the Earth since formation or rejuvenated sulfur
volatilized from recycled crustal material. Sulfuric acid vapour rapidly condenses as the fume cools and represents an essentially primary emission of aerosol sulfate, $\text{SO}_4^{2-}$.

Volcanic $\text{SO}_2$ is photo-oxidized in the marine environment to produce $\text{H}_2\text{SO}_4$ and represents a source of secondary aerosol sulfate.

Sulfate constitutes the third most abundant ion in seawater (2.71 g/kg of seawater for a salinity of 35%). Sea salt aerosol produced mechanically at the ocean surface by wind and breaking waves has the same bulk ionic composition as seawater at the time of its formation. Thus the ocean is a primary source of aerosol sulfate whose concentration can be calculated by its ratio to sodium, a conservative tracer, and the second most abundant ion in seawater. The ratio of primarily produced sea salt sulfate (ss$\text{SO}_4^{2-}$) to $\text{Na}^+$ is 0.060 mol mol$^{-1}$ (0.252 g g$^{-1}$).

The third natural source of sulfur in the marine atmosphere is biogenic. Photoautotrophic and chemoautotrophic microbial communities produce the reduced sulfur compounds; carbonyl sulfide ($\text{OCS}$), hydrogen sulfide ($\text{H}_2\text{S}$) and dimethylsulphoniopropionate (DMSP) the metabolic precursor to dimethylsulfide (DMS).

Carbonyl sulfide is chemically stable throughout the troposphere with practically no vertical gradient. OCS is an important source of sulfur in the stratosphere where its oxidation to form $\text{H}_2\text{SO}_4$ is responsible (along with episodic injections of sulfur from volcanoes) for maintaining the stratospheric sulfate aerosol layer [Crutzen, 1976; Kettle et al., 2002].

Hydrogen sulfide is produced by methanogens under anoxic conditions typically found in marine sediments. Coastal environments, especially those with well-developed tidal flats and estuaries, are significant sources of hydrogen sulfide. In the open ocean
the surface is decoupled from the sediments and \( \text{H}_2\text{S} \) concentrations are relatively low. After production, dissolved \( \text{H}_2\text{S} \) is rapidly oxidized in oxic surface waters. As a result, the contribution of \( \text{H}_2\text{S} \) to total sulfur in the remote ocean is small (<10%) compared to DMS [Saltzman and Cooper, 1989].

Open-ocean DMSP/DMS production is dominated by *Dinophyceae* (dinoflagellates) and *Prymnesiophyceae* (prymnesiophytes, including coccolithophores) with smaller contributions from chromophyte algae (those possessing both chlorophyll-a and chlorophyll-c) [Keller et al., 1989]. In oligotrophic waters dinoflagellates are abundant at the deep chlorophyll maximum. Coccolithophores are also important members of the microbial community in oligotrophic waters, where they can form large blooms which can be tracked using satellite observations. Diatoms are not major producers of DMS however their numerical abundance, particularly in temperate and polar regions, and their species diversity indicate they may be seasonally or regional important.

Seawater DMS concentrations range over an order of magnitude exhibiting both horizontal and vertical heterogeneity as well as diurnal and seasonal variation. Diversity between different biogeochemical provinces are linked to the differences in the microbial communities’ species composition and the relationships between phytoplankton producing DMSP/DMS and the grazing habits of their predators [Wolfe et al., 1997]. Although the distribution of DMS is broadly similar to that of ocean primary productivity [Bates et al., 1987], concentrations of DMS are not well correlated with physical (temperature and salinity), chemical (DMSP) or biological (chlorophyll) tracers [Kettle, 1999].
Finally, anthropogenic combustion of sulfur containing solid and liquid fuels produces primary aerosol sulfate and SO₂. The combustion-derived sulfur can be produced in the remote marine environment by ships [Capaldo et al., 1999; Ferek et al., 1998] or transported long range from their continental source regions. Natural and anthropogenic biomass burning also produces SO₂, sulfate and other aerosol species [Sinha et al., 2003; Whitlow et al., 1994]. However, in at least one study [Koch et al., 2006] estimates of pre-industrial biomass burning sulfur emissions were assumed to be half their current values. This estimate is based on assumptions about global trends in agriculture and silviculture. As a result, the contribution of biomass burning derived sulfur to the atmospheric budget over the remote ocean is expected to be small.

1.2.3. Atmospheric oxidation of reduced sulfur

The in-situ atmospheric oxidation of sulfur in the atmosphere occurs in both the gas and aqueous phases. In the gas phase, SO₂ is converted to H₂SO₄ according to the following photo-oxidation reaction series:

\[
SO_2 + OH + M \rightarrow HOSO_2 + M
\]

\[
HOSO_2 + O_2 \rightarrow HO_2 + SO_3
\]  

(1.2)

\[
SO_3 + H_2O + M \rightarrow H_2SO_4
\]

Once formed, H₂SO₄ condenses on pre-existing aerosol to form secondary aerosol sulfate. Under favourable conditions, H₂SO₄ will homogeneously or heterogeneously nucleate to form new particle number. This population of newly formed secondary
aerosols can grow through a combination of condensation and coagulation, eventually becoming effective as cloud condensation nuclei in the remote marine environment.

$SO_2$ has a relatively high rate of dry deposition ($\sim$1 cm s$^{-1}$) resulting in effective removal by dry deposition. Its solubility is also high increasing from an effective Henry's law ($H^+_S(IV)$) constant of $\sim$10$^4$ M atm$^{-1}$ for a cloud water pH of $\sim$5.8 to a value of $\sim$10$^7$ M atm$^{-1}$ for seawater pH of $\sim$8.0. Dissolution of $SO_2$ follows the reversible acid-base dissociation:

$$SO_2(g) + H_2O \leftrightarrow SO_2 \cdot H_2O$$

$$SO_2 \cdot H_2O \leftrightarrow H^+ + HSO_3^-$$

(1.3)

$$HSO_3^- \leftrightarrow H^+ + SO_3^{2-}$$

In activated aerosol droplets or cloud water, pH is typically $<$6.0 and hydrogen sulfite ($HSO_3^-$) is the dominant aqueous S(IV) ion. Aqueous phase oxidation of hydrogen sulfite by dissolved hydrogen peroxide ($H_2O_2$) proceeds according to the following reaction:

$$HSO_3^- + H_2O_2 \leftrightarrow SO_2O0H^- + H_2O$$

(1.4)

$$SO_2O0H^- + H^+ \rightarrow O_2 + H_2SO_4$$

Aqueous phase oxidation of S(IV) also occurs in cloud droplets by dissolved ozone ($O_3$) according to:

$$O_3 + SO_3^{2-} \rightarrow O_2 + SO_4^{2-}$$

(1.5)
Since the sulfite ($\text{SO}_3^{2-}$) fraction of S(IV) is only above \(10\%\) for $\text{pH} > 6.5$, aqueous phase oxidation via dissolved $\text{H}_2\text{O}_2$ is considered the dominant pathway for in-cloud sulfate production and reaction 1.5 has been omitted from some models [Chin et al., 1996; Koch et al., 1999].

Recently produced sea salt aerosols have pH similar to the bulk composition of seawater ($\text{pH}=8.0$). Under these conditions the sulfite ion ($\text{SO}_3^{2-}$) is the dominant form of S(IV) and can be oxidized according to reaction 1.5. This reaction is some $10^5$ times faster than in-cloud oxidation by $\text{H}_2\text{O}_2$ and the overall reaction rate appears to be limited by $\text{SO}_2$ transfer from the gas to aqueous-aerosol phase [Jacob, 2000]. Note that this reaction and condensation of other acidic gases (H$_2$SO$_4$ and HNO$_3$) rapidly (~hours) consumes sea salt aerosol alkalinity, shutting down the availability of this S(IV) oxidation pathway. Except for open-ocean regions with strong sea salt aerosol fluxes, excess (biogenic) alkalinity [Sievering et al., 2004], and/or low availability of acidic gases or $\text{H}_2\text{O}_2$, the reaction 1.4 oxidation pathway remains the dominant mechanism for producing non-seasalt sulfate in the marine boundary layer.

Atmospheric oxidation of dimethylsulfide in the marine atmosphere is a complex reaction pathway initially split between an OH addition and an H-atom abstraction reaction pathway. DMS oxidation reactions can also be initiated by NO$_3$ through H-atom abstraction. Oxidation via OH addition is favoured near the equator and has a pronounced diel cycle while NO$_3$ oxidation is more prevalent under high latitude low-light conditions or where the marine atmosphere is relatively polluted.
The products of the multi-stage DMS oxidation pathways are dimethyl sulfoxide (DMSO), dimethyl sulfone (DMSO₂), methane-sulfonic acid (MSA), methane-sulfinic acid (MSIA) and SO₂ [Davis et al., 1999; Toon et al., 1987]. Once formed, SO₂ is oxidized according to one of the previously mentioned reaction pathways. Similarly, DMSO, and DMSO₂ are oxidized by OH and lead to further production of MSA. MSA has a high vapour pressure but is also highly water-soluble. This results in short gas-phase lifetimes as it rapidly condenses onto pre-existing aerosol surface area under high RH's typically observed in the MBL [Huebert et al., 1993]. Due to the temperature and light dependence of the reaction pathways, ratios of the production of MSA to SO₂ vary with temperature and light such that it is ~0.1 near the equator and ~0.4 near Antarctica [Seinfeld and Pandis, 1998]. The oxidation of DMS is primarily a daytime phenomenon although there is evidence for nighttime ([OH]= 0) production of MSA and H₂SO₄ in the coastal [Berresheim et al., 2002] and remote [Mauldin et al., 2003; Nowak et al., 2001] marine environments. Oxidation of DMS and daughter products in both the gas and aerosol-phases remain an active field of study.

1.2.4. Cycling of atmospheric sulfur over the remote ocean

Figure 1.2 contains a conceptual representation of the cycling of sulfur over the remote oceans. In this schematic reduced sulfur from biogenic DMS is released from the surface ocean into the marine boundary layer. During the day, oxidation of DMS can occur in both the gas phase as well as through aqueous phase reactions in activated aerosols and cloud drops. Some oxidation products are removed by dry deposition with the bulk being removed by precipitation and below-cloud scavenging. DMS (largely
insoluble), aerosol and cloud-droplet sulfur compounds not removed during precipitation are lofted and detrained into the FT as convective clouds evaporate. Altitudes to which the sulfur compounds are lofted are latitude dependent with the highest altitudes corresponding to deep convection near the equator.

After the cloud evaporates low pre-existing aerosol surface area, low temperature and relatively high concentrations of SO₂ (and therefore H₂SO₄) result in particle nucleation [Clarke et al., 1999]. After equatorial airmasses are lofted they generally subside over the mid-latitudes due to Hadley cell circulation patterns. An example of this pattern is deep convection at the intertropical convergence zone (ITCZ) of the Pacific compared to synoptic scale subsidence in the “East Pacific High”. While subsiding, the number of newly formed secondary aerosols is reduced through coagulation. Geometric mean diameter of the aerosol population increases as a result of condensation and coagulation while the geometric standard deviation of the distribution decreases (i.e. the width of the distribution becomes narrower). This trend can be seen in the panel at right which is derived from in-situ airborne measurements off the coast of Peru during the PEM-Tropics mission.

Finally, the subsiding FT aerosol population is eventually entrained into the MBL where they contribute new particle number that can participate in the hydrological cycle through their role as CCN.
Figure 1.2 – (a) Sulfate aerosol cycling in the remote MBL from Clarke et al. [1998] illustrating the process of scavenging of MBL aerosol by precipitation and pumping of air aloft into colder regions where nucleation is favored (and observed). This is followed by growth during subsidence and entrainment of this aerosol into the MBL where it replenishes MBL CN and CCN. (b) – Observed vertical profile of subsiding size distributions reflecting both nucleation and gradual growth in FT. Entrainment of monomodal FT aerosol into the MBL is followed by cloud processing that adds mass heterogeneously to sizes activated as CCN and making them larger while the smaller inactivated sizes grow little. This result in the concentration minimum near 0.1 μm that is an indication of sizes activated at prevailing MBL cloud saturations.
1.2.5. Seasalt aerosol in the remote marine boundary layer

From the preface of Lewis and Schwartz, [2004]:

*Sea salt aerosol exerts a major influence over a broad reach of geophysics. It is important to the physics and chemistry of the marine atmosphere and to marine geochemistry and biogeochemistry generally. It affects visibility, remote sensing, atmospheric chemistry, and air quality. Sea salt aerosol particles interact with other atmospheric gaseous and aerosol constituents by acting as sinks for condensable gases and suppressing new particle formation, thus influencing the size distribution of these other aerosols and more broadly influencing the geochemical cycles of substances with which they interact. As the key aerosol constituent over much of the Earth’s surface at present, and all the more so in pre-industrial times, SSA is central to description of Earth’s aerosol burden.*

In their recent intercomparison assessment of 20 aerosol modules used in global climate models, Kinne et al., [2006] report that the median value of annual, globally averaged, dry sea salt mass is 13 mg m\(^{-2}\). This value is second only to dust aerosol mass whose globally averaged value is 39 mg m\(^{-2}\). Yet the contribution of sea salt aerosol and dust to globally averaged aerosol optical depth at 550 nm is comparable; 0.030 for sea salt and 0.032 for dust. This is due mainly due to the hygroscopic nature of sea salt aerosol whose dry diameter doubles at 80% RH, the average value in the marine boundary layer over much of the World Ocean.

However, the accuracy with which these aerosol models predict the direct effect of sea salt aerosols is difficult to assess because their influence is combined with other aerosol components which are also significant optically. Kinne et al., note that all-model
average total aerosol optical depth (AOD = 0.13) is comparable to that derived from AERONET (0.14) and satellite\(^2\) remote sensing (0.15) but that the inter-model variability of the component-specific contributions to aerosol optical depth is high. Their measure of this variability is the model diversity which is expressed as the ratio of the maximum and minimum annual global averages simulated. Model total diversity (TD) refers to all 20 AEROCOM models whereas the central diversity (CD) refers to the central 2/3 (i.e. extremes are eliminated). For simulations of sea salt mass, TD = 5.4 and CD = 2.3 while for dust, TD = 6.6 and CD = 1.8. For sea salt AOD, TD = 3.3 and CD = 2.3 while for dust AOD, TD = 4.5 and CD = 2.5.

Based on the central diversity measure this implies that in global simulations the models are predicting more similar AOD's than predictions of aerosol mass while also predicting more similar burdens of dust mass than sea salt mass. The conclusions to be drawn here is that we do not have an accurate estimate of annual, globally averaged, sea salt mass because our estimates based on state-of-the-art model simulations differ by at least a factor of 2 and by as much as a factor of 5.

The AEROCOM models evaluate the inter-model difference between their microphysical parameterizations and its effect on optical properties by computing the annual globally averaged extinction efficiency of each aerosol type. This intensive aerosol property, mass extinction efficiency, ME, is calculated in Kinne et al., as the ratio between the component specific AOD and the component's mass. The all model median for seasalt is 3.0 m\(^2\) g\(^{-1}\) while the median for dust is 0.95 m\(^2\) g\(^{-1}\). For sea salt the TD = 7.7 and CD = 2.9 while for dust the TD = 15 and the CD = 2.3. This suggests that a few

\(^2\) MODIS data for oceanic retrievals, MISR data over land.
models have parameterizations that are relative outliers while the remainder are very similar.

A closer examination indicates that several, well cited models are those with extinction efficiencies much lower than the all models median. For example the NCAR MATCH model and the NASA-GSFC GOCART model report sea salt extinction efficiencies of 1.8 and 1.0 m² g⁻¹ respectively. Inter-model variability for extinction efficiency of an order of magnitude implies that our description of the microphysical and optical properties are poorly constrained despite the fact that their direct effect, as measured by AOD, are close to the observed values. Said another way, compensating errors in modeling the direct radiative forcing of each aerosol component result in a somewhat accurate (compared to AERONET and MODIS/MISR) estimates of direct radiative forcing for the total aerosol. As will be demonstrated, poorly simulated microphysical properties affect aerosol optical properties but they have can have a more profound impact on our ability to simulate the aerosol indirect effects, i.e. CCN.

1.3. Asian Dust Aerosol

1.3.1. The Iron Hypothesis

Martin [1990] noted that CO₂ minima during glacial periods coincide with maxima in dust deposition based on geological records. His “Iron Hypothesis” proposed a positive climate feedback whereby the cold arid climate of the glacial period enhanced aeolian deposition of iron-bearing dust to the ocean surface. Presently, biological productivity in several large marine ecosystems is to some degree limited by low concentrations of iron. Martin proposed that higher inputs of iron-rich wind-borne dust will enhance ocean primary productivity. This biogeochemical feedback is self-
reinforcing as the drawdown of atmospheric CO\textsubscript{2} sustains the cold arid conditions encountered during glacial periods. Similar to the CLAW Hypothesis, the Iron Hypothesis remains an intense field of interdisciplinary study resulting in collaborations between scientific disciplines as disparate as marine microbial ecology and satellite’s optical sensor design.

1.3.2. The Asian Dust source regions

Vast regions of Central and Western China are semi-arid to arid. Moist air is blocked from entering the central Asian basins by tall mountain ranges including the Himalaya to the south, the Pamir to the West and Altay mountains to the north. Distance to the coast is also a factor. Many regions experience a severe continental climate and contain two of the Earth’s largest deserts, the Gobi and the Taklamakan.

The Taklamakan is the world’s 13\textsuperscript{th} largest desert (320,000 km\textsuperscript{2}), ranges in elevation from 1500 m ASL in the southwest to 800 m in the northeast and experiences seasonal temperatures extremes of -20 to +40\degree C. The Taklamakan is one of the world’s largest sand deserts with deposits as thick as 300 meters and dunes systems reaching up to 300 meters in height (Figure 1.3). The Taklamakan is sometimes considered a western extension of the much larger Gobi desert.

The Gobi is the world’s fourth largest desert (1,300,000 km\textsuperscript{2}), resides at a mean elevation of 900 m and experiences temperature extremes of -40\degree C in winter to +50\degree C in summer. For at least the past 2.6 million years, prevailing winds over the Gobi have been from the northeast toward the southwest. As a result of surface deflation the Gobi desert is mostly a stone desert with a surface pavement of cobbles and gravel.
To the southeast of the main Gobi desert lie several smaller sandy desert subunits, the Badain Jaran, the Tengger (Figure 1.4), the Ulan Buh and the Mu Us deserts. These subunits straddle the Huang He (Yellow River) and were formed by the aeolian deposition of sand grade material sourced in the Gobi. At their southeast margin the sand deposits are interbedded with silt deposits of the Chinese “Loess Plateau”.

The Loess Plateau covers an area of 640,000 km², resides at a mean elevation of 1200 m ASL and is the world’s largest deposit of loess; a sedimentary deposit of wind blown silt and clay sized material. Northeast to Southwest transects of the Loess Plateau indicate gradation from sandy-silt, to silt, to silty-clay along the axis of the prevailing winds [Liu, 1985]. The loess-paleosol sequence of the Loess Plateau has a relatively continuous deposition character over the past 2.4-2.6 million years. Underlying the oldest loess-soil units is reddish clay-silt sized sediment named the red-clay formation. Using major and trace metal analysis Ding et al., [2001] determined that the last glacial-interglacial loess-soil units were compositionally similar to a red clay section in Jiaxian. This finding extends the geological time scale of the Loess Plateau’s Aeolian formation to ~7.0 million years.

The desert regions of China as well as the Loess Plateau are direct sources of natural mineral aerosol (Asian Dust). The Loess Plateau is bound in the southeast by the Wei He, a tributary of the Yellow river which itself bounds the plateau to the northwest. Highly erodable, the silt and clay give the Huang He its characteristic yellow colour.

The fertile soils of the plateau are considered the birthplace of Chinese agriculture [Liu, 1985]. Due to its fertility the Loess Plateau and alluvial loess deposits are subject to intense agricultural pressure. As a result of poor land use practices and diversions for
irrigation, a secondary source of Asian Dust is former riparian ecosystems after undergoing desertification. Since the source provenance of the material is the same, compositionally the alluvial deposits of Chinese Loess is relatively uniform. Alluvial “loess like” deposits vary most in calcite concentrations and organic carbon content [Liu, 1985].
Figure 1.3 – Dune field in the south-central Taklamakan, 40 km north of the ancient silk-road city of Khotan (Hetian, Xinjiang Province, Peoples Republic of China).

Figure 1.4 – Dune field in the Tengger Desert, Inner Mongolia Autonomous Province, Peoples Republic of China.
1.3.3. Bulk Density of Chinese Loess

Electron microscope analysis of Chinese Loess show that the upper part of the stratigraphy is comprised of a meta-stable microfabric of plate-like aliminosilicates 10's of μm in size [Derbyshire, 1983]. The matrix is bound by calcium carbonate (calcite) and, occasionally, siliceous cement.

Zhen Yanwu (1982) and Zhai Lisheng (1983) tabulated dry bulk densities and void ratios of four loess-like soil deposits to get a bulk density of loess material of 2.06 g cm⁻³. This bulk density is used throughout this dissertation with regard to correcting supermicrometer mineral aerosol aerodynamic to geometric diameters and when converting aerosol volume to mass and vice versa. This is equivalent to assigning a shape factor, χ, of 1.10-1.25 for dust particles with aerodynamic diameters between 0.5 and 10.0 μm assuming a bulk density for crustal material of 2.6 g cm⁻³. The loess value (2.06 g cm⁻³) is nearly identical to the “effective density” of 2.0 g cm⁻³ proposed by Reid et al., [2003] but smaller than the value used in McNaughton et al. [2007] to evaluate DC-8 inlet passing efficiencies. When recalculated, the 50% passing efficiency diameters of the UH and UNH inlets are no less than 3.5 μm and 2.8 μm when sampling Asian dust at the surface and 2.2 μm and 1.8 μm when sampling at the DC-8 ceiling of 12 km.
1.3.4. Geochemistry of Chinese Loess

Table 1.4 summarizes the elemental composition of Loess Plateau loess deposits, paleosols and red clay from several different sources. Note that due to the analysis technique the concentration of each trace element is recalculated on a volatile-free basis. In this manner interlayer water is removed, carbonate is converted to CO$_2$, iron oxides, including FeO, are converted to Fe$_2$O$_3$, mineral sulfate (gypsum – CaSO$_4$) is liberated as SO$_2$, and atmospheric O$_2$ is consumed.

Calcium carbonate concentration varies with grain size (3.6-21% with an average of 12%), and is contained predominantly in the medium to coarse, 6-60 μm, silt grains [Qizhong et al., 1964]. Aluminosilicates in the clay size fraction (< 6.0 μm) are composed mostly of illite (51 +/- 6%) with a smaller fraction of kaolinite (19 +/- 2.8%) and montmorillinite (8.6 +/- 3.7%). Calcite is the fourth most abundant mineral in the clay size fraction (<6 μm) but is also the most variable (6.5 +/- 6.2%).

Iron oxides are surface bound to the clay minerals and account for ~50% of the total iron (Fe$_2$O$_3$). Goethite and hematite account for 75% and 25% (+/-10%) of the iron oxides respectively and are the only two minerals responsible for visible light absorption by Asian dust aerosol [Lafon et al., 2006]. Goethite (FeOOH) is a yellowish to red-brown mineral while hematite is grey or earthy reddish in colour. Chinese loess contains a higher proportions of goethite to hematite than dusts from Niger (65:45 G:H) or Tunisia (70:30 G:H) which may account for the “yellow sand” moniker applied to dust storms in both modern and historical Asian texts.
Table 1.5 summarizes the weight percentages of the iron compounds in Chinese Loess. The ratio of total iron to ferrous iron (Fe$_2$O$_3$/FeO) is variable with values of 3:1 in the uppermost soil unit and an average of ~7:1 for the 2.4 million year sequence. Reports of elemental total iron content of the loess and paleosols varies between 3-9 wt% [Ding et al., 2001; Liu, 1985]. Assuming ferrous iron constitutes 15% of total iron, the ferrous iron content is ~0.5-1.5 wt%. Structural iron refers to iron atoms incorporated into the crystalline structure of the aluminosilicates. Structural iron is neither optically active, biologically available or likely to be solubilized during ion-chromotography analysis of the University of New Hampshire aerosol filter samples used in this dissertation.

Both goethite and hematite are optically active at visible wavelengths. Hematite and goethite are both extremely insoluble with minimum solubilities near seawater pH. Iron oxides present in Asian dust are aggregated with the loess aluminosilicates [Lafon et al., 2006; Liu, 1985]. They are likely surface bound through partial isomorphous substitution of Fe(III) by Al(III). This reaction further lowers their solubility [Kraemer, 2004] however their solubility also increases with decreasing particle diameter.

Cornell and Schwertmann [1993] reported soil goethite and hematites are in the 10-150 nm size range. Solutions in equilibrium with 100 nm cubic goethite at pH 8.0 is in the pico-molar range (10^{-12} M). However, many bacteria synthesize then secrete chemicals of low molecular weight, called siderophores, which bind to iron and can make it soluble in seawater. These bacteria then take up these iron-siderophore complexes and remove the iron for biological processes. Oxalate (C$_2$O$_4^{2-}$) also forms iron complexes below pH 8.0. At a concentration of 10^{-3} M and at rainwater pH of 5.6, oxalate increases the soluble iron concentration in equilibrium with Goethite from 10^{-12} to 10^{-6} M.
[Kraemer, 2004]. Oxalate is the simplest, most abundant organic aerosol compound that can be measured using the University New Hampshire ion-chromatography technique.

1.3.5. Geochemistry of Asian Dust

There are no direct measurements of aerosol iron aboard the NASA DC-8. Weak-acid soluble aerosol calcium is measured by ion chromatography (IC) by the University of New Hampshire system. Due to the limitations of the IC technique the only calcium that will be measured is probably that which occurs as calcite. Structural calcium, magnesium, and iron will remain as part of the aluminosilicate crystalline matrix and will therefore not be recorded in the anion-cation balance of the IC measurement.

Bioavailable iron and light absorption by iron oxides is associated with the unmeasured aluminosilicate-bound particulate not the measurable calcite. Thus in order to infer the aerosol concentration of iron we are required to establish a link between the aerosol calcium (as calcite) and iron oxides. The first half of Table 1.6 summarizes the molar ratios of Ca:Al, Fe:Al and Fe:Ca for the Chinese Loess parent material. Total calcium to aluminum ratios are more variable than iron to aluminum. In the central panel of Table 1.6 we summarize the same elemental ratios but instead from measurements of Asian dust aerosol. Similar to its parent material, aerosol Ca:Al is more variable than the Fe:Al ratio. Note the deficit or depletion of Ca:Al in the aerosol samples compared to the parent material. This results in an apparent enrichment of total Fe:Ca while the ratio of Fe:Al is conserved between the loess deposits and the mineral aerosol.

Calcite associated with the Chinese Loess is in the medium to coarse, 6-60 \( \mu \text{m} \), silt grains [Qizhong et al., 1964]. While aluminosilicates and quartz grains are also a
component of the silt sized loess material, the iron oxides are surface-bound to the clay
grade (< 6.0 µm) aluminosilicates. Lafon et al. [2006] investigated the apparent Fe:Ca
enrichment by separating their wind-tunnel generated aerosol samples into a ‘clay size
fraction’ (< 2.0 µm) and a ‘fine silt fraction’ (2-20 µm). Their results indicated that the
Total and Free Fe:Al ratios were in fact higher (0.97, 0.49) for the particulate associated
with the coarse mode cascade impactor plate (d_{50, aero}=10.2 µm) than for their fine mode
impactor plate (0.47, 0.18 at d_{50, aero}=2.5 µm). Their conclusion that coarse particles
contain a significantly larger proportion of Fe:Al should be viewed with some caution as
a 50% aerodynamic cut size of 10.2 micrometers corresponds to a geometric size of 7.1
µm indicating that both the “clay” and “fine-silt” mass they analyzed would be defined as
‘clay grade’ by soil scientists studying the Chinese Loess deposits. The important
conclusion is that lofting of mineral dust winnows the dust resulting in a relative
enrichment of clay-grade iron oxides compared to calcite.

The bottom panel of Table 1.6 compares the Ca:Al, Fe:Al and Fe:Ca ratios
measured in East Asian pollution plumes. The elemental ratios of the PM9 pollution
aerosol collected by Alfaro et al. [2003] in April 2002 at Zhenbeitai are no different than
the PM2.5 ratios of Cohen et al. [2004], collected at three separate ground stations in East
Asia from January-July 2001. And while the Fe:Ca ratios are 30% lower than the ratios
when sampling dust, anthropogenic sources of iron appear to be more soluble than crustal
sources [Hand et al., 2004] potentially enhancing their bioavailability.

As a result of the considerations discussed above I employ a Fe:Ca conversion
ratio of 0.90 when estimating the total aerosol iron concentration. The optically active
iron compounds hematite and goethite are assumed to represent 25% and 75% of the total
free iron which is 46.5% of the total iron based on the bulk aerosol values measured at Zhenbeitai ([Lafon et al., 2006] table 4). Uncertainty in the Fe:Ca ratio is 25%. For the Free:Total Fe ratio uncertainty is 11% and for partitioning between hematite and goethite the uncertainty is 10%. This results in an overall uncertainty of ~30%.
Table 1.4 - Major element compositions (wt\%) of Chinese Loess, Loess-Paleosols and the Pliocene Red Clay

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO2</td>
<td>67</td>
<td>66</td>
<td>63</td>
<td>66</td>
<td>&gt; 50</td>
</tr>
<tr>
<td>Al2O3</td>
<td>14</td>
<td>14</td>
<td>13</td>
<td>15</td>
<td>&gt; 10</td>
</tr>
<tr>
<td>CaO</td>
<td>5.8</td>
<td>6.6</td>
<td>11</td>
<td>4.2</td>
<td>7.5-10.5</td>
</tr>
<tr>
<td>Fe2O3</td>
<td>5.5</td>
<td>6.1</td>
<td>4.8</td>
<td>5</td>
<td>3.0-6.0</td>
</tr>
<tr>
<td>FeO</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.4-1.5</td>
</tr>
<tr>
<td>MgO</td>
<td>2.5</td>
<td>2.8</td>
<td>3.8</td>
<td>2.2</td>
<td>1.5-5.0</td>
</tr>
<tr>
<td>K2O</td>
<td>2.5</td>
<td>2.4</td>
<td>2.3</td>
<td>3.4</td>
<td>1.5-2.6</td>
</tr>
<tr>
<td>Na2O</td>
<td>1.8</td>
<td>1.1</td>
<td>1.7</td>
<td>3.9</td>
<td>1.2-2.3</td>
</tr>
<tr>
<td>CaCO3</td>
<td>99.1</td>
<td>99.0</td>
<td>99.6</td>
<td></td>
<td>3.6-21 (12)</td>
</tr>
<tr>
<td>Sum</td>
<td>98.1</td>
<td>99.0</td>
<td>99.6</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 1.5 - Breakdown of iron mineral compounds in Chinese Loess (wt%). Data are for paleosols, red clay, loess and wind tunnel generated aerosols from source material in the Ulan Buh region as well as direct aerosol samples from Zhenbeitai. Calculated wt%'s of FeO (in red) are computed by using the a ratio of 7:1 as per the Fe2O3/FeO average from Liu, [1985]. The FeO wt% is then subtracted from the Lafon et al., [2006] in order to compute the 'Corrected Structural-Fe'. Labile Fe is computed as the sum of Goethite and FeO.

<table>
<thead>
<tr>
<th>Material and Reference</th>
<th>Fe2O3 (wt%)</th>
<th>Structural-Fe (wt%)</th>
<th>Hematite (wt%)</th>
<th>Goethite (wt%)</th>
<th>Corrected Structural-Fe</th>
<th>FeO (wt%)</th>
<th>Labile (?) Fe (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paleosols [Ding et al., 2001]</td>
<td>5.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.8</td>
</tr>
<tr>
<td>Jiaxian Red Clay [Ding et al., 2001]</td>
<td>6.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.9</td>
</tr>
<tr>
<td>Loess [Ding et al., 2001]</td>
<td>4.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.7</td>
</tr>
<tr>
<td>Ulan Buh Wind Tunnel - Bulk [Lafon et al., 2006]</td>
<td>7.0</td>
<td>4.0</td>
<td>0.8</td>
<td>2.3</td>
<td>2.9</td>
<td>1.1</td>
<td>3.3</td>
</tr>
<tr>
<td>Ulan Buh Wind Tunnel - Fine [Lafon et al., 2006]</td>
<td>6.0</td>
<td>3.8</td>
<td>0.6</td>
<td>1.7</td>
<td>2.1</td>
<td>0.9</td>
<td>2.6</td>
</tr>
<tr>
<td>Ulan Buh Wind Tunnel - Coarse [Lafon et al., 2006]</td>
<td>8.7</td>
<td>4.3</td>
<td>1.1</td>
<td>3.3</td>
<td>4.5</td>
<td>1.3</td>
<td>4.6</td>
</tr>
<tr>
<td>Zhenbeitai Bulk Aerosol [Lafon et al., 2006]</td>
<td>7.7</td>
<td>4.1</td>
<td>0.9</td>
<td>2.7</td>
<td>3.5</td>
<td>1.2</td>
<td>3.8</td>
</tr>
<tr>
<td>Luochuan Loess [Liu, 1985]</td>
<td>3.0-6.0</td>
<td>2.7-3.9</td>
<td></td>
<td></td>
<td>0.4-1.5</td>
<td></td>
<td>3.1-5.4</td>
</tr>
</tbody>
</table>
Table 1.6 - Summary of elemental ratios for Chinese Loess, aerosol samples of Asian dust, and for East Asian regional pollution.

<table>
<thead>
<tr>
<th>Dust Parent Soils</th>
<th>Ca/Al</th>
<th>Fe/Al</th>
<th>Fe/Ca</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chinese Desert Regions</td>
<td>1.9</td>
<td>0.82</td>
<td>0.43</td>
<td>Zhang et al., [1998]</td>
</tr>
<tr>
<td>Loess Plateau</td>
<td>2.7</td>
<td>0.77</td>
<td>0.29</td>
<td>Zhang et al., [1993]</td>
</tr>
<tr>
<td>Tibetan Plateau</td>
<td>0.91</td>
<td>0.81</td>
<td>0.67</td>
<td>Zhang et al., [2001]</td>
</tr>
<tr>
<td>Ulan Buh - WT (fine)</td>
<td>1.23</td>
<td>0.47</td>
<td>0.38</td>
<td>Lafon et al., [2006]</td>
</tr>
<tr>
<td>Ulan Buh - WT (coarse)</td>
<td>1.96</td>
<td>0.97</td>
<td>0.49</td>
<td>Lafon et al., [2006]</td>
</tr>
<tr>
<td>Ulan Buh - WT (bulk)</td>
<td>1.38</td>
<td>0.60</td>
<td>0.43</td>
<td>Lafon et al., [2006]</td>
</tr>
<tr>
<td>mean</td>
<td>1.72</td>
<td>0.70</td>
<td>0.46</td>
<td></td>
</tr>
<tr>
<td>stdev</td>
<td>0.77</td>
<td>0.11</td>
<td>0.16</td>
<td></td>
</tr>
<tr>
<td>coeff var</td>
<td>45%</td>
<td>16%</td>
<td>35%</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Dust Aerosol Samples</th>
<th>Ca/Al</th>
<th>Fe/Al</th>
<th>Fe/Ca</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gosan 11-15 April 2001</td>
<td>0.56</td>
<td>0.48</td>
<td>0.90</td>
<td>Arimoto et al., [2006]</td>
</tr>
<tr>
<td>Gosan 25-26 April, 2001</td>
<td>0.41</td>
<td>0.45</td>
<td>1.10</td>
<td>Arimoto et al., [2006]</td>
</tr>
<tr>
<td>Mt. Halla 11-15 April 2001</td>
<td>0.72</td>
<td>0.67</td>
<td>0.98</td>
<td>Arimoto et al., [2006]</td>
</tr>
<tr>
<td>Mt. Halla 25-26 April 2001</td>
<td>0.51</td>
<td>0.58</td>
<td>1.15</td>
<td>Arimoto et al., [2006]</td>
</tr>
<tr>
<td>Zhenbeitai, China (Dust)</td>
<td>0.79</td>
<td>0.63</td>
<td>0.80</td>
<td>Alfaro et al., [2003]</td>
</tr>
<tr>
<td>Zhenbeitai, China (Dust)</td>
<td>1.00</td>
<td>0.59</td>
<td>0.48</td>
<td>Arimoto et al., [2004]</td>
</tr>
<tr>
<td>Zhenbeitai, China (WS-Ca)</td>
<td>0.54</td>
<td>0.48</td>
<td>0.87</td>
<td>Lafon et al., [2006]</td>
</tr>
<tr>
<td>Zhenbeitai, China (Dust)</td>
<td>0.69</td>
<td>0.60</td>
<td>0.87</td>
<td>Lafon et al., [2006]</td>
</tr>
<tr>
<td>mean</td>
<td>0.65</td>
<td>0.57</td>
<td>0.90</td>
<td></td>
</tr>
<tr>
<td>stdev</td>
<td>0.19</td>
<td>0.08</td>
<td>0.22</td>
<td></td>
</tr>
<tr>
<td>coeff var</td>
<td>29%</td>
<td>14%</td>
<td>25%</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Pollution Aerosol Samples</th>
<th>Ca/Al</th>
<th>Fe/Al</th>
<th>Fe/Ca</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zhenbeitai, China (Pollution) - PM9</td>
<td>1.14</td>
<td>0.64</td>
<td>0.56</td>
<td>Alfaro et al., [2003]</td>
</tr>
<tr>
<td>Hong Kong - PM2.5</td>
<td>1.29</td>
<td>0.70</td>
<td>0.54</td>
<td>Cohen et al., [2004]</td>
</tr>
<tr>
<td>Cheju Island - PM2.5</td>
<td>1.10</td>
<td>0.69</td>
<td>0.63</td>
<td>Cohen et al., [2004]</td>
</tr>
<tr>
<td>Sado Island - PM2.5</td>
<td>0.97</td>
<td>0.60</td>
<td>0.62</td>
<td>Cohen et al., [2004]</td>
</tr>
<tr>
<td>mean</td>
<td>1.13</td>
<td>0.66</td>
<td>0.59</td>
<td></td>
</tr>
<tr>
<td>stdev</td>
<td>0.14</td>
<td>0.05</td>
<td>0.04</td>
<td></td>
</tr>
<tr>
<td>coeff var</td>
<td>12%</td>
<td>7%</td>
<td>7%</td>
<td></td>
</tr>
</tbody>
</table>
1.4. Improving model simulations of tropospheric aerosols using in-situ airborne measurements

Both the previous and the most recent Intergovernmental Panel on Climate Change reports [IPCC, 2001; IPCC, 2007] have identified aerosols as one of the largest uncertainties in our efforts to model the Earth’s radiation balance. The goal of this PhD dissertation is to provide the atmospheric science community with robust measurements of aerosol size distributions, which can be used to validate/calibrate climate model simulations of the ambient atmospheric aerosol. Results from climate models that accurately simulate the vertical distribution of both aerosol number and mass, as well as the time-scales for processes which affect them, can be viewed with a higher degree of confidence than those that fail to adequately replicate observations such as those presented here.

Data presented in this dissertation was measured in-situ via aircraft on five separate NASA and NSF funded field campaigns. My approach is to evaluate aerosol properties in the Earth’s troposphere by stratifying the data into airmasses of unique character based on their physical (altitude, temperature, relative humidity) and chemical (gas- and aerosol-phase tracers) characteristics. After stratification, aerosol properties for each airmass type are then evaluated and analyzed. One of the prime goals of the analysis is to provide climate modelers with information that will directly assist them in simulating aerosol concentrations as a function of particle size, size dependent optical properties, and where possible, chemical composition. This dissertation will provide the broader scientific community with data that can be used to reduce uncertainties associated with determining:
1. the direct radiative effects of tropospheric aerosols, including comparative analysis between aerosol of natural and anthropogenic origin;
2. the indirect effect of aerosols on cloud properties through their role as cloud condensation nuclei;
3. the influence of aerosols on Earth's biogeochemical processes.

Chapter 2 summarizes the instrumentation used to measure the microphysical, optical and chemical characteristics of tropospheric aerosol. This includes consideration of all recognized and relevant phenomenon that may affect airborne sampling (e.g. inertial and turbulent losses in airborne inlet systems). Whenever appropriate, I have corrected and/or standardized this analysis so that it remains comparable to similar studies using ground- or ship-based measurements. Where relevant, error and uncertainty analysis is included.

Chapter 3 summarizes vertical profiles of trace gases, aerosol number, mass and optical properties for three separate geographic locations, the Eastern North Pacific, Eastern North America, as well as the Mexico/Gulf of Mexico region. Aerosol size distributions and optical properties for biomass burning emissions from boreal forest fires and anthropogenic pollution from North America are discussed in detail as these aerosol are responsible for large increases in tropospheric light extinction compared to clean background conditions. The chapter compares observed size distribution and their optical properties with those derived from the OPAC parameterization [Hess et al., 1998] and includes a discussion of ambient aerosol optical depth and the spectral dependence of light scattering and absorption.
Chapter 4 focuses on the aerosol indirect effect by first evaluating the extent to which the airborne measurements can identify “clean” background aerosol in the marine boundary layer and free troposphere. Identifying aerosol number concentrations, mixing state and size distributions under suitably clean conditions is of use to modelers when attempting to simulate ambient aerosol during “pre-industrial” times. The measured background distributions are then compared to ship-based observations, the OPAC parameterization and a 1-D column model in order to evaluate discrepancies in aerosol number which will directly affect estimates of natural CCN. Finally, the effects of entrainment, specifically the entrainment of polluted airmasses into the clean marine boundary layer, are examined in order to assess the effect of pollution on MBL CCN concentrations.

Chapter 5 focuses on the optical and geochemical characteristics of Asian pollution and dust transported to the remote Eastern North Pacific (ENP) marine boundary layer. Data from a case study and an examination of the long-term record from the Mauna Loa Observatory are both discussed. Finally, wet deposition of Asian pollution and dust can potentially alter the nutrient dynamics of the surface ocean mixed layer through the addition of nutrients such as nitrogen and iron. Percent increases in surface ocean nitrate and iron concentrations are estimated for both the oligotrophic waters of the Eastern North Pacific subtropical gyre and for the high-nutrient, low-chlorophyll waters of the ENP subpolar gyre.

This research is funded through a NASA Earth System Science Fellowship and addresses NASA’s Earth Science goals associated with atmospheric composition and
climate change by attempting to reduce uncertainties in modeling the direct, indirect and biogeochemistry of both natural and anthropogenic aerosols.
1.5. References


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AT THE TIME OF MICROFILMING
2.0 In-situ Airborne Aerosol Measurements

2.1. NASA and NSF sponsored field campaigns

Data presented in this dissertation was collected during five airborne field campaigns funded by either the United States’ National Aeronautics and Space Administration (NASA) or the United States’ National Science Foundation (NSF). The field campaigns are listed in the Table 2.1 and include the relevant overview references.

Table 2.1 – Airborne field campaigns included in this dissertation

<table>
<thead>
<tr>
<th>Agency</th>
<th>Acronym</th>
<th>Date</th>
<th>Region</th>
<th>Overview</th>
</tr>
</thead>
<tbody>
<tr>
<td>NASA</td>
<td>TRACE-P</td>
<td>Spring, 2001</td>
<td>East Asia</td>
<td>[Jacob et al., 2003]</td>
</tr>
<tr>
<td>NSF</td>
<td>ACE-Asia</td>
<td>Spring, 2001</td>
<td>East Asia</td>
<td>[Huebert et al., 2003]</td>
</tr>
<tr>
<td>NASA</td>
<td>DICE</td>
<td>Spring, 2003</td>
<td>California</td>
<td>[McNaughton et al., 2007]</td>
</tr>
<tr>
<td>NASA</td>
<td>INTEX-NA</td>
<td>Summer, 2004</td>
<td>Eastern North America</td>
<td>[Singh et al., 2006]</td>
</tr>
<tr>
<td>NASA</td>
<td>INTEX-B</td>
<td>Spring, 2006</td>
<td>Mexico, Eastern North Pacific</td>
<td>[Singh et al., 2008, in prep]</td>
</tr>
</tbody>
</table>

Together TRACE-P and ACE-Asia were designed as inter-agency, multi-national collaborative efforts to characterize the growing emissions in rapidly industrializing Eastern Asia [Huebert et al., 2003; Jacob et al., 2003]. Four aircraft, the NASA DC-8, NASA P3-B, the NSF/NCAR C-130 and the CIRPAS Twin Otter were stationed in East Asia from February until May of 2001 where they carried out extensive measurements over the East China Sea, Yellow Sea and Sea of Japan. Airmasses sampled during these flights allowed detailed studies of aerosols associated with biomass burning in southeast Asia [Ma et al., 2003], anthropogenic pollution from mainland China [Bahreini et al., 2003; Clarke et al., 2004; McNaughton et al., 2004] as well as the characteristics of a Asian Dust [Conant et al., 2003; Kahn et al., 2004; Tang et al., 2004]. These studies were carried out with careful consideration of instrument accuracy and precision.
[Anderson et al., 2003] as well as the meteorological settings under which the observations were made [Fuelberg et al., 2003; Merrill and Kim, 2004].

Platform intercomparisons were periodically conducted between the NASA DC-8, the P3-B, and the NSF/NCAR C-130 [Doherty et al., 2005; Ma et al., 2004; Moore et al., 2004]. Additionally the airborne platforms were used for comparison to ship-based measurements aboard the R/V Ron Brown and ground-based stations such as the Gosan Supersite at Jeju Island South Korea [Doherty et al., 2005]. As a result of these intercomparisons Moore et al. [2004] identified serious discrepancies between the NASA DC-8 and the NASA P3-B measurements of optically relevant aerosols. The same discrepancy did not exist between the measurements aboard the P3-B compared to those aboard the NSF/NCAR C-130. The probable source of this discrepancy was differing inlet performance between the NASA Langley solid diffuser type inlet used aboard the NASA DC-8 (LaRC inlet), and the University of Hawai'i solid diffuser type inlet (UH inlet) used aboard the P3-B. Aboard the NSF/NCAR C-130 optically relevant aerosol are sampled behind the University of Denver low-turbulence inlet (LTI) [Wilson et al., 2004]. In preparation for TRACE-P and ACE-Asia the UH inlet deployed aboard the NASA P3-B had been evaluated in conjunction with the LTI aboard the C-130 aircraft [Huebert et al., 2004]. The UH solid diffuser and the LTI were found to sample comparably up to dry aerodynamic diameters of ~5.0 μm; a significant improvement over a previous aerosol inlet design used aboard the NSF/NCAR C-130 [Blomquist et al., 2001].

In response to Moore et al. [2004], NASA funded the DC-8 inlet characterization experiment (DICE). This experiment was nominally an engineering evaluation of the
University of New Hampshire solid diffuser inlets (UNH inlet), the UH inlet and the LaRC inlet used aboard the DC-8 and P3-B aircraft during TRACE-P. During DICE the DC-8 sampled pollution and mineral dust aerosol over the Mojave Desert of California and marine aerosol off the coast of California near Trinidad Head. In both sampling locations the inlets were compared to ground-based measurements whose turbulent losses due to inlet sampling inefficiencies were assumed to be much less than the airborne inlets. The results from the DICE experiment were summarized and published as McNaughton et al. [2007]. This manuscript is included as Appendix-A to this dissertation.

The conclusions drawn from the DICE experiment were that the UNH and the UH solid diffuser inlets sampled comparably with 50% sampling efficiency ($\alpha=0.05$)$^1$ diameters of no less than 4.1 and 5.0 $\mu$m while sampling near the surface at a true air speed of 150 m s$^{-1}$. At the DC-8 flight ceiling (near 12 km) the 50% cutoff diameters were calculated to be 2.2 and 3.2 $\mu$m at a true airspeed of 220 m s$^{-1}$. DICE results showed that the NASA Langley inlet did not effectively transmit all of the optically relevant aerosols to the airborne instrumentation. This resolved the source of the discrepancy noted in Moore et al. [2004]. Based on the DICE results McNaughton et al. conclude that in-situ airborne measurements of atmospheric aerosols behind either the UNH or the UH inlet systems were comparable to ground- or ship-based measurements that meet the EPA’s PM$_{2.5}$ sampling standard and that the aircraft inlets did so over the entire performance envelope of the aircraft. They note that sampling of aerosol beyond

$^1$ Here and throughout this dissertation statistical significance and significant differences between means are evaluated using the Student's $t$-test. Additional information on the test and its validity for use can be found in the appendix of McNaughton et al., [2007].
PM$_{2.5}$ may be compromised when sampling dust storm events near their source regions and when sampling sea salt aerosols under high wind speed and high ambient relative humidity (RH > 90%).

Following the DICE campaign the UNH and UH inlets were installed aboard the NASA DC-8 for aerosol measurements during the Intercontinental Chemical Transport Experiment (INTEX-NA) conducted in summer of 2004 [Singh et al., 2006]. INTEX-NA was the NASA funded component of the larger International Consortium for Atmospheric Research and Transport and Transformation (ICARTT 2004) experiment [Fehsenfeld et al., 2006]. The intensive observation period was scheduled for summer when photochemical production of ground-level ozone is typically a maximum over Eastern North America (ENA). During the summer of 2004 a deep trough formed over ENA resulting in a series of frontal passages that precluded airmass stagnation and the buildup of high concentrations of ground-level ozone [Fuelberg et al., 2006]. Nevertheless a persistent high over Alaska and Northwestern Canada led to record-breaking forest fires [Turquety et al., 2007]. Smoke from these boreal forest fires was transported over Eastern North America to as far south as Texas [Morris et al., 2006] and as far as Western Europe [Fehsenfeld et al., 2006]. Additionally frontal storm systems lead to abundant deep convection and lightning induced production of NO$_x$ [Bertram et al., 2007; Singh et al., 2007b]. Results from in-situ aerosol measurements during INTEX-NA have already been published in Clarke et al., [2007] and Shinozuka et al. [2007]. The Clarke et al. publication is also included in Appendix-A. Additional analysis of the INTEX-NA data is included within this dissertation.
During spring of 2006 the NASA DC-8 participated in Phase B of the Intercontinental Chemical Transport Experiment (INTEX-B) part of the much larger Megacities Impact on Regional and Global Climate Experiment (MIRAGE). The NSF/NCAR C-130 also participated in MIRAGE and the Pacific phase of INTEX-B (IMPEX) with funding provided by the NSF. During March of 2006 the DC-8 was stationed in Houston while the C-130 was stationed in Veracruz, Mexico. Both aircraft were used to characterize the near-field trace gases and aerosols from the Central Highlands of Mexico and their regional transport out over the Gulf of Mexico. During the last two weeks of April and the first two weeks of May 2006 the DC-8 was stationed in Honolulu, Hawai‘i and then Anchorage, Alaska while the NSF/NCAR C-130 was stationed in Seattle, Washington. During this period both aircraft sampled the marine boundary layer and free troposphere to study the long-range transport of Asian dust and pollution to the west coast of North America.

INTEX-B/MIRAGE summary publications and a meteorological overview are in preparation [Molina et al., 2007; Singh et al., 2007a]. The meteorological setting during the Mexico and Hawai‘i phases of INTEX-B was climatologically average. During the Alaskan phase of INTEX-B the region was climatologically “wet” with more frequent than average transport of low pressure cyclonic weather systems across the North Pacific (H. Fuelberg, pers. comm.). Results from both the Mexico and Pacific Phases of INTEX-B are included in each chapter of this dissertation.
2.2. Measuring aerosol size distributions

In-situ measurements of the aerosol size distribution are fundamental to our understanding of aerosol effects on climate. In this section I discuss how atmospheric aerosols are delivered from the ambient environment to the aerosol instrumentation aboard NASA and NSF research aircraft and how the size distribution is measured over 3 orders of magnitude in diameter.

Aboard the NASA DC-8 the UH solid diffuser inlet delivers ambient air to the combined NASA Langley Research Center (LaRC) and Hawai‘i Group for Environmental Aerosol Research (HiGEAR) aerosol sampling package. During MIRAGE/IMPEX sample air is delivered to the HiGEAR instrument package via the NSF/NCAR C-130 solid diffuser inlet. Figure 2.1 is a sample flow diagram for the LaRC/HiGEAR instrument rack deployed aboard the NASA DC-8 during the INTEX-B field campaign. The flow pattern can be divided into two sample streams, the high and low pressure-drop streams. The high pressure-drop stream requires sample flow to be augmented with mechanical pumps while the low-drop stream uses only suction from the passive venturi pumps to draw sample through the instruments. Instrument flow rates are included as the numeric values below the instrument names. The instruments and their functions and capabilities are discussed in detail in the following sections.

During each of the field campaigns total and refractory (300°C) aerosol number (Dp > 10 nm) are measured using two TSI model 3010 condensation nuclei counters. These are labeled ColdCN and HotCN [Clarke et al., 1997]. The CN counters can detect particle concentrations of 1-10,000 cm⁻³ with a lower detection limit size of ~10 nm when
operating at a saturator/condenser temperature differential, $\Delta T$, of 22°C (the flown configuration). When particle concentrations exceed 10,000 cm$^{-3}$ the data are coincidence-count corrected according to the methods outlined in the user's manual.

Ultrafine ($D_p > 3$ nm) particle number concentration is measured using a TSI model 3025 condensation nuclei counter and is labeled (UCN). The instrument lower detection limit is 3 nm and can measure concentrations of 1-100,000 cm$^{-3}$. Data from these instruments are recorded at 1-Hz by the HiGEAR LabView program.

Aerosol size distributions are measured over 3 orders of magnitude (0.010-10.0 µm) using a combination of differential mobility particle sizing, optical particle sizing, and aerodynamic particle sizing. These instruments are discussed in the following subsections. Aerosol optical properties including aerosol light scattering, light absorption and the increase in light scattering as a function of relative humidity are also measured and are discussed in section 2.3.
Figure 2.1 – Flow diagram for the LaRC/HiGEAR aerosol sampling system installed aboard the NASA DC-8 during INTEX-B.
2.2.1. Differential Mobility Analysis

During each field campaign custom built differential mobility analyzers (DMA) were used to establish the size distributions of aerosol in the 0.010 – 0.20 μm size range. These sizes typically dominate aerosol number and often most CCN. Each DMA system is equipped with a lagged aerosol grab sampler (LAG chamber) which is periodically filled and holds up to three sample volumes for analysis [Clarke et al., 1998]. Each DMA system is also equipped with a heater assembly or, thermo-optical aerosol discriminator (TOAD), which pre-heats the aerosol to 150°C or 360°C prior to analysis [Clarke, 1991]. This thermal conditioning is designed to drive off volatile aerosol components so that the refractory aerosol size distribution can be evaluated separately. In polluted airmasses the internally mixed refractory aerosol is comprised of the “soot” components responsible for light absorption [Clarke et al., 2007; Clarke et al., 2004; Mayol-Bracero et al., 2002]. Preheating the aerosol to 360°C does not affect the analysis of sea salt or dust, the most common natural refractory primary aerosol species.

The normal operating procedure for the DMA system is to collect a LAG chamber sample over a 20-second interval and to then sequentially analyze the aerosol at dry ambient conditions (Relay 1 or R1), after preheating to 150°C (R2) and after preheating to 360°C (R3). Scan time for the DMA system is 90-seconds with a 30-second wait time after each scan. Thus a full, three-cycle (R1-2-3) DMA scan requires 360 seconds. During the final 30-second wait time the LAG chamber is flushed for 20 seconds and the relays again cycle, R1-2-3. During vertical profiling the DMA only samples using the unheated relay (R1) to improve temporal resolution of the aerosol’s vertical distribution.
During INTEX-B the DC-8 aerosol package was equipped with an additional unheated “long” DMA (lDMA). With the additional lDMA the thermal DMA could be cycled between unheated and 360°C scans (R1-3) without sacrificing vertical resolution. This allows more detailed characterization of the vertical distribution of the refractory aerosol. The lDMA measures unheated aerosol only between 0.010 and 0.50 μm, operated continuously using a 90-second scan followed by a 30-second wait period, and employed a smaller LAG Chamber (mini-LAG).

In the laboratory and during field deployments sizing accuracy of both DMA's was evaluated using PSL microspheres. Multiple charging corrections were applied and diffusion losses where estimated and corrections applied. Laboratory tests and tests aboard the aircraft were performed in order to evaluate how well the instruments compared. Figure 2.2 compares DMA and lDMA integral number (top row) and volume (bottom row) over two discrete size ranges 0.020-0.060 μm (left) and 0.060-0.16 μm (right). As indicated the two instruments agree to within 10% as deployed aboard the NASA DC-8 during INTEX-B.
Figure 2.2 – Comparison of DMA and IDMA performance. Top row compares integral number while the bottom row compares integral volume. The left two panels compare the integrals over the size range 0.02-0.06 \( \mu \text{m} \) while the right hand panels compare the integrals over the 0.06-0.16 \( \mu \text{m} \) size ranges.

2.2.2. Optical Particle Sizing

During each field deployment a custom modified PMS LAS-X optical particle counter is used to measure the aerosol size distribution between 0.1 and 20.0 \( \mu \text{m} \) at a resolution of 112 channels per logarithmic decade (\( d_{\text{log}D_{\text{oc}}} = 0.009 \)). Each OPC is also equipped with a 4-channel TOAD assembly operating at dry ambient temperature, 150\(^\circ\)C, 360\(^\circ\)C and 420\(^\circ\)C [Clarke et al., 2007]. These sizes typically dominate the optical properties and aerosol mass.
The OPC instruments are calibrated using monodisperse polystyrene spheres with a density of 1.05 g cm\(^{-3}\) and a refractive index of 1.59 @ 589 nm. OPC sizing accuracy is also assessed using borosilicate glass beads with a density of 2.52 g cm\(^{-3}\) and a refractive index of 1.56 @ 589 nm and silicon dioxide (SiO\(_2\)) spheres with a density of 2.01 g cm\(^{-3}\) and a refractive index of 1.40 @ 589 nm. The aerosol size determined by the OPC instrument are optically effective diameters (\(D_{\text{oe}}\)) as discussed in Clarke et al. [2004].

During post-processing the unheated OPC size distributions are adjusted to account for sizing errors due to aerosol refractive indices that differ from those of the PSL calibration spheres (1.59 @ 589 nm). OPC data over the 0.12-0.53 \(\mu\)m size range is adjusted assuming an ammonium sulfate composition with a refractive index of 1.53-0.0i. When sampling mineral dust the OPC data over the size range 0.53-8.0 \(\mu\)m is adjusted assuming a refractive index of 1.53-0.0006i. When sampling sea salt aerosol no size adjustment is made to the data in the 0.53-8.0 \(\mu\)m size range because the dry sea salt refractive index (1.588-0.0i) is essentially identical to that of PSL (1.59-0.0i) at the He-Ne laser wavelength of 633 nm. No optical to geometric size adjustments are made for the heated OPC channels as information regarding chemical composition, and thus refractive index, is a relative unknown. Since counting statistics and sizing accuracy of the OPC and UH solid diffuser inlet passing efficiency is poor beyond 8.0 \(\mu\)m, data above this size range is typically eliminated from the data sets.

In Figure 2.3 I evaluate the degree to which the IDMA and the OPC number and volume integrals agree. Here I use level leg averages from the entire INTEX-B campaign regressing OPC optically effective integrals (i.e. no refractive index correction) against the mobility diameter integrals from the IDMA. Between 0.12 and 0.30 \(\mu\)m integral
number (top-left) and volume (bottom-left) are within 5%. Between 0.30 and 0.50 µm
OPC derived number (top-middle) is under-estimated by 30% due to Mie oscillations.
Poor counting near the Mie oscillation results in a 40% underestimate of aerosol volume
(bottom-middle). When integrated over the full region of overlap (0.12-0.50 µm) the
OPC integral number and volume agree to within 15% of the IDMA integrals for all data
collected during INTEX-B regardless of aerosol composition (i.e. no refractive index
correction).

Note that when adjusting the OPC optically effective sizes to geometric sizes for
an ammonium sulfate aerosol over the 0.12-0.53 µm size range the average increase in
particle diameter is ~4%. Since number is conserved (and within 8% of IDMA number –
top-right of Fig. 2.3) this results in ~12% increase in aerosol volume after correcting the
OPC data. This increase essentially eliminates the ~15% discrepancy between
uncorrected OPC volume compared to aerosol volume measured using particle mobility
(bottom-right panel of Fig. 2.3).

A separate example of this is shown in Figure 2.4 where the average area
distributions for each of the DMA, IDMA, OPC and APS are plotted against one another.
Here the distributions represent the average distributions measured in airmasses
dominated by anthropogenic emissions from Asia but with a small amount of Asian Dust.
OPC optically effective diameters were adjusted using an ammonium sulfate composition
(m=1.53-0.0i) which results in slightly better agreement between the IDMA and OPC
area integrals over the 0.12-0.5 µm size range. Adjusting OPC size distribution in the
0.5-8.0 µm size range using a mineral dust refractive index (1.53-0.0006i, [Clarke et al.,
2004]) results in a smaller adjustment. No sizing adjustment is applied to the heated
(420°C) OPC size distribution because refractive index of the aerosol after pre-heating is unknown. The agreement in the region of refractory DMA/OPC overlap (0.1-0.2 μm) indicates that no adjustment is required for the heated distributions.
Figure 2.3 – Comparison between OPC integral number (top row) and volume (bottom) to IDMA integrals over three size intervals. Differences between the integral numbers are the result of Mie oscillation in the optically effective OPC size distribution. However, over the full region of overlap 0.12-0.50 μm the discrepancy is no larger than 15% for all data collected during INTEX-B level flight legs.

Figure 2.4 – Average area distribution for airmasses dominated by Asian pollution as measured over the Pacific during INTEX-B. Accumulation mode (0.12-0.50 μm) OPC distributions are adjusted (acc-shift) from optically effective diameters to geometric diameters using a refractive index of 1.53-0.01 (i.e. ammonium sulfate). Adjustment to the coarse mode (coa-shift) distributions use a refractive index of 1.53-0.0006. APS area distributions are corrected using a Chinese Loess density of 2.06 g cm⁻³. No size adjustments have been made to the heated (420°C) channel of the OPC as refractive index after heating is unknown. The overlap with the heated DMA channel indicates no Dₜₐₑ to Dₜ adjustment is required.
2.2.3. Aerodynamic Particle Sizing

Aerodynamic aerosol size distributions in the 0.5-20.0 μm size range are measured using a TSI model 3321 aerodynamic particle sizer (APS). Data from the first 5 channels (0.50-0.78 μm) were discarded due to poor instrument performance in this size range. Ignoring slip correction factors ($C_{c,a}/C_{c,g}$) by approximating them as unity [Baron and Willeke, 2001] aerodynamic diameters ($D_{ae}$) were adjusted to geometric diameters ($D_g$) during post processing according to:

$$D_g = D_{ae} \left( \frac{\rho_e}{\rho_p} \right)^{\frac{1}{2}}$$

(2.1)

For sea salt particles a dry aerosol particle density of 2.2 g cm$^{-3}$ was used. If APS instrument relative humidity exceeded the deliquescence point of sea salt (41%) then the appropriate density for the diameter adjustment is derived from Tang et al. [1997]. For mineral dust particles a bulk aerosol particle density of 2.06 g cm$^{-3}$ was applied [Liu, 1985]. This Chinese Loess value is slightly less than the bulk density of crustal material 2.56 g cm$^{-3}$ [Craig, 1997] but close to the effective density of 2.0 g cm$^{-3}$ suggested by Reid et al., [2003] for correcting APS data. No shape factor correction, $\chi$, was applied to the APS size distributions. APS flow and sizing calibrations were routinely performed during each field campaign using PSL, borosilicate and SiO$_2$ calibration spheres. Periodically flow adjustments were performed according to the procedures outlined in McNaughton et al., [2007].
2.2.4. Performance Characteristics of the HiGEAR impactor plates

When measuring aerosol optical properties it is often advantageous to eliminate the supermicrometer aerosol component from the sample in order to investigate the extensive and intensive properties of the submicrometer aerosol only. After subtracting the extensive submicrometer aerosol optical properties from the total aerosol optical properties we can often perform a more detailed investigation of both the extensive and intensive optical properties of the supermicrometer aerosol as well.

Removing the supermicrometer aerosol is accomplished using two aerodynamic impactors, one for the TSI nephelometer system (TSI Neph impactor) and one for the RRNeph/PSAP/f(RH) system (RRNeph impactor). The RRNeph impactor is shown as the diamond-shaped element in the figure 2.1 flow diagram and is plumbed with a bypass valve so that total aerosol can periodically be measured.

Each impactor is designed to eliminate 50% of the aerosol number at a specific aerodynamic diameter (~1 μm @ ρ=1.0 g cm⁻³). Figure 2.5 plots optically effective volume distributions for four monodisperse sizes of SiO₂ calibration spheres measured by the OPC during a laboratory test with the TSI Neph impactor in line (black) and without the impactor (blue). During the same test the APS instrument was used to assess the aerodynamic particle passing efficiency, defined here as the ratio of the particle number with the impactor in-line divided by the particle number with the impactor offline (Figure 2.6). Distributions have been adjusted using the densities indicated in the legend for each SiO₂ calibration sphere. The solid black line in Figure 2.6 is the passing efficiency curve derived from these measurements.
Figure 2.7 plots the optically effective size distribution measured by the OPC with the impactor (black) and without the impactor as well as the predicted distribution (red) using the impactor efficiency curve derived in Figure 2.6. Based on the results of this test the 50% aerodynamics (\(\rho=1.0\ \text{g cm}^{-3}\)) efficiency of the TSI nephelometer impactor is 0.88 \(\mu\text{m}\) when operating at a flow rate of 30 lpm. A similar analysis was carried out for the RRNeph impactor assembly resulting in a 50% efficiency diameter of 1.0 \(\mu\text{m}\) for a flow rate of 20 lpm. These impactor efficiency curves are used throughout this dissertation to compute the submicrometer aerosol size distribution. One minus the efficiency curves is used to compute the supermicrometer aerosol size distributions. 

![Diagram](https://example.com/diagram.png)

**Figure 2.5** – OPC volume distributions measured through the TSI Neph impactor (blue) and without the impactor (black).
Figure 2.6 – TSI nephelometer impactor efficiency curve for particles with a density of 2.0 g cm\(^{-3}\). Curve is generated as the fit to the ratio of the SiO\(_2\) calibration spheres passing efficiencies corrected for their respective densities.

Figure 2.7 – Verification of the accuracy of the TSI Neph impactor efficiency curve derived from APS measurements. OPC volume distribution when the impactor is in-line is shown in black and without the impactor is shown in blue. The predicted impactor distribution based upon data collected without the impactor is shown in red.
2.3. Measuring aerosol optical properties

2.3.1. Measurements of aerosol light scattering

For each of the experiments listed in Table 2.1 total aerosol light scattering is measured using a TSI model 3563, 3-λ integrating nephelometer [Anderson et al., 1996; Anderson and Ogren, 1998]. During TRACE-P submicrometer aerosol scattering was measured during level legs by switching the TSI nephelometer impactor into the aerosol sample flow (see §2.2.4). During ACE-Asia, DICE and INTEX-NA submicrometer aerosol light scattering was measured using a second model 3563 TSI nephelometer (TSI Neph). During MIRAGE and INTEX-B submicrometer aerosol light scattering was measured using a Radiance Research model 903 single-wavelength nephelometer. Additionally dry and humidified aerosol light scattering is measured using two Radiance Research nephelometers operating in parallel (dry and wet RRNephhs) during ACE-Asia, INTEX-NA & B (see §2.3.3).

The chief limitation of the RRNephhs is their instrument specific truncation of forward light scattering in the sample volume. Anderson et al., [2003] developed an empirical correction for this deficiency:

\[
RRNeph\sigma_{sp,corr} = \frac{RRNeph\sigma_{sp}}{(0.94 - 0.25 \cdot (1 - FMF))}
\] (2.2)

where,

\[
FMF = \frac{\sigma_{sp,submicrometer}}{\sigma_{sp,total}}
\] (2.3)
RRNeph data collected during DICE was corrected according to this formula and results in a discrepancy of less than 5% between TSI Neph and RR Neph supermicrometer scattering (see figure 7 of McNaughton et al. [2007]). The Anderson and Ogren [1998] correction has been applied to the TSI Neph data while the empirical correction of Anderson et al., [2003] has been applied to the RR Neph data presented in this dissertation.

Calibrations using filtered CO₂ and Refrigerant 134A (higher Rayleigh scattering calibration gas than CO₂) were performed prior to each deployment and every 3-5 flights. No significant (<5%) calibration adjustments were required for the TSI nephelometers while slight (5-10%) adjustments were often required for the zero and span of the RR Neph. These corrections have been applied to the data.

Every 3-5 flights an in-flight Rayleigh zero was performed on the TSI nephelometers. No significant changes were noted. During each flight at least one 300-second filtered air sample was collected to check for leaks and/or deviations from zero. No significant deviations from zero were noted for the TSI nephelometers. Problems with RR Neph leakage is discussed in detail in §2.3.3.

During INTEX-NA a TSI nephelometer instrument comparison was carried out between the LaRC and UH TSI Nephs which nominally operated as the total and submicrometer nephelometers during the campaign. The results of the two-hour comparison (Figure 2.8) of the 1-Hz data indicate that discrepancies in the blue and green channels are <1% while the red channels differ by about 5%. Zero intercepts for the regressions are 0.7, 0.3 and 0.1 Mm⁻¹ an acceptable value for data collected at 1-Hz. Regressions of the backscattering coefficient contain slightly higher offsets between the
instruments but are less than 15%. Typically this data is averaged over a minimum of 60-300 seconds which results in much lower noise and a smaller backscattering offset (~8% @ 60-seconds). These findings are consistent with previously published accuracy and precision estimates for these instruments [Anderson et al., 2003; Anderson and Ogren, 1998].
Ground Test - 2004/07/07 - 17:15 to 19:00
TSI Neph Intercomparison

Figure 2.8 – Linear regressions of aerosol light scattering (left) and backscattering (right) recorded by the UH TSI Neph compared to the LaRC TSI Neph measurements. Rows correspond to the values at 450 (top), 550 and 700 nm wavelengths. Data are recorded at 1-Hz and indicate accuracy and precision comparable to that reported previously for these instruments.
2.3.2. Measurements of aerosol light absorption

During TRACE-P and ACE-Asia total and submicrometer aerosol absorption were measured using a single-wavelength ($\lambda = 532$ nm) Radiance Research particle soot absorption photometer (PSAP) which were corrected according to Bond et al., [1999]. During INTEX-NA flights 6-20, total aerosol absorption was measured using a new 3-wavelength ($\lambda = 470, 530$ and 660 nm) PSAP while submicrometer scattering was measured using a single wavelength PSAP. The raw data from INTEX-NA is corrected according to the formulation of [Virkkula et al., 2005] rather than the Bond et al., [1999] correction applied to the TRACE-P and ACE-Asia data sets [Anderson et al., 2003].

During INTEX-B, MIRAGE and IMPEX total and submicrometer aerosol absorption is measured using new 3-$\lambda$ PSAP's corrected according to [Virkkula et al., 2005].

In laboratory tests prior to the INTEX-B experiment three of the four 3-$\lambda$ PSAPs were tested in the laboratory for instrument noise while sampling filtered air. The average instrument noise ($\delta_{300}$) is computed as the average standard deviation for six, 300 second (5-minute) averages of the 1-Hz data (Table 2.2). These values are comparable to instrument noise ($\delta_{240} = 0.72$ Mm$^{-1}$ and 0.33 Mm$^{-1}$) reported for the single-wavelength PSAPs used to measure total and submicrometer absorption during ACE-Asia (figure 3 of [Anderson et al., 2003]). PSAP #4 was not delivered from the manufacturer until after the November 2006 intercomparison and has not been evaluated.
Table 2.2 – Laboratory comparison of PSAP instrument noise while sampling filtered air.

<table>
<thead>
<tr>
<th>Unit</th>
<th>Owner</th>
<th>Experiment</th>
<th>Total or Submicrometer Sampling</th>
<th>Blue $\delta_{300}$ (Mm$^{-1}$)</th>
<th>Green $\delta_{300}$ (Mm$^{-1}$)</th>
<th>Red $\delta_{300}$ (Mm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSAP1</td>
<td>HiGEAR</td>
<td>INTEX-NA, B &amp; MIRAGE</td>
<td>total</td>
<td>0.56</td>
<td>0.56</td>
<td>0.56</td>
</tr>
<tr>
<td>PSAP2</td>
<td>LaRC</td>
<td>INTEX-B</td>
<td>total</td>
<td>0.36</td>
<td>0.34</td>
<td>0.36</td>
</tr>
<tr>
<td>PSAP3</td>
<td>LaRC</td>
<td>INTEX-B</td>
<td>submicrometer</td>
<td>0.51</td>
<td>0.50</td>
<td>0.55</td>
</tr>
<tr>
<td>PSAP4</td>
<td>HiGEAR</td>
<td>MIRAGE</td>
<td>submicrometer</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

During MIRAGE/INTEX-B there were three intercomparison flights where the NASA DC-8 and the NSF/NCAR C-130 flew in formation. Total and submicrometer aerosol absorption was compared during these time periods (Figure 2.9). The first column of Figure 2.9 compares C-130 versus DC-8 total aerosol absorption at 470 (top), 530 (middle) and 660 nm (bottom). The center column compares the measurement of submicrometer 3-Å absorption measurements. Note the large discrepancy between the two measurements of submicrometer aerosol absorption.

During level flight the RRNeph/PSAP impactor assembly aboard the DC-8 and the C-130 are switched from “submicrometer” mode to “total” mode. This periodically allows the instruments to be compared while both measure total aerosol absorption. Results from these time periods are shown in Figure 2.10 for the DC-8 and Figure 2.11 for the C-130. Note that “total” PSAP is always denoted PSAP #1 while the nominally “submicrometer” PSAP is denoted PSAP #2.

Figure 2.10 shows that the DC-8 PSAP #2 absorption is significantly higher than PSAP #1 while for the C-130, PSAP #2 records only slightly less absorption than PSAP #1 (Figure 2.11). Based on the inter-platform comparison I assume the two total PSAP’s are the most accurate and perform a robust (underweights statistical outliers) multiple
linear regression to determine an empirical correction for the two submicrometer PSAP's. The submicrometer PSAP data for each experiment were then corrected according to these regressions.

Comparing the third column of Figure 2.9 to the second column of Figure 2.9 shows the correction eliminates the discrepancy noted during the intercomparison flights and ensures that aerosol absorption and quantities derived from them (e.g. single scatter albedo) will be comparable between the two platforms. The source of this discrepancy was not identified although it is most likely related to errors in sample flow rate. Note that while instrument noise and thus precision of the PSAP's can be assessed [Anderson et al., 2003], we have no way to calibrate the instruments for absolute accuracy.
Figure 2.9 – Comparison of 3-wavelength PSAP absorption values measured aboard the C-130 versus those measured aboard the DC-8 during intercomparison flights. The first column of data compare total aerosol absorption at 470, 530 and 660 nm. The second column compares the submicrometer aerosol absorption. The discrepancies were evaluated independently (see Figs. 2.10 and 2.11) and the data were empirically corrected. The corrected data are shown in the third column. Close agreement between the measurements on the two separate platforms lends confidence to the overall integrity of the data collected while the aircraft are sampling independently.
Figure 2.10 – Robust multiple linear regression of PSAP2 absorption values compared to PSAP1 values while both were sampling total aerosol aboard the NASA DC-8. Regressions were used to adjust the PSAP2 submicrometer absorption values and result in closer comparability between the DC-8 and C-130 submicrometer measurements of aerosol absorption (see figure 2.9).
Figure 2.11 – Robust multiple linear regression of PSAP2 absorption values compared to PSAP1 values while both were sampling total aerosol aboard the NSF/NCAR C-130. Regressions were used to adjust the PSAP2 submicrometer absorption values and result in closer comparability between the DC-8 and C-130 measurements (see figure 2.9).
2.3.3. Measuring light scattering as a function of relative humidity – f(RH)

During INTEX-NA & B the increase in light scattering as a function of relative humidity, so called f(RH), is measured. The system deployed aboard the NASA DC-8 is identical to the system flown aboard the NSF/NCAR C-130 during ACE-Asia [Howell et al., 2006].

Two model 903 Radiance Research nephelometers (RR Neph) are used to measure aerosol light scattering at 532 nm. Air sampled by one nephelometer (RRwet) is preconditioned to a relative humidity of 80% +/- 7% using a custom designed f(RH) system employing a GORE-TEX™ membrane. The second nephelometer (RRdry) was plumbed in parallel and outfitted with a commercial blanket heater. The blanket heater raises the nephelometer temperature by 5-10°C reducing the relative humidity to values below 40% in the humid (RH_{amb} > 90%) marine boundary layer and often below 5% in the free troposphere.

During INTEX-NA the f(RH) system nominally sampled the “total” aerosol. During level flight legs where the real time data indicated the presence of supermicrometer aerosol (i.e. sea salt and/or mineral dust) the RR Neph impactor valve is switched on allowing us to characterize the submicrometer f(RH) values. During INTEX-B the instrument nominally sampled behind a 1-μm aerodynamic impactor. Thus during INTEX-B the impactor assembly valve is periodically switched off allowing us to characterize the total f(RH) values. During a typical 20-minute level leg this impactor switching would be performed at least once, often twice, resulting in two 5-minute “total” f(RH) measurements and two 5-minute “submicrometer” f(RH) measurements. Since
there was very little dust sampled during INTEX-NA, “total” free troposphere (FT) \( f(RH) \) values over North America can be directly compared to the “submicrometer” \( f(RH) \) values collected in the FT over Mexico and the North Pacific (i.e. the submicrometer only data collected during INTEX-B).

Due to their construction RR Nephs are prone to leaks when there is a large pressure differential (\( \Delta P \)) between the aircraft cabin and the ambient atmosphere. Early in the Mexico phase of INTEX-B an unacceptably high leak rate resulted in non-zero scattering values during filtered air tests at high altitude. On March 15\(^{th} \) the RRNephs were resealed and the leak rates recalculated (Figure 2.12). Average \( \Delta P \) for the INTEX-B campaign was 350 mb with a range between -25 and 600 mb. After resealing the RRNephs the leak rates were reduced to \(~4\%\) and \(~8\%\) of the total flow (6 vlpm) for the dry and wet nephs respectively (Figure 2.12). After re-sealing the instruments, filter-zero tests performed at high altitude were no different than zero (\( \alpha=0.05 \)). This indicates that the sites of the leakage were effectively acting as filters and did not adversely affect aerosol composition, an effect that would alter the \( f(RH) \) measurement. The leakage does affect the determination of aerosol scattering in the ambient environment.

As a result of these considerations, \( f(RH) \) data recorded prior to flight 7 (March 17\(^{th} \), 2006) have not been used in this dissertation. The remainder of the scattering data is corrected assuming particle free air is introduced to the sample volume at the RRNeph leak rate determined as a function of \( \Delta P \). And while the leak will add some uncertainty to the measurement I later show that the variability in \( f(RH) \) observed during INTEX-NA and B are comparable to variability reported during ACE-Asia indicating that this uncertainty is less than the observed variability in the ambient environment.
During post-processing the relevant calibration coefficients are applied to the scattering data collected by the f(RH) system’s nephelometers. Then, using the RH values recorded by the RRdry and RRwet nephelometers a two point fit is used to compute $\gamma$, the exponential term in the $f(RH)$ equation:

$$
\sigma_{sp,amb} = \sigma_{sp,dry} \cdot \left( 1 - \frac{RH_{dry}}{100} \right)^\gamma
$$

(2.4)

where, $\sigma_{sp,dry}$ and $\sigma_{sp,amb}$ are light scattering at the indicated “dry” and “ambient” relative humidities [Carrico et al., 2003; Howell et al., 2006]. Total, $\gamma_T$, and submicrometer, $\gamma_S$, values are used throughout this dissertation to estimate ambient light scattering at 550 nm.
2.3.4. Evaluating the accuracy of the f(RH) measurements

The increase in light scattering as a function of relative humidity depends on the aerosol size distribution as well as the aerosols’ composition. Anderson et al. [2003], tabulated precision (δ_P, ave for α=0.05), total uncertainty (δ_U, ave) and standard deviation (SD) of the f(RH) measurements during ACE-Asia. However, they did not include an analysis of the accuracy of the f(RH) measurements by testing measurements of an aerosol of known composition against f(RH) predicted from size distributions. During INTEX-B a ground-based test of the f(RH) system accuracy was performed with the f(RH) system in its flight configuration aboard the NASA DC-8.

During the test the IDMA, OPC and APS sizing instruments recorded the aerosol size distribution while the RRdry and RRwet nephos recorded aerosol light scattering at two different RH’s. Two separate aerosol types were generated using a commercially available nebulizer. Sea salt aerosol (Figure 2.13) was generated from a filtered (Dp > 0.2 μm) seawater sample from Station ALOHA [Karl and Lukas, 1996]. Ammonium sulfate aerosol [(NH₄)₂SO₄] was generated from a 10 wt% solution (Figure 2.14). During the test the impactor assembly was cycled between the on and off positions allowing both the total and submicrometer f(RH) values to be recorded. Since the size instruments were not located behind the RRNeph impactor assembly the shape of the size distribution is calculated from the impactor efficiency curves which adds some uncertainty (see section 2.2.4).

After the test, APS size distributions were density corrected based on the ratio of APS to RRdry and RRwet instrument RH’s values from the work [Tang, 1997; Tang and
The IDMA and APS size distributions were combined into one set of distributions while the OPC and APS size distributions were combined into a separate set of distributions. Scattering from the size distributions were calculated using Tang et al., refractive indices at the RRNeph instrument RH's. No corrections for size dependent losses in the OPC, APS or f(RH) systems were considered, however the RRNeph scattering data have been corrected using the empirical formulation of Anderson et al. [2003].

The results shown in Figures 2.13 and 2.14 indicate that scattering measurements for two aerosols of known composition are within ~+/-25% of the values calculated from size distributions measurements after applying experimentally determined salt densities and optical properties as a function of relative humidity. Since f(RH) is computed from the ratio of these two uncertain quantities the f(RH) measurement could be low by up to a factor of 0.67 or overestimated by up to a factor of 1.5.

In Appendix-B I tabulate f(RH) values for various airmass types including clean marine conditions where the aerosol composition is relatively well constrained by other measurements. The results presented in this dissertation are consistent with values previously published using this f(RH) system [Anderson et al., 2003; Howell et al., 2006] as well as independent measurements using a separate instrument system [Carrico et al., 2003]. Thus I conclude that the accuracy of the f(RH) determination is limited by RRNeph instrument noise, 0.6 Mm⁻¹ for a 240 second level leg average [Anderson et al., 2003], rather than poor performance of the f(RH) system’s preconditioner. Size dependent losses in the sample lines is also a potential source of error, especially when
sampling hydrated (80% RH) supermicrometer sea salt without the RRNeph impactor.

These losses have not been evaluated.
Figure 2.13 - Sea salt comparison of dry (RH<40%) and humidified (RH=82-85%) light scattering measured by the RRdry (left) and RRwet (right) nephs compared to theoretical values calculated from size distributions. The top two panels are the values calculated from the combined OPC + APS distributions while the bottom two panels are for the combined IDMA + APS distributions. Dashed lines indicate values +/- 25%.

Figure 2.14 - Ammonium sulfate, $(\text{NH}_4)_2\text{SO}_4$, comparison of dry (RH<40%) and humidified (RH=82-85%) light scattering measured by the RRdry (left) and RRwet (right) nephs compared to theoretical values calculated from size distributions. IDMA + APS distributions are shown as open squares while the OPC + APS distributions are shown as open circles.
2.4. Fitting aerosol size distributions using lognormal distributions

In general aerosol size distributions can be represented using log-normal curves [Baron and Willeke, 2001; Seinfeld and Pandis, 1998]. Throughout this dissertation aerosol size distributions are summarized using log-normal curves of the form:

\[
\frac{dN}{d \ln D_p} = \frac{N}{(2\pi)^{1/2} \ln \sigma_g} \exp \left( -\frac{(\ln D_p - \ln D_{pg})^2}{2 \ln^2 \sigma_g} \right)
\]

(2.5)

where \( N \) is the total particle number, \( D_p \) is particle diameter, \( D_{pg} \) is the geometric mean diameter and \( \sigma_g \) is the geometric standard deviation of the distribution. For plotting and analysis purposes it is easier to use a base 10 logarithm to express the aerosol size distribution rather than the natural logarithm. When plotted as \( dN/d\log D_p \) versus \( \log D_p \) the area under the curve is equal to total particle number, \( N \). The distribution using the natural logarithm is converted to base 10 using:

\[
\frac{dN}{d \log D_p} = \ln(10) \frac{dN}{d \ln D_p}
\]

(2.6)

The geometric mean for the number distribution is easily converted to the corresponding area and volume geometric mean diameter according to:

\[
\ln \overline{D}_{pgn} = \ln \overline{D}_{pg} + 2 \ln^2 \sigma_g
\]

\[
\ln \overline{D}_{pgv} = \ln \overline{D}_{pg} + 3 \ln^2 \sigma_g
\]

(2.7, 2.8)

The geometric mean diameter of the aerosol population is also referred to as the median diameter, or the diameter below which one-half of the particle number reside.
Throughout this dissertation the number, area, volume and mass median diameters are abbreviated as: NMD, AMD, VMD and MMD.

Integral number, N, is converted to integral area, S, or integral volume, V, according to:

\[
S = \pi N \exp\left(2 \ln \overline{D_{pg}} + 2 \ln^2 \sigma_g\right)
\]

\[
V = \frac{\pi}{6} N \exp\left(3 \ln \overline{D_{pg}} + \frac{9}{2} \ln^2 \sigma_g\right)
\]

Note that the volume median and mass median diameters are the same but that the integral volume, V, is multiplied by a particle bulk density, \(\rho\), to compute mass, M. The geometric standard deviation of the distributions, \(\sigma_g\), is the same whether the distribution is expressed as number or volume etc. This mathematical expression of the distribution is convenient because it allows description of any distribution using just three parameters, N, \(D_{pg}\) and \(\sigma_g\) rather than as a vector of \(dN/d\log D_p\) values with as many elements as there are diameters.

The 60-second resolution data collected during the field campaigns is stratified into airmasses of similar character using gas- and aerosol-phase tracers as discussed in Chapter 3. For generating size distributions the same stratification is carried out using the NASA generated 300- to 600-second resolution University of New Hampshire aerosol chemistry data set (UNHaero). Once the UNHaero time intervals are selected, the log-normal fitting procedure is completed in the eight steps summarized below.
1. Fast data averaged to UNHaero time intervals

Over a 300 second interval there is typically at least one full, unheated, 150°C and 360°C DMA distribution measurement. For INTEX-B there is also at least one IDMA distribution per 300 second chemistry sample. The DMA systems bin data into even, logarithmically spaced, diameter arrays between 0.010 and 0.20 μm (0.010 to 0.50 μm for the IDMA) with a dlogDp value of 0.022. OPC size distributions are saved every 3 seconds and the TOAD cycles between each temperature every 30 seconds. The OPC data are collected over the 0.10 and 20.0 μm size range with a dlogDp value of 0.009. OPC data < 0.12 μm are discarded due to poor performance; OPC data > 8.0 μm are typically discarded due to poor counting statistics. The APS also records distributions every 3 seconds. The APS assigns aerosol size over the 0.50 and 20.0 μm size range with a dlogDp value of 0.031. APS data below 0.78 μm is discarded due to poor instrument performance. For each instrument all the available distributions are averaged over the UNHaero sampling interval before starting the log-normal fitting routine.

2. OPC diameters adjusted for refractive index and relative humidity

The OPC diameters are first adjusted for refractive index (see section 2.2.2). Relative humidity is checked but never exceeded 25% so no RH size adjustments are necessary.

3. APS diameters adjusted for density and relative humidity

APS diameters are first adjusted according to Eqn. 2.1. Particle density is assigned a value of 2.06 g cm⁻³ for dust whereas sea salt particle densities are calculated
based on instrument RH [Tang et al., 1997]. Instrument RH only exceeded 40% during some level legs in the MBL near Hawai‘i.

4. Unheated and refractory distributions combined using joindists.m

In order to construct a single size distribution for each time interval the data from each instrument is combined using a MATLAB routine, joindists.m. This routine combines an arbitrary number of aerosol size distributions by interpolating the \( \frac{dN}{d\log D_p} \) values to a specified, even, logarithmically-spaced vector of diameters which are specified by the user. Overlap regions are optionally weighted resulting in smooth transition over the regions of instrument overlap. I specify a logarithmically spaced output diameter array between 0.01 and 60.0 \( \mu \text{m} \) with a \( d\log D_p \) value of 0.02. The upper limit of 60.0 \( \mu \text{m} \) is useful because calculation of size distribution properties under ambient relative humidity conditions occasionally result in ambient diameters greater than a factor of two compared to their dry diameters. The joindists.m routine is run consecutively for unheated and the refractory (360°C) distributions for each UNHaero time interval for the airmass type being analyzed.

Then, for each sample,

5. The unheated distribution is fit using a least squares optimization,
6. the unheated fit is visually checked and reiterated as necessary,
7. the refractory distribution is fit using a least squares optimization,
8. and the refractory fit is visually checked and reiterated as necessary.

Other researchers have reported using log-normal fitting routines using least squares optimization [Hand and Kreidenweis, 2002; Osborne and Haywood, 2005;
Porter and Clarke, 1997]. However, in the cases cited only one moment of the aerosol size distribution is considered during the fit. The problem with this approach is that when minimizing using least squares the error term is computed based on the magnitude of the difference for each data point. Since aerosols exist over three to four orders of magnitude in number this corresponds to nine to twelve orders of magnitude in volume. Thus when fitting the number distribution [Osborne and Haywood, 2005; Porter and Clarke, 1997] the tail of the distribution contains an insignificant number and therefore insignificant error. But the tail of the number distribution contains all of the volume and will be poorly constrained. Similarly, when fitting using the volume distribution [Hand and Kreidenweis, 2002] aerosol number will be poorly fit.

To avoid this commonly overlooked pitfall we (S. Howell) developed a least squares fitting routine in MATLAB, NLAV.m, which simultaneously evaluates the least squares error for the number, length, area and volume distributions (i.e. the zeroth through third moments). Using this algorithm results in better fits which do not bias the results by large errors contributed from a single mode, e.g. number or volume. After the fit is computed it is visually displayed. I then decide whether additional modes are required to describe the aerosol population and if necessary reiterate the fit. Between one and three modes (termed the Aitken, accumulation and coarse modes), were required to fit the unheated distribution. In general only two fits, Aitken and coarse mode, are required to fit the refractory aerosol distributions. Note that in general the refractory Aitken mode aerosol is the internally mixed component of the unheated accumulation
mode aerosol\textsuperscript{2}, the unheated Aitken mode aerosol being nearly completely volatile at 360°C. An example of typical 2-mode fits to an unheated and a refractory distribution are included in figures 2.15 and 2.16. Locally poor fits in the number distribution (top panels) are prevented from skewing the fit in volume distribution (bottom panels) and vice-versa. This level of agreement is typical of fits used throughout this dissertation and shows small potentially real variations in unheated Aitken mode number as well as poor counts and the effects of OPC Mie oscillations on the unheated and refractory volume distributions.

After each distribution is fit the values for each mode are saved into separate ASCII files for later use. For example if 15 distributions were fit then a 15 row, 3 column matrix of $N$, $N_{MD}$ and $\sigma_R$ is generated. If the unheated and refractory distributions each required a 1-mode fit, two, $15 \times 3$ files are saved. If each fit required two modes then four files are saved.

The following chapters include summary plots of the number and volume distributions for the unheated and refractory distributions. The distributions plotted correspond to the average values tabulated in Appendix-C. Note that the ASCII files generated contain more fits to the distributions than those used to compute the plotted averages. This is because some distributions are missing data (e.g. no refractory DMA distribution) and it is not appropriate to generate averages using unequal numbers of unheated and refractory distributions.

\textsuperscript{2} This is determined using the tandem differential mobility capability of the HiGEAR DMA instruments, data which are not discussed in this dissertation.
Figure 2.15 – Two-mode log-normal fit for an unheated aerosol size distribution measured in mixed Asian pollution and dust.

Figure 2.16 – Two-mode log-normal fit for a refractory aerosol size distribution measured in mixed Asian pollution and dust.
2.5. References


over the Pacific and Gulf of Mexico, *Atmospheric Chemistry and Physics, in prep.*, 2007a.


3.0 Aerosol size distributions and the aerosol direct effect

Aerosols directly affect the Earth's radiation balance by scattering and absorbing solar radiation. Recent modeling efforts compute an annual globally averaged aerosol optical depth (AOD) between 0.11 and 0.14. These estimates are slightly lower than globally averaged AERONET and satellite estimates (~0.14 and ~0.15). However, large discrepancies remain with respect to simulating carbonaceous aerosol and mineral dust absorption which both exert a profound influence on radiative forcing [Kinne, 2006; Schulz et al., 2006]. Assessing aerosol influence on the Earth's radiation balance requires knowledge of the vertical distributions of the aerosol. Since most data are from ground-based observations or satellite retrievals, aircraft measurements provide the link between these measurements and the aerosol properties of the atmospheric column [Shinozuka et al., 2007].

In this chapter I summarize vertical profiles of trace gases, aerosol number, mass and optical properties for airmasses which dominate aerosol extinction in the troposphere over North America and the North Pacific. I compare average aerosol size distributions for these airmass types with parameterizations and discuss their differences with respect to aerosol optical properties. Average values of the increase in light scattering as a function of relative humidity and their effect on ambient AOD are discussed. Finally, I close the discussion with a preliminary analysis of the wavelength dependence of light absorption by carbonaceous aerosols and mineral dust; a source of considerable uncertainty in modeling the radiative effects of tropospheric aerosols.
3.1 Airmass classification over the North Pacific and North America

In our 2007 publication, [Clarke et al., 2007], we compared biomass burning and anthropogenic aerosols in 84 separately identified “plumes”. These plumes were identified when selected gas and aerosol phase tracers exceeded their 95th percentile compared to all other data measured within a 1 km altitude bin. This classification scheme effectively isolates the dominant properties for these two plume types and constitutes ~17% of the INTEX-NA flight data.

Using merged DC-8 datasets from INTEX-NA & B I have further stratified airmasses over North America and the North Pacific into 25 airmass types. These are grouped by experiment:

\[
\begin{align*}
IA &= \text{INTEX-NA} \\
IB &= \text{INTEX-B}
\end{align*}
\]

region,

\[
\begin{align*}
ENA &= \text{Eastern North America} \\
MEX &= \text{Central Highlands and Gulf of Mexico} \\
HI &= \text{Hawaiian trade wind regime (East Pacific High)} \\
AK &= \text{Alaskan Low}
\end{align*}
\]

atmospheric compartment,

\[
\begin{align*}
FT &= \text{Free troposphere (2-12 km)} \\
LT &= \text{Lower free troposphere (2-6 km)} \\
UT &= \text{Upper free troposphere (6-12 km)}
\end{align*}
\]

\[
\begin{align*}
BL &= \text{Boundary Layer (alt < 2 km)} \\
CBL &= \text{Continental boundary layer (alt < 2 km)} \\
MBL &= \text{Marine boundary layer (alt < 1.5 km)}
\end{align*}
\]
and finally by airmass type. The nomenclature of the airmass types include:

IA_ENA_steUT: Airmasses from the region of UT/LS airmass exchange.

IA_ENA_cleanLT: Clean conditions in the lower troposphere (2-6 km).
IA_ENA_cleanUT: Clean conditions in the upper troposphere (6-12 km).

IA_ENA_antbroLT: Anthropogenic pollution in the lower troposphere (2-6 km).
IA_ENA_antbroUT: Anthropogenic pollution in the upper troposphere (6-12 km).

IA_ENA_bbLT: Biomass burning in the lower troposphere (2-6 km).
IA_ENA_bbUT: Biomass burning in the upper troposphere (6-12 km).

IA_ENA_conv1UT: 0-12 hrs since deep (> 6 km) convection.
IA_ENA_conv2UT: 12-48 hrs since deep convection.
IA_ENA_conv3UT: 48-108 hrs since deep convection.

IA_ENA_age1BL: "Fresh" anthropogenic pollution in the boundary layer.
IA_ENA_age2BL: "Intermediate" anthropogenic pollution in the boundary layer.
IA_ENA_age3BL: "Aged" anthropogenic pollution in the boundary layer.

IB_Mexico_cleanFT: Clean background conditions in the FT including evidence of airmass exchange with the Southern Hemisphere.

IB_Mexico_anthroLT: Anthropogenic pollution over the Gulf of Mexico for altitudes greater than 1.5 km.

IB_Mexico_anthroCBL: Pollution over the Central Highlands of Mexico.
IB_Mexico_anthroMBL: Pollution over the Gulf of Mexico below 1.5 km altitude.

IB_Hawaii_mixedFT: Long range transport of mixed Asian pollution and Asian Dust in the FT (altitude > 1.5 km) south of 40°N.
IB_Hawaii_anthroFT: Long range transport of Asian Pollution in the FT.

IB_Hawaii_anthroMBL: Asian Pollution in the remote marine boundary layer.

IB_Hawaii_backMBL: Airmasses in the remote MBL with aerosol composition the same as seawater.

IB_Hawaii_steUT: Airmasses from the region of UT/LS airmass exchange.

IB_Alaska_dustyLT: Long range transport of mixed Asian pollution and Asian Dust in the FT (altitude > 1.5 km) north of 40°N.

IB_Alaska_anthroLT: Long range transport of Asian Pollution in the FT.

IB_Alaska_anthroMBL: Asian Pollution in the remote MBL.

IB_Alaska_backMBL: Airmasses in the remote MBL with aerosol composition the same as seawater.

IB_Alaska_steUT: Airmasses from the region of UT/LS airmass exchange.

Airmasses selected for analysis are identified according to one or more Boolean criteria. These criteria were selected in order to simply but effectively isolate airmasses of unique character but in a manner that can easily used to evaluate model output in future comparisons.

Summary tables of thermodynamic, gas phase and aerosol tracers are included in Appendix B. Trace gases are reported in mixing ratios whereas aerosol properties are reported at standard atmospheric temperature and pressure (SATP = 298.15K; 1013.25 mb). Appendix-C contains tables of the lognormal fitting statistics for the aerosol size distributions that relate to each of these airmass types.

With respect to the aerosol direct effect I am most interested in determining how large the perturbations are compared to clean background conditions, i.e. conditions expected to be the norm in a pre-industrial model simulation [Schulz et al., 2006]. When summarizing the statistics for the “clean” airmasses I use the median (50th percentile)
value so as to reduce the influence of large outlier values that positively skew the mean value. When computing the influence of anthropogenic pollution, biomass burning and properties of the marine aerosol it is more appropriate to consider the mean value in order to evaluate the average perturbation these plumes have on the background atmosphere. Note however that airborne sampling is not random. Thus the frequency of plume occurrences and to some extent our mean values can be biased by our sampling strategy. I do not consider this further as there is insufficient long-term in-situ measurements of the FT with which to make this determination. I begin by summarizing the characteristics associated with vertical profiles of trace gases, aerosol number, mass and aerosol optical properties. Descriptive summaries of each airmass types can be found in the chapter sections that pertain to them.

3.2 Vertical Profiles of selected trace gases, aerosol number, mass and optical properties

Providing the modeling community with vertical profiles of aerosol mass and optical properties will reduce uncertainties associated with modeling the aerosol direct effect [Kinne, 2006; Kinne et al., 2003; Reddy et al., 2005; Schulz et al., 2006]. Vertical profiles of aerosol number are key to constraining the indirect effect, i.e. the aerosols as cloud condensation nuclei (CCN) [Penner et al., 2006]. Vertical profiles of mass can be used to test our understanding of aerosol life-cycles, particularly their transport from the continental and marine boundary layers (CBL, MBL) to the free troposphere (FT) [Raes et al., 2000; Textor et al., 2006]. Also, estimates of the vertical distribution of volatile and refractory organic carbon mass (VolOC and RefOC) as well as light absorbing black
carbon (BC) will provide much needed data on carbonaceous aerosols in the FT
[Kanakidou et al., 2005; Liousse et al., 1996].

The chief advantage of airborne atmospheric sampling platforms is their ability to
take in-situ measurements of the vertical distribution of trace gases and aerosols. The chief
disadvantage is that the data essentially represent a point measurement in both space and
time (x, y, z, and t). The extensive ground-based network of measurements in continental
North America provide time series at a fixed location on the Earth’s surface [Malm et al.,
2004]. However these measurements as well as ground-based remote sensing [Holben et
al., 2001; Murayama et al., 2003] cannot be used to provide a truly global estimate of the
ambient aerosol field. Space-borne remote sensing [Kahn et al., 2004; Kaufman et al.,
2002] can be used to provide global measurements of the aerosol field every few days.
However their radiance retrievals must be related to the underlying properties of the
ambient aerosols’ size distribution. Since these are not measured directly by the satellites,
each sensor requires rigorous calibration and validation exercises that ultimately rely on a
host of a priori assumptions about the structure of the atmosphere and the trace-gases and
aerosols found within it. This calibration/validation can only be done by compiling data
using in-situ measurements, which are not available globally. Climate models are used to
forecast the global aerosol field and to test our hypothesis regarding the direct and
indirect effects of aerosols on past, present and future climate [Liousse et al., 1996;
Penner et al., 2002; Tang et al., 2004b]. Global climate models rely on assumptions
regarding sources, sinks and processes that govern atmospheric residence times for trace-
gas and aerosol species. Thus they also require extensive calibration and validation using
in-situ measurements. Often these models must employ coarse spatial and temporal
resolution as well as parameterizations in order to reduce the computational demands required to simulate the atmosphere on a global scale. Using parameterizations of subgrid-scale processes can lead to significant errors [Petch, 2001] resulting in large uncertainties in modeling important atmospheric phenomenon such as direct radiative forcing by aerosol [IPCC, 2007].

Vertical profiles of trace gases have been compared to model simulations to evaluate model performance in the FT. This analysis is limited due to our inability to make long-term in-situ measurements in the FT. Comparing vertical profiles of component specific aerosol properties has received less attention for two main reasons. First, many models do not contain dynamic aerosol modules capable of simulating aerosol population dynamics at the global scale. Second, robust in-situ measurements of component specific aerosol properties in the free troposphere are not readily available to the modeling community in a form suitable for their general use.

The series of figures contained in the following subsections summarize vertical profiles of trace gases (CO, O₃, HNO₃ and SO₂), aerosol number, aerosol mass and aerosol optical properties measured over North America and the North Pacific. Data for each airmass type are pooled and then binned by altitude so that differences between the airmasses can be evaluated. This is a somewhat poor representation of conditions in the ambient atmosphere, especially for large episodic plumes like biomass burning, as discrete airmasses are interleaved as layers with relatively sharp boundaries. The coarse spatial resolutions of GCM's cannot be repetitively compared to numerous aircraft profiles at what amount to points in both space and time within the model domain. Thus
an aggregate representation, like those presented here, is more appropriate for comparison to spatial and temporal averages generated by GCM’s.

3.2.1 Profiles over Eastern North America

During INTEX-NA (summer 2004) the FT over Eastern North America (ENA) was heavily influenced by forest fire plumes transported long-range from their source regions in Alaska and Northern Canada [Fuelberg et al., 2006; Singh et al., 2006]. Anthropogenic pollution from Asia and North America also contaminated the FT over Eastern North America [Liang et al., 2007].

The median concentration of CO, O₃ and HNO₃ measured under clean ENA FT conditions are ~1σ lower than the average concentrations measured when the FT is influenced by anthropogenic emissions or smoke from boreal forest fires (Figure 3.1). Median SO₂ under clean conditions is 28 pptv in the LT and 13 pptv in the UT compared to average values of 111 pptv and 63 pptv when the airmass is dominated by anthropogenic emissions (data summaries can be found in Appendix B - Table B.1). Summertime CO in the background upper and lower troposphere is 77-83 ppbv whereas in the biomass burning plumes the concentrations average 160 and 140 ppbv.

In section 3.3.3 I discuss the aging of anthropogenic pollution in the Eastern North American continental boundary layer. In the analysis airmasses are separated into three age classes based on the ratio of aerosol sulfate, SO₄²⁻, to total sulfur, SO₄²⁻ + SO₂. As the ENA BL airmasses ages, SO₂ can dry deposit to the Earth’s surface and onto pre-existing aerosol surface area. SO₂ is also photo-oxidized and/or formed during activation in cloud to form sulfate aerosol (see Section 3.3.3 for more detail). Each of these processes
lead to an overall increase in the S_{ratio} with time. Here “Fresh” airmasses are arbitrarily defined as those with S_{ratio} values less than 0.25 and appear as dotted red lines in Figures 3.1 through 3.4. Airmasses of “Intermediate” age have an S_{ratio} between 0.25 and 0.5 and are represented with dashed red lines, while relatively “Aged” airmasses have an S_{ratio} greater than 0.5 and are plotted as solid lines in Figures 3.1 - 3.4. As expected, the relatively conservative tracer CO (first panel of Figure 3.1) shows little difference (< 10%) between airmasses of different ages. Ozone increases 25% while nitric acid concentrations increase by about a factor of 2 as the airmasses age. This is consistent with our understanding of photo-chemical production of ground-level ozone and nitric acid from anthropogenic emissions of VOC’s and NO_x [Seinfeld and Pandis, 1998]. SO_2 is depleted such that the “Aged” column burden is only 34% of the ”Fresh” value.

Figure 3.2 plots CO in the first panel, ambient (not SATP) aerosol number in the center two panels and the RCN ratio in the far right panel. Free troposphere profiles of ultrafine (Dp > 3 nm) particle concentrations tend to increase with altitude over the remote ocean [Clarke and Kapustin, 2002]. The ultrafine particle number under background FT conditions over Eastern North America are low, 600 std cm^{-3}, but increase with altitude to concentrations of 2400 std cm^{-3} (Figure 3.2). This range of concentrations is consistent with UCN number concentrations from PEM-Tropics A & B for conditions where the RCN ratio is low (<0.2) [Clarke and Kapustin, 2002]. Figure 3.2 shows CN > 3 nm (UCN) for anthropogenically influenced airmasses increases with altitude from average values of ~1,700 std cm^{-3} in the LT to an average value of 15,000 std cm^{-3} in the UT (Table B.1). More abundant particle number is likely the result of gas-to-particle-conversion after photo-oxidation of SO_2 whose concentrations are higher in polluted compared to
background airmasses (far right panel of Figure 3.1). The shape of the vertical profile and the range of concentrations is similar to values measured over the remote ocean during PEM-Tropics A & B when the RCN ratio exceeds 0.2 [Clarke and Kapustin, 2002].

Condensation and coagulation during subsidence lowers particle number [Clarke et al., 1998b], but the lower troposphere value is still triple (1700 std cm⁻³) the background value in the ENA LT. The significance of this new particle number is discussed in more detail in Chapter 4. Ultrafine aerosol number in airmasses influenced by BB varies relatively little with altitude. SATP concentrations are in the 1400-2300 std cm⁻³ range.

In the boundary layer secondary aerosol formation from anthropogenic emissions are responsible for high concentrations of aerosol number > 3 nm [McNaughton et al., 2004]. Over continental North America these concentrations were found to decrease from 12,000 to 3,000 std cm⁻³ as the airmass ages. Later I investigate the evolution of the aerosol size distributions as a function of S_ratio (section 3.3.3).

Refractory aerosol number in FT biomass burning and pollution plumes are comparable and have SATP concentrations of 800-1200 std cm⁻³. These values are well in excess of the 200-300 std cm⁻³ observed under background FT conditions (summaries in Appendix B - Table B.1). Refractory CN concentrations in the boundary layer are between 2400 and 5800 std cm⁻³ and decrease by about a factor of 2 as the airmasses age.

Reduction of primary soot aerosol number in the BL can occur via a combination of processes including coagulation, dilution and wet/dry deposition.

In the final panel of Figure 3.2 I plot the ratio of refractory aerosol number (> 10 nm) to total aerosol number (> 10 nm). Near the surface this refractory CN ratio (RCN ratio) is high (> 0.70). The RCN ratio tends to increase with airmass age so long as the
airmass does not mix with air having low refractory number. This is because externally mixed secondary aerosols formed from gas-to-particle conversion coagulate with refractory aerosols of primary origin, i.e. soot. Under both clean and anthropogenically influenced conditions in the FT the ratio tends to decrease with altitude. We understand this trend to be the result of two processes. First, the concentration of refractory aerosol number is stable or decreases slightly with altitude as a result of wet removal processes, scavenging and dilution. Also, secondary aerosol production results in high concentrations of new, externally mixed volatile aerosol. The formation mechanism is most efficient under cold and humid conditions commonly present at high altitude near cloud outflow where there is little pre-existing aerosol surface area [Clarke et al., 1998a].

The forest fire plumes sampled over Eastern North America during INTEX-NA were sourced in the boreal forests of North America. SO$_2$ in the BB airmasses is higher than background conditions. However, these airmasses also contain high concentrations of primary soot particulate resulting in a relatively high RCN ratio (> 0.50) throughout the atmospheric column. Biomass burning aerosol can be injected directly into the FT through pyroconvection. This dry lofting of forest fire plumes results in large total aerosol surface area (i.e. light extinction) and likely contributes to the suppression of new particle formation and high RCN ratios.

Figure 3.3 plots CO along with vertical profiles of aerosol mass. The profiles highlight the surface source of aerosol mass which decreases with altitude. Total aerosol sulfate is lowest under background conditions but have similar profiles for Anthro and BB influenced airmasses. At the surface we see a buildup of aerosol sulfate, the result of sulfur
being irreversibly transferred from the gas phase reservoir, \(\text{SO}_2\), to the aerosol phase with time.

No direct measurements of organic aerosols were conducted aboard the NASA DC-8 during either INTEX-NA or B. However, in [Clarke et al., 2007] we demonstrate that organic carbon volatile below 360\(^\circ\)C (VolOC) can be calculated as the difference between submicrometer aerosol volume less the sum of submicrometer inorganic ionic volume and refractory aerosol volume. This operationally defined property was shown to exhibit the same magnitude and variation as water soluble organic carbon (WSOC) [Sullivan et al., 2006]. This VolOC term is calculated according to:

\[
\frac{M_{\text{volOC}}}{\rho_{\text{volOC}}} = V_{\text{volOC}} = V_{\text{sub}} - \left( \frac{\sum [\text{SO}_4^{2-}],[\text{NO}_3^-],[\text{NH}_4^+]}{\rho_{\text{ions}}} + V_{\text{refOC}} \right) 
\]

where, \(\rho_{\text{volOC}} = 1.6\) and \(\rho_{\text{ions}} = 1.8\) g \(\text{cm}^{-3}\). Where refractory mineral dust or seasalt can be excluded, refractory aerosol composition is inferred to be refractory organic carbon, RefOC.

Total aerosol mass for BB profiles is larger than the Anthro values. However, their sulfate mass profiles are nearly identical. Figure 3.3 plots VolOC (RefOC not shown) for each airmass type and indicates the higher mass fractions of volatile organic carbon in the biomass burning airmasses compared to VolOC in aerosol of anthropogenic origin. Note that since the OPC measurements of total and refractory aerosol are consecutive, sample timing within the plumes can adversely affect averages when there are few samples. This can be seen in the 9 km bin of the BB profile. Here VolOC mass appears to exceed the total mass by a factor of 2. Plotted as the dashed black line is the
VolOC mass based on the total aerosol mass using the Clarke et al. [2007] average BB VolOC mass fraction of 0.60. In the boundary layer the data tend to indicate an increase in VolOC mass as the airmasses age. Note that there are no direct measurements of organic aerosol aboard the DC-8. Nevertheless this behavior is consistent with the formation of WSOC, which Sullivan et al. [2006], found to have a time constant on the order of 1 day.

Figure 3.4 plots the vertical profiles of dry aerosol light scattering, absorption and ambient extinction. Ambient aerosol extinction is calculated using in-situ measurements of the increase in light scattering as a function of relative humidity and campaign average (all data) ambient RH. Average SATP dry scattering and absorption values for the UT, LT and BL are tabulated in Appendix B - Table B.1. The vertical profiles of aerosol optical properties demonstrate the large perturbations anthropogenic and biomass burning emissions have on light extinction in the FT. Under background conditions light scattering seldom exceeds ~3 Mm$^{-1}$ and absorption is not statistically different than zero ($\alpha=0.05$)$^1$. In the lower troposphere Anthro and BB aerosols have average extinction values of 16 and 59 Mm$^{-1}$. In the upper troposphere their averages are 2.8 and 59 Mm$^{-1}$.

Compare the vertical profiles of relatively hygroscopic anthropogenic pollution to the relatively hydrophobic biomass burning aerosol in Figure 3.4. UT and LT water vapour mixing ratios and RH’s are lower in the BB layers (432, 3200 ppmv; 38, 30%) than the Anthro layers (530, 7500 ppmv; 51, 62%). The reductions in anthropogenic aerosol extinction with altitude associated with enhanced water vapour data may reflect

---

$^1$ Here and throughout this dissertation statistical significance and significant differences between means are evaluated using the Student's t-test. Additional information on the test and its validity for use can be found in the appendix of McNaughton et al., [2007].
aerosol removal during vertical transport via relatively wet convective processes.

Refractory BB aerosol number as well as the concentrations of relatively hydrophobic RefOC are slightly higher than in the Anthro airmasses and may reflect direct aerosol injection into the FT by relatively dry pyroconvection.

Boundary layer aerosol scattering measurements show significant increases as the airmass ages (Figure 3.4). This is consistent with condensation of sulfuric acid, ammonium, nitric acid as well as secondary organic aerosol. Significant ($\alpha=0.05$) changes in aerosol absorption as a function of airmass age cannot be determined due to relatively large uncertainties ($\pm 0.5 \, \text{Mm}^{-1}$ - see section 2.3.2) compared to the average BL PSAP measurements ($\sim 1.0 \, \text{Mm}^{-1}$). Average $f(RH)$ values tabulated in the Appendix B (Table B.5) are used to compute ambient extinction at the campaign average relative humidity. This highlights the evolving nature of visible light extinction as polluted North American airmasses age during BL transport. The evolution of the size distribution is discussed in more detail in section 3.3.3.
Figure 3.1 - Vertical profiles of trace gases measured over Eastern North America during INTEX-NA.
**Figure 3.2** – Same as Figure 3.1 but for aerosol number.
Figure 3.3 – Same as Figure 3.1 but for aerosol mass.
Figure 3.4 - Same as Figure 3.1 but for aerosol extinction.
3.2.2 Profiles over the Mexican Highlands and over the Gulf of Mexico

Trace gas profiles over Mexico and the Gulf during the spring of 2006 show that anthropogenic emissions are affecting atmospheric composition up to at least 5.5 km. Above this altitude the majority of the data meet the “clean” airmass criteria of CO < 90 ppbv and O₃ < 40 ppbv. At this location prevailing winds are from the west meaning airmasses sampled over Mexico would be transported from the East Asian region and should contain East Asian pollution tracers. MOPITT satellite observations of column CO during the intensive observation period appear to support this hypothesis but show a local minimum between Hawai‘i and Mexico (Figures 3.5). The median CO concentrations under clean conditions over Mexico (72 ppbv) are much lower than the minimum values measured over the Hawai‘i (CO > 90 ppbv) during the same campaign (see Figure 3.11). Airmass back trajectories confirm that some air (3 of 4 trajectory clusters analyzed) is sourced over East Asia but show limited interaction with surface (Figure 3.6 – left). One set of back trajectories (Figure 3.6 - right) are sourced in the Southern Hemisphere (SH) indicating inter-hemispheric airmass exchange. Dilution of CO rich NH air (averaging 120 ppbv over Hawai‘i) by CO poor SH air (averaging ~60 ppbv; [Seinfeld and Pandis, 1998]) would partially account for the lower values observed over Mexico. Since CO lifetime is on the order of months, reductions due to photolysis during Hawai‘i to Mexico transport are expected to be small have not been evaluated.

HNO₃ and SO₂ concentrations are also extremely low in the clean MEX FT (45 pptv; 16 pptv) with SO₂ often below the instrument detection limit of 10 pptv (Figure 3.7). In
contrast HNO$_3$ and SO$_2$ concentrations in anthropogenically influenced airmasses are $\sim$1-2 orders of magnitude higher.

The elevated MEX FT concentrations of SO$_2$ in polluted FT air leads to greater ultrafine particle number in the upper troposphere (Figure 3.8). Elevated refractory number in the LT (likely soot from combustion) exceeds the clean FT values by at least a factor of 5 but contributes little to aerosol number and therefore light absorption above 6 km (Figure 3.10). Volatile number in the polluted MBL is comparable to the average in the lower FT while refractory aerosol is $\sim$60% higher. Mean RCN ratio is highest in the MBL and lowest in the CBL near Mexico City where gas-phase precursors lead to abundant new particle formation.

The average aerosol mass measured in polluted airmasses over the central highlands of Mexico and in the FT over the Gulf of Mexico exceed 5 $\mu$g m$^{-3}$ below 4 km and steadily increase towards the surface (Figure 3.9). This average is however somewhat misleading. Near Mexico City two, 300-second level leg averages of aerosol mass were as high as 225 $\mu$g m$^{-3}$ even at a DC-8 radar altitude of 1.1 km. The refractory aerosol mass for these cases is 198 $\mu$g m$^{-3}$ indicating that the distribution is dominated by dust and that the volatile aerosol mass itself is $\sim$27 $\mu$g m$^{-3}$. In fact the total supermicrometer mass is much larger than the measured value because robust counting statistics were recorded even in the uppermost channels of both the OPC and the APS instruments ($\sim$20.0 $\mu$m). These diameters are well above the UH inlet’s 50% efficiency diameter (3.5 $\mu$m for $\rho$=2.06 g cm$^{-3}$).

These high concentrations, particularly over the Central Highlands, allow a relatively robust estimate of the vertical distribution of both volatile and refractory OC.
Whereas the ratio of Vol:Ref OC is approximately 1:1 in the polluted FT and MBL the aerosol over the central highlands (i.e. Mexico City) has a ratio of ~4:1. For dusty cases, some portion of the submicrometer refractory aerosol is mineral dust. Separating these aerosol types requires analysis of the size distribution [Clarke et al., 2004]. This has not been performed on the bulk 60-second resolution data processed to compute the average vertical profiles. As a result the RefOC values over the central highlands is an overestimate of refractory OC. Sulfate aerosol concentrations are comparable between the highlands and the lower FT and by difference with the total mass illustrate the relatively large contribution of aerosol nitrate and volatile OC to the total mass of aerosol in this heavily polluted region.

Vertical profiles of dry aerosol scattering and absorption are elevated compared to the clean background up to 6-8 km. Values near the surface in the polluted CBL and MBL reach dry average values of 50-100 Mm⁻¹. Ambient extinction values in the arid CBL over the Mexican Highlands change little due to low ambient RH (26%) and suppression of total fRH (γ_T=0.32; γ_S=0.39) by mineral dust. In contrast, RH in the polluted MBL averaged 70% while γ_T and γ_S are 0.63-0.65. Thus when the CBL extinction values are integrated over ~2-6 km the aerosol optical depth (AOD) of 0.19 is similar to that of the MBL, 0.17, even though the MBL values are only integrated over 1.5 km.
Figure 3.5 – MOPITT column integrated CO for April 15\textsuperscript{th} – May 15\textsuperscript{th} 2006. Note the CO minima between Hawai'i and Mexico.
Figure 3.6 - Airmass back trajectories for clean upper troposphere air sampled over Mexico during INTEX-B. Back trajectories from East Asia (left) remain in the upper troposphere while some trajectories are sourced in the southern hemisphere (right) after being convected from the mid- to lower- troposphere (courtesy M. Porter and H. Fuelberg).
Figure 3.7 – Vertical profiles of trace gases for the Central Highlands and Gulf of Mexico regions sampled by the DC-8 during INTEX-B.
Figure 3.8 – Same as Figure 3.7 but for aerosol number.
Figure 3.10 – Same as Figure 3.7 but for aerosol extinction.
3.2.3 Profiles over the Eastern North Pacific

Using a temporal resolution of 60-seconds per sample there are 5127 data points collected over the Eastern North Pacific (ENP) during INTEX-B. Of these, just 24, or 0.5% of the data meet the “clean” background conditions of CO < 90 ppbv and O3 < 40 ppbv. While the CO and O3 selection criteria are arbitrary, will vary seasonally and may have different background values in different regions, the paucity of low CO, low O3 data over the ENP indicate that very few data points can be used to describe what might be considered “clean background” conditions suitable for comparison to a “pre-industrial” type simulation in a global climate model. Thus for these profiles the “clean” conditions measured in the FT over Mexico are included for reference instead.

The trace gas profiles of CO and O3 illustrate the impact Asian emissions have on the FT over the remote North Pacific (Figure 3.11). Values over Hawai‘i (127 and 63 ppbv) and Alaska (137 and 71 ppbv) are effectively double the values observed over Mexico (72 and 34 ppbv). HNO3 and SO2 values are similar except for the UT where both Hawaiian and Alaskan SO2 values exceed the clean FT values by a factor of 2-5. HNO3 in the MBL is highest in the polluted boundary layer near Alaska while SO2 is highest in the clean Hawaiian MBL. The high SO2 values below the trade wind inversion can likely be attributed to Kilauea volcano’s Pu‘u O’o vent complex [Porter et al., 2002] while a few samples from Alaska also contain high SO2 when sampling emissions from the Augustine volcano.

Remarkably the FT refractory and total aerosol number is similar in each region (Figure 3.12 and Table 3.1). Below the MBL inversion clean conditions are defined as
those where the aerosol chemistry is dominated by a seasalt type composition. For clean conditions the refractory number is significantly less (HI RCN = 170 std cm\(^{-3}\); AK RCN = 330 std cm\(^{-3}\)) than under polluted conditions (HI RCN = 320 std cm\(^{-3}\); AK RCN = 560 std cm\(^{-3}\)). Differences in refractory seasalt CN due to higher wind speeds can likely be ruled out as wind speeds were not significantly different (\(\alpha=0.05\)) under “clean” and polluted conditions for either region.

Table 3.1 – Comparison of aerosol number in the FT over Mexico, Hawai‘i and Alaska during INTEX-B.

<table>
<thead>
<tr>
<th>Region</th>
<th>CN &gt; 3 nm (# cm(^{-3}))</th>
<th>CN &gt; 10 nm (# cm(^{-3}))</th>
<th>Hot CN (# std cm(^{-3}))</th>
<th>RCN Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mexico</td>
<td>1399</td>
<td>1099</td>
<td>250</td>
<td>0.24</td>
</tr>
<tr>
<td>Hawai‘i</td>
<td>1507</td>
<td>884</td>
<td>329</td>
<td>0.51</td>
</tr>
<tr>
<td>Alaska</td>
<td>1723</td>
<td>903</td>
<td>384</td>
<td>0.54</td>
</tr>
</tbody>
</table>

ENP FT total sulfate is similar in each region indicating that larger total aerosol mass is due to the presence of Asian dust (Figure 3.13). Volatile OC cannot be reliably derived using equation 3.1 because measurements of submicrometer aerosol mass and submicrometer sulfate are near the level of instrument precision for a 60-second sample. Likewise, in the MBL robust estimates of RefOC cannot be determined because a portion of the submicrometer mass is seasalt not refractory organic carbon [Clarke et al., 2006; Martensson et al., 2003].

Light scattering by aerosols in the FT over the ENP is elevated compared to clean background conditions (Figure 3.14). Light absorption is above background values below ~6 km. Above 6 km PSAP instrument precision precludes obtaining values statistically different than zero. The influence of Asian dust can be seen in the Hawaiian
profile data which is skewed in the 2-3 km altitude range by repetitive sampling of a dusty layer capping the MBL on April 23rd, 2006. MBL extinction near Hawai'i is about double the Alaskan values. This may be the result of enhanced wet deposition in Alaska as rainfall in the region during the sampling period was higher than the climatological average (H. Fuelberg, pers. comm.).
Figure 3.11 – Vertical profiles of trace gases over the North Pacific and Mexico during INTEX-B. Background values in the MBL (blue, cyan) are for cases when the aerosol composition is no different than seawater.
Figure 3.12 – Same as Figure 3.11 but for aerosol number.
Figure 3.9 – Same as Figure 3.7 but for aerosol mass. Volatile and refractory organic carbon (OC) are shown as the dashed and solid lines respectively.
Figure 3.13 – Same as Figure 3.11 but for aerosol mass.
Figure 3.14 – Same as Figure 3.11 but for aerosol extinction.
3.3 Natural and anthropogenic aerosol that affect light extinction over continental North America

Quantifying the perturbations to the Earth's radiation balance by natural and anthropogenic aerosols is still uncertain compared to perturbations due to green-house gases and natural variations in solar insolation [IPCC, 2007]. Summarized in this chapter are in-situ measurements of aerosol size distributions and their optical properties. Evaluating model simulations of size distributions and associated optical properties against these observations will better constrain these models and potentially reduce uncertainty associated with modeling the direct effect of aerosols on climate.

3.3.1 Biomass burning in the North American free troposphere

Airmasses influenced by biomass burning emissions were identified when either hydrogen cyanide (HCN) or acetonitrile (ACN) exceeded one standard deviation of the INTEX-NA average FT values (156, 332 pptv). The corresponding threshold values of HCN and ACN are 220 and 500 pptv.

HCN data was measured independently aboard the NASA DC-8 by the California Institute of Technology and the NASA Ames Research Center. When the two independent data sets are combined 74% of the 3658 FT data points\textsuperscript{2} contain HCN data. ACN data are only available for 56% of the data points. Due to sample timing etc. several of the largest biomass burning plumes were not selected using the HCN and ACN tracers alone. Adding sample times for which either total or submicrometer aerosol gamma, $\gamma_t$ or $\gamma_s$, is less than 0.3 retrieves these missing BB plumes.

\textsuperscript{2} Based on the University of New Hampshire mist chamber data merge; temporal resolution is 90-seconds.
Liang et al., also separated UT biomass burning plumes for the INTEX-NA data. A comparison of several tracers is included in Table 3.2.

### Table 3.2 - Comparison of Liang et al., UT “Biomass Burning” airmass type to our “BB” UT conditions.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>McNaughton et al.</th>
<th>Liang et al.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mean</td>
<td>median</td>
</tr>
<tr>
<td>RH (%)</td>
<td>38</td>
<td>34</td>
</tr>
<tr>
<td>CO (ppbv)</td>
<td>181</td>
<td>119</td>
</tr>
<tr>
<td>O₃ (ppbv)</td>
<td>87</td>
<td>83</td>
</tr>
<tr>
<td>HCN (pptv)</td>
<td>640</td>
<td>510</td>
</tr>
<tr>
<td>ACN (pptv)</td>
<td>270</td>
<td>180</td>
</tr>
</tbody>
</table>

In Clarke et al. [2007], we also identified biomass burning plumes using a statistical classification. The data presented in this dissertation are an extension of that work. This analysis excludes boundary layer BB plumes because they are often mixed with pollution and in some cases were mis-classified as pollution using the Clarke et al. classification scheme.

Not surprisingly the size distributions of biomass burning aerosol over North America exhibited a high degree of variability. Fitting the distributions using log-normal curves requires between one and three modes to fit aerosol in the Aitken, accumulation and coarse modes. Let’s consider the difference between the distributions obtained at 5.4 km, approximately 50 km east of the Grand Canyon on July 6th, 2004 and the distributions measured at 3.8 km above Huntsville, AL on July 20th, 2004. Figure 3.15 and 3.16 plot visible and infrared aerosol scattering measured by the airborne DIAL LIDAR [Browell et al., 2001] for both the Grand Canyon (Fig. 3.15) and Huntsville (Fig. 3.16) BB plumes. The Grand Canyon plume can be seen as a thick smoke plume emanating from the basin-and-range region of Western North America. The Huntsville
plume can be seen as a thin filament subsiding over the Southeast US after being transported long-range from fires burning in Alaska and Northwestern Canada.

The Grand Canyon forest fire plume was retrieved from the dataset using the $\gamma_T$ value because no measurements of acetonitrile or hydrogen cyanide were available during this 5-minute level leg average (Table 3.3). The summary of gas phase tracers measured in the Huntsville plume highlight its intensity even though the Grand Canyon plume was sampled nearer its source. Lognormal fitting (Figure 3.17) of the Huntsville BB aerosol results in a volumetric mean diameter (VMD) of 0.44 $\mu$m compared to only 0.23 $\mu$m for the Grand Canyon plume.

The pie charts in Figure 3.17 show that chemically the distributions differ in their mass fractions of inferred organic carbon species (VoOC, RefOC, BC) but have similar mass fractions of inorganic ions ($SO_4^{2-}$, $NO_3^-$, $NH_4^+$). The composition of these distributions is organic rich compared to the average reported in Clarke et al. [2007] and the very low $\gamma_T$'s (0.11 and 0.17) reported in Table 3.3 are the result. The refractory volume fraction for biomass burning aerosols is typically high, averaging ~10-25% of the total accumulation mode volume. In contrast anthropogenic refractory aerosol volume fractions are ~2-10% [Clarke et al., 2007]. Model simulations of these aerosol should replicate this difference as it directly affects the optical properties of the aerosol [Kirchstetter et al., 2004] and the increase in light scattering as a function of relative humidity [Quinn et al., 2005].

Because of their differing source regions and the heterogeneity of aerosols in the BB plumes mean distributions such as those presented in Figure 3.18 do not actually represent all aerosol of this type. This heterogeneity can be evaluated by looking at the
variation in the NMD and $\sigma_g$ for the fits. Twenty-six accumulation mode fits were generated with a mean NMD of 0.11 $\mu$m, mean $\sigma_g$ of 1.77 and a mean VMD of 0.27 $\mu$m (Appendix C). Computing the standard deviation of the NMD the range of NMD’s is 0.062 – 0.20 $\mu$m. Using a fixed $\sigma_g$ of 1.77 this results in a range of VMD’s between 0.16 and 0.52 $\mu$m. $\sigma_g$ also varies between the fits 1.77 +/- 0.28. For a fixed NMD of 0.11 $\mu$m (the average value) this could result in VMD’s between 0.18 and 0.52 $\mu$m. The characteristics of biomass burning aerosols will depend on more factors than can be constrained from the airborne data, e.g. fuel type, fire temperature, transport pathway and season etc. Based on my analysis summertime North America forest fire aerosol in the FT have an average VMD of 0.27 $\mu$m ranging between 0.16 and 0.52 $\mu$m with an $\sigma_g$ value of 1.77 +/- 0.28. This is a relatively broad range of values for comparison to models but in the absence of additional FT data can be used as a constraint.

Table 3.3 – Comparison of gas and aerosol phase tracers for two biomass burning plumes measured over North America.

<table>
<thead>
<tr>
<th>Region</th>
<th>Altitude (km)</th>
<th>CO (ppbv)</th>
<th>HCN (pptv)</th>
<th>ACN (pptv)</th>
<th>gamma</th>
<th>N</th>
<th>NMD ($\mu$m)</th>
<th>$\sigma_g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grand Canyon</td>
<td>5.4</td>
<td>254</td>
<td>no data</td>
<td>no data</td>
<td>0.11</td>
<td>9835</td>
<td>0.15</td>
<td>1.47</td>
</tr>
<tr>
<td>Huntsville</td>
<td>3.8</td>
<td>325</td>
<td>2087</td>
<td>959</td>
<td>0.17</td>
<td>1328</td>
<td>0.31</td>
<td>1.41</td>
</tr>
</tbody>
</table>

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Figure 3.15 – Visible and infrared aerosol scattering ratio measured by DIAL LIDAR during INTEX-B flight 4. A plume of smoke over the Grand Canyon was sampled at 5.4 km between 17:05 and 17:25 UTC on July 6th.
**Figure 3.16** – Visible and infrared aerosol scattering ratio measured by DIAL LIDAR during INTEX-B flight 10. A filament of forest fire smoke was sampled over Huntsville Alabama at 3.8 km between 17:15 and 17:30 UTC on July 20th 2006.
Figure 3.17 – Comparison of two biomass burning aerosol size distribution measured during INTEX-NA. The two distributions have nearly identical volume integrals but their mean volume diameters differ by a factor of 2. Chemically they are similar but the Huntsville distribution contains a higher mass fraction of refractory material.

Figure 3.18 – Lognormal fits of unheated (top) and refractory (bottom) aerosol number (left) and volume (right) distributions for biomass burning aerosol measured in the North American FT. These aerosol have diverse sources and have a wide range of NMD’s and $\sigma g$ (see text). Averages are plotted for overview purposes.
3.3.2 Anthropogenic pollution in the North American free troposphere

Anthropogenically influenced FT airmasses were identified after excluding the clean, STE and BB data sets. I analyzed the statistics associated with the FT concentrations of Ethane, Ethyne and Benzene. When any of these parameters exceeded 1σ the data point was identified as "anthropogenically influenced". The corresponding threshold values are 1100, 180 and 60 pptv for ethane, ethyne and benzene. This stratification technique is compared to Liang et al. [2007] in Table 3.4.

Table 3.4 - Comparison of Liang et al., UT "Asian" airmass type to our "Anthropogenic" UT conditions.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>McNaughton et al.</th>
<th>Liang et al.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mean</td>
<td>median</td>
</tr>
<tr>
<td>RH (%)</td>
<td>52</td>
<td>45</td>
</tr>
<tr>
<td>CO (ppbv)</td>
<td>113</td>
<td>113</td>
</tr>
<tr>
<td>O3 (ppbv)</td>
<td>86</td>
<td>83</td>
</tr>
<tr>
<td>C2H6 (pptv)</td>
<td>1350</td>
<td>1240</td>
</tr>
<tr>
<td>C2H4 (pptv)</td>
<td>120</td>
<td>100</td>
</tr>
<tr>
<td>Benzene (pptv)</td>
<td>19</td>
<td>17</td>
</tr>
</tbody>
</table>

The size distributions of anthropogenic pollution aerosol in the North American free troposphere also exhibited a high degree of variability. For the unheated accumulation mode aerosol the mean NMD, σₚ and VMD's are 0.069 μm, 1.80 +/- 0.21, and 0.19 μm. These are shown in Figure 3.19 which summarizes the average distributions and their fit.

The 1 standard deviation range of unheated accumulation mode NMD's is 0.051-0.093 μm with corresponding VMD's of 0.14-0.26 μm for a fixed σₚ of 1.80. For a fixed NMD of 0.069 μm (the average value) but allowing σₚ to vary +/- 0.21 the corresponding VMD's are 0.13 - 0.30 μm. This range of variability can be shown visually by
considering the four distributions plotted in Figure 3.20. These distributions were measured at 2.8, 4.8, 9.3 and 11.1 km. A summary of gas phase tracer values and the lognormal fit parameters are included in Table 3.5 and indicate that these plumes are definitively of anthropogenic origin.

Table 3.5 – Gas phase tracers and lognormal fits parameters for sample distributions of anthropogenic pollution in the North American free troposphere.

<table>
<thead>
<tr>
<th>Date</th>
<th>Altitude (km)</th>
<th>CO (ppbv)</th>
<th>Ethane (ppbv)</th>
<th>CH$_3$O (ppbv)</th>
<th>N</th>
<th>NMD (µm)</th>
<th>$\sigma_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>8-Jul</td>
<td>2.8</td>
<td>no data</td>
<td>858</td>
<td>1425</td>
<td>2,121</td>
<td>0.087</td>
<td>1.67</td>
</tr>
<tr>
<td>14-Aug</td>
<td>4.8</td>
<td>111</td>
<td>579</td>
<td>1007</td>
<td>2,884</td>
<td>0.110</td>
<td>1.59</td>
</tr>
<tr>
<td>28-Jul</td>
<td>9.3</td>
<td>123</td>
<td>1020</td>
<td>184</td>
<td>13,418</td>
<td>0.049</td>
<td>1.42</td>
</tr>
<tr>
<td>11-Aug</td>
<td>11.1</td>
<td>117</td>
<td>2622</td>
<td>274</td>
<td>32,308</td>
<td>0.015</td>
<td>1.39</td>
</tr>
</tbody>
</table>

Aerosol in the distributions measured at 11.1 km number 32,000 cm$^{-3}$ and contain ~200 refractory aerosol (RCN ratio < 0.01). As this distribution subsides, condensation and coagulation will increase total aerosol mass while reducing aerosol number. This general behaviour can be seen in the ENA aerosol number and mass profiles discussed in the section 3.2.1.

For the lower troposphere, Figure 3.20 shows that some aerosol distributions resemble those commonly observed in the polluted BL. The distributions from 4.8 and 2.8 km have RCN number ratios of ~0.6. The RCN volume ratio computed from the size distribution is ~8% of the accumulation mode aerosol volume. Additionally, the distribution from 4.8 km includes a supermicrometer dust mode possibly indicating dry lofting as opposed to wet convection. Observations of FT mineral dust over ENA was relatively rare occurring in just 3 of the 66 distributions.
Figure 3.19—Lognormal fits of unheated (top) and refractory (bottom) aerosol number (left) and volume (right) for anthropogenic pollution measured over Eastern North America during INTEX-NA.

Figure 3.20—Example number (left) and volume (right) distributions of anthropogenic pollution in the North American free troposphere. The bottom two panels summarize the chemical composition of the 9.3 and 4.8 km distributions.
3.3.3 Aging pollution in the North American boundary layer

Gas phase SO\textsubscript{2} is converted to H\textsubscript{2}SO\textsubscript{4} through photo-oxidation and reaction with the OH radical (Equation 1.3) and can dry deposit to pre-existing aerosol surface area and the Earth’s surface. In activated aerosol droplets and cloud, sulfate can be formed via reaction with H\textsubscript{2}O\textsubscript{2} (Equation 1.4) or O\textsubscript{3} (Equation 1.5). Sulfate formation via the reaction with H\textsubscript{2}O\textsubscript{2} is less pH dependent than the O\textsubscript{3} reaction and thus the H\textsubscript{2}O\textsubscript{2} reaction is considered the dominant pathway for sulfate formation in and near cloud. Once formed, H\textsubscript{2}SO\textsubscript{4} in the polluted continental boundary layer either condenses on pre-existing aerosol to form secondary aerosol sulfate, or it forms new particle number through gas-to-particle conversion [McNaughton et al., 2004].

The rate of sulfate formation is controlled by several factors including emission rates and concentrations of aerosol precursor gases [Kulmala et al., 2002; Napari et al., 2002], pre-existing aerosol surface area [Clarke et al., 1998a; Clarke et al., 1999], solar insolation, temperature and relative humidity [Easter and Peters, 1994], and atmospheric dynamics [Nilsson et al., 2001].

Here I separate BL pollution into three age classes; fresh, intermediate and aged, based on the molar ratio of sulfate to total sulfur, (S\textsubscript{ratio}). The S\textsubscript{ratio} is defined as:

\[
S_{\text{ratio}} = \frac{[SO_4^{2-}]_{aq}}{([SO_4^{2-}]_{aq} + [SO_2^-]_g)}
\]  

(3.2)

The threshold S\textsubscript{ratio} values used to define the three airmasses are; Fresh \( S_{\text{ratio}} \leq 0.25 \); Intermediate \( 0.25 < S_{\text{ratio}} \leq 0.5 \); and Aged \( S_{\text{ratio}} > 0.5 \). Originally I tested the data for a fourth age, \( S_{\text{ratio}} > 0.75 \). After compiling the tracer statistics and fitting the
size distributions I found that there was no significant difference between the NMD’s of aerosol with an \( S_{\text{ratio}} \) of 0.5-0.75 compared to \( S_{\text{ratio}} > 0.75 \). Instead the differences simply represented reductions in total aerosol number and mass as a result of airmass dilution and wet/dry removal processes. Based on this analysis the “Age 4” data was combined with “Age 3” and are collectively referred to as “Aged” pollution.

Strictly speaking, the \( S_{\text{ratio}} \) cannot be used to derive a “time since emission” index since the rate of sulfate formation will be uniquely determined for every air parcel based on its history. The fastest conversion rates occur in the presence of cloud or fog and can reach 30\% hr\(^{-1}\) [Dittenhoefer and De Pena, 1980; Eatough et al., 1984; Gillani et al., 1983; Gillani et al., 1981; Gillani and Wilson, 1983]. Depending on season and the availability of oxidants, mid-latitude SO\(_2\) conversion rates reported for coal-fired power plants and smelter plumes range between \( \sim 0.1\% \text{ hr}^{-1} \) and 10\% hr\(^{-1}\) [Hewitt, 2001; Newman, 1981]. Mid-latitude conversion rates are highest \( \sim 1-3\% \text{ hr}^{-1} \) during summer under sunny, cloud free conditions and lowest \( < 0.5\% \text{ hr}^{-1} \) in winter and at night [Forrest et al., 1981; Gillani, 1978; Husar et al., 1978; Lusis et al., 1978; Richards et al., 1981]. Due to higher solar insolation, we expect subtropical and tropical conversion rates to be higher than at midlatitudes. Porter et al. [2002] reported an SO\(_2\) half life in the fresh volcanic plume from Kilauea to be as short as 6 hours, an SO\(_2\) to sulfate conversion rate of \( \sim 8\% \text{ hr}^{-1} \). Models estimate global SO\(_2\) lifetimes are on the order of 1-3 days [Benkovitz et al., 2004; Feichter et al., 1996; Koch et al., 1999], an average conversion rate of 0.9\% hr\(^{-1}\) to 2.6\% hr\(^{-1}\).

During the 2004 ICARTT study, Brock et al. [2008] measured \( S_{\text{ratios}} \) of 0.12 +/- 0.03 and 0.22 +/- 0.06 over Long Island, NY. They estimated these fresh emissions to be
3-4 hrs and 4-5 hrs downwind of New York City. The following day they measured a
more aged plume, a mixture of Baltimore, MD, Washington DC and New York City
emissions, with an $S_{ratio}$ of 0.41 +/- 0.11 and an estimated age of ~40 hours. Brock et al.,
also discuss a well aged North American plume sampled over the maritime provinces of
Canada. In this airmass they recorded an $S_{ratio}$ of 0.56 +/- 0.15. Overall they found the
conversion of gas-phase SO$_2$ to aerosol sulfate is consistent with gas-phase oxidation by
OH with a time constant of ~3-4 days, or a conversion rate of 0.6% hr$^{-1}$ to 0.9% hr$^{-1}$
values commensurate with diurnally averaged values of ~1% hr$^{-1}$ [Hewitt, 2001; Newman,
1981].

Using an average conversion rate of 1% hr$^{-1}$ results in an airmass age of <25 hrs
for “Fresh” plumes ($S_{ratio} < 0.25$). For intermediate plumes ($S_{ratio} = 0.25-0.50$) the
airmass age is ~1-2 days while airmasses with an $S_{ratio} > 0.50$ are more than 2 days old.
The result is that the $S_{ratio}$ tracer can be viewed as a quasi-lagrangian indicator of airmass
age provided evolution of the aerosol size distribution is dominated by sulfate aerosols
under cloud free conditions. And although conversion rates at high RH or in cloud or fog
will be much higher, they also tend to produce aged size distributions with a well
developed accumulation mode. The $S_{ratio}$ is also advantageous as it can be easily
extracted from a GCM model domain for analysis (D. Koch, pers. comm).

Figure 3.21 summarizes the unheated and refractory aerosol number and volume
distribution for each of the three Eastern North American boundary layer airmass ages
defined using the $S_{ratio}$ (Eqn. 3.2). As expected the unheated accumulation mode aerosol
number is reduced through coagulation while total aerosol volume (mass) increases via
condensation (Table 3.6). As a result of these dynamics the NMD and VMD of the distribution increase while the accumulation distribution narrows (i.e. reduced \( \sigma_a \)).

Submicrometer refractory aerosol of anthropogenic origin is primarily soot. As volatile material condenses on this preexisting aerosol surface area we expect their coagulation rates will be lower than secondary aerosol formed from gas-to-particle conversion. As the ENA BL airmasses age the volatile CN (VCN) decrease from 47% to 29% and then 18% of total CN. During ACE-Asia and TRACE-P the VCN fraction decreased from \( \sim -49\% \) of total CN \( \sim 24 \text{ hours downwind of China (Yellow Sea)} \) to \( \sim -32\% \) of total aerosol after 48 hours of transport (South of Japan) [McNaughton et al., 2004].

The results from McNaughton et al. near East Asia and Brock et al. from Eastern North America provide a consistent constraint on the \( S_{ratio} \) ages. Fresh emissions, \( S_{ratio} < 0.25 \), appear to have ages less than 24 hours while an \( S_{ratio} \) between 0.25 and 0.50 corresponds to moderately aged pollution approximately 24-48 hours downwind from their sources. “Aged” pollution with an \( S_{ratio} > 0.5 \) are likely more than 2 days downwind of their source regions provided that sulfate production is dominated by OH oxidation and not cloud processing.

Many GCM’s model primary and secondary aerosol as external mixtures. Those attempting to model soot, and secondary aerosols (e.g. sulfates and organic carbon) as internal mixtures using coagulation and condensation should be able to reproduce the observed increase in RCN ratio, i.e. degree of internal mixing as a function of time as well as the \( S_{ratio} \). The INTEX-NA observations show increasing NMD of the refractory distribution while narrowing the distribution but there is no clear increase in refractory volume or VMD. This behavior is consistent with inter-particle coagulation. Table 3.6
and Figure 3.22 summarize the mass fractions of volatile inorganic ions, volatile OC, refractory OC and inferred BC for each of the BL distributions. As indicated in Figure 3.22 the mass fraction of inorganic ions increases as these species continues to condense. This result is consistent with Brock et al. [2008] who found that fresh aerosol is dominated by volatile organic species which then accumulate higher mass fractions of inorganic ions as they age.

Figure 3.21 – Unheated (top) and refractory (bottom) number (left) and volume (right) distributions for aging anthropogenic pollution in the North American boundary layer. Coagulation leads to reductions in aerosol number while condensation increases total aerosol volume. Together coagulation and condensation lead to larger NMD and VMD’s with time. Supermicrometer dust mass is slightly lower in the most aged airmass, likely the result of gravitational settling of these aerosol.
Table 3.6 – Summary of the accumulation mode aerosol fit statistics for each of the three airmass ages in the polluted North American boundary layer.

<table>
<thead>
<tr>
<th>Airmass Age</th>
<th>N  (# cm⁻³)</th>
<th>NMD (µm)</th>
<th>V (µm³ cm⁻³)</th>
<th>VMD (µm)</th>
<th>σp (⁻)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh</td>
<td>9993</td>
<td>0.050</td>
<td>5.8</td>
<td>0.21</td>
<td>2.00</td>
</tr>
<tr>
<td>Intermediate</td>
<td>6171</td>
<td>0.068</td>
<td>6.4</td>
<td>0.23</td>
<td>1.89</td>
</tr>
<tr>
<td>Aged</td>
<td>2976</td>
<td>0.10</td>
<td>6.8</td>
<td>0.27</td>
<td>1.77</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Airmass Age</th>
<th>N  (# cm⁻³)</th>
<th>NMD (µm)</th>
<th>V (µm³ cm⁻³)</th>
<th>VMD (µm)</th>
<th>σp (⁻)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh</td>
<td>5266</td>
<td>0.021</td>
<td>0.54</td>
<td>0.16</td>
<td>2.28</td>
</tr>
<tr>
<td>Intermediate</td>
<td>3989</td>
<td>0.028</td>
<td>0.73</td>
<td>0.18</td>
<td>2.18</td>
</tr>
<tr>
<td>Aged</td>
<td>2227</td>
<td>0.037</td>
<td>0.64</td>
<td>0.18</td>
<td>2.08</td>
</tr>
</tbody>
</table>

Figure 3.22 – Aerosol chemistry for aging anthropogenic aerosol in the North American boundary layer. Total aerosol mass increases from the condensation of inorganic ions, predominantly sulfate, which account then account for a larger mass fraction of total aerosol.

Reducing the organic carbon mass fraction of submicrometer aerosol through the condensation of hygroscopic inorganic ions results in a larger γ₅ [Quinn et al., 2005]. Clarke et al. [2007], also showed γ increased (decreased) as the inorganic ion (organic carbon) mass fraction increased (see Figure 5 of Clarke et al.). The 90-second averages of γ₅ in the Eastern North American boundary layer do not show a significant increase as
the aerosols age (Table 3.7 and Appendix Table B.5). The 300-second averages of $\gamma_S$ increase from 0.44 to 0.46 but are not significantly different ($\alpha=0.05$). If this difference were significant it would represent a 5% increase in $\gamma_S$ for an 18% decrease in the organic mass fraction (sum of VolOC, RefOC, and BC). The Quinn et al., parameterization predicts a 12% increase in $\gamma_S$ for an 18% change in POM. If sampled in a Lagrangian fashion the $\gamma_S$ of an aging aerosol population will change as ionic and organic species continue to condense. In this case however the sample variability ($\delta\gamma_S = 0.6-0.10$) is larger than the change we expect to observe. Considering the precision of the RRNeph and the spatial and temporal scales over which these samples were obtained it is therefore not surprising that we cannot detect a significant change in $\gamma_S$.

A second notable feature of the anthropogenic aerosol in the Eastern North American BL is the presence of supermicrometer urban/industrial dust. There is little difference in the dust mass between fresh and intermediate plumes while for the aged plumes the supermicrometer mass is reduced by about one third. At the same time the FMF$_{scat}$ increases slightly from 83% to 88%. The growing influence of submicrometer light scattering and a reduction in dust aerosol results in a significant ($\alpha=0.05$) increase in $\gamma_T$ regardless of whether the data are analyzed at the 90-second or the 300-second resolution. This finding is consistent with other observations of the influence of dust on the f(RH) [Howell et al., 2005].
Table 3.7 – Summary statistics for the increase in light scattering as a function of relative humidity over Eastern North America.

<table>
<thead>
<tr>
<th>Eastern N. America</th>
<th>Submicrometer</th>
<th>Total Aerosol</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N</td>
<td>gamma</td>
</tr>
<tr>
<td>UT BB mc</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anthro mc</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LT BB (UNHmc)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anthro (UNHmc)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Age 1 (UNHmc)</td>
<td>27</td>
<td>0.44 (0.09)</td>
</tr>
<tr>
<td>Age 2 (UNHmc)</td>
<td>92</td>
<td>0.43 (0.09)</td>
</tr>
<tr>
<td>Age 3 (UNHmc)</td>
<td>70</td>
<td>0.44 (0.07)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Eastern N. America</th>
<th>Submicrometer</th>
<th>Total Aerosol</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N</td>
<td>gamma</td>
</tr>
<tr>
<td>UT BB mc</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anthro mc</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LT BB (UNHae)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anthro (UNHae)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Age 1 (UNHae)</td>
<td>11</td>
<td>0.44 (0.10)</td>
</tr>
<tr>
<td>Age 2 (UNHae)</td>
<td>42</td>
<td>0.43 (0.10)</td>
</tr>
<tr>
<td>Age 3 (UNHae)</td>
<td>23</td>
<td>0.46 (0.06)</td>
</tr>
</tbody>
</table>
3.3.4 Anthropogenic pollution over the Central Highlands of Mexico and the Gulf of Mexico

Mexico's industrialization and the more than 22 million people residing in the Valley of Mexico are substantially altering the atmospheric environment over the Central Highlands and Gulf of Mexico. This is easily seen in the March 19th, 2006 photo (Figure 3.23) taken from the NASA DC-8. Future population growth, further urbanization and the unique geographic setting of the Mexico City basin make it a contemporary analog for current and future air quality problems in other Latin American cities (Bogota Colombia, Santiago Chile, La Paz Bolivia, etc.). The central highlands of Mexico are an arid alpine plateau with seasonally dry playa and active volcanoes. These natural sources of volcanic ash, mineral salts and dust also contribute to aerosol extinction in the region. As shown in Figure 3.24 the results can be impressive.
Figure 3.23 – Anthropogenic pollution and forest fires in the Valley of Mexico as viewed from the NASA DC-8 on March 19th, 2006 during INTEX-B.
Figure 3.24 – Dust storm over the Central Highlands of Mexico photographed from the NASA DC-8 during INTEX-B. *Pico de Orizaba*, the 3rd highest peak in North America, has a topographical prominence of 4922 meters indicating the depth of this dust storm is in excess of 3000 m.
Figure 3.25 shows the DC-8 flight tracks during the Mexico phase of INTEX-B. The region identified in red is classified as the Central Highlands of Mexico. These data are bound by Cartesian coordinates and where the difference between GPS and radar altitude exceeds 750 m (i.e. the "highlands"). Where CO and O₃ exceed their clean background values the data are labeled as anthropogenically influenced airmasses in the continental boundary layer (MEX Anthro CBL). The measurements indicate that this influence did not extent beyond ~5.5-6.0 km mASL during INTEX-B (see profiles). Data collected over the Coastal Lowlands of the US and Mexico or the Gulf of Mexico is shown in blue. These data are separated by altitudes into two groups, anthropogenically influenced free troposphere air (MEX Anthro FT; GPS_ALTITUDE >= 1.5 km) and the anthropogenically influenced marine boundary layer air (MEX Anthro MBL; GPS_ALTITUDE < 1.5 km).

The emissions from the central highlands of Mexico can be put into a broader context using the DIAL LIDAR aboard the DC-8. Figure 3.26 illustrates visible and infrared light scatting during the March 19th, 2006 INTEX-B flight. From 17:30-19:30 UTC the DC-8 made a series of FT and BL measurements enroute to a missed approach at the Mexico City airport at 19:50 UTC. As indicated by the LIDAR measurements and the photo in Figure 3.23 a dense plume of anthropogenic pollution and dust caps the Valley of Mexico. Prevailing wind from the Southwest is blowing the Mexico City plume over the coastal lowlands and out over the Gulf of Mexico. Additionally the dust component of the plume can be tracked using the aerosol depolarization ratio plotted in Figure 3.27. Here dust from the arid central highlands is being blown with the anthropogenic pollution out over the Gulf.
Figure 3.25 - DC-8 flight tracks highlighting the region classified as "Central Highlands" of Mexico compared to "Gulf of Mexico" region. A difference of 750 m between DC-8 GPS altitude and DC-8 radar altitude were used to identify the highlands regions.
Figure 3.26 – Visible and infrared aerosol scattering ratio measured by DIAL LIDAR during INTEX-B flight 8. Anthropogenic pollution from the Central Highlands of Mexico is being blown Northeast out over the Gulf Mexico at 2-6 km altitude.
Figure 3.27 – Aerosol depolarization ratio measured by DIAL LIDAR during INTEX-B Flight 8 on March 19th, 2006. Mineral dust depolarizes the DIAL LIDAR return and defines a central highlands plume moving from the Mexico City area out over the Gulf of Mexico.

Figure 3.28, 3.29 and 3.30 plot the DC-8 flight path between 17:00 and 20:00 UTC for the March 19th, 2006 INTEX-B Flight. Along the trajectory the data points are coloured according to the scattering angstrom exponent (Figure 3.28), the angstrom exponent of absorption (Figure 3.29) and according to submicrometer gamma, γ_s (Figure 3.30). The size of the data marker is proportional to total aerosol light scattering providing a relative measure of the signal strength used to derive each of the intensive properties. The scattering angstrom exponent is high, 1.5-2.0, for most of the flight and reflects an aerosol population dominated by pollution. However the level leg above Mexico City and the descent for the missed approach at the Mexico City airport show the enormous quantity of dust (Angstrom exponent ~ = 0.0) which resides in the CBL (Figure 167).
3.28). This finding is repeated when the trajectory is coloured by Angstrom exponent of absorption. In the FT over the Gulf and the coastal lowlands the value is between ~2.0-2.5, consistent with an aerosol population dominated by pollution with some dust. At Mexico City the steep wavelength dependence of dust absorption results in Angstrom exponents between 3.5 and 4.0 (Figure 3.29).

Submicrometer aerosol hygroscopicity plotted in Figure 3.30 are high in the MBL where sulfates and submicrometer sea salt lead to $\gamma_s$ values of 0.6-0.7. The FT aerosol over the Gulf of Mexico has values more typical of pollution aerosol with some dust (0.4-0.5). In the Mexico City CBL the dust suppresses $\gamma_s$ to values as low as 0.2.

Now that the March 19th, 2006 flight has been put into a spatial context, I examine aging of the Mexico City pollution plume by selecting three of the level legs for size distribution analysis. The “Gulf of Mexico” leg was recorded at 3.1 km ASL between 18:18 and 18:27 UTC and is the leg with the right hand turn centered at 97.5°W, 23.5°N in Figure 3.28. The second leg is over the Sierra Madre Oriental Mountains, 0.7 km AGL (2.6 km ASL) at 18:52 to 19:08 UTC above 98.25°W, 21.5°N. The final leg is near Mexico City at 1.1 km AGL (3.3 km ASL) between 19:40 and 19:51 UTC and centered 99°W, 20°N. The aerosol depolarization from the DIAL LIDAR in Figure 3.27 shows that these level legs along the DC-8 flight track intercept this large urban plume.

The aerosol number and volume distributions associated with each of these level legs are plotted in Figure 3.31. Aerosol number is shown with a linear y-axis whereas the volume distributions require a logarithmic scale to compare aerosol volumes. The unheated fits to the distribution each require 4-modes; one Aitken mode fit, one accumulation mode fit and two coarse mode fits. The refractory distributions also
required 4-mode fits except the Gulf of Mexico region which requires no refractory
Aitken mode fit. The statistics associated with these fits are summarized in Table 3.8.

Several features of the distributions deserve description. First, the nature of the
refractory Aitken mode aerosol in the Mexico City and Sierra Madre Oriental is unknown.
It is possible that the DMA TOAD does not fully volatilize all of the Aitken mode
number resulting in a false Aitken-mode refractory peak. The 1-Hz measurements of
refractory aerosol number are consistent with the integrals derived from the size
distributions but use the same measurement technique; a preheater followed by counting
in a TSI model 3010 CN counter. Thus either both preheaters and CN counters are not
removing all the volatile aerosol or this particle mode is real. Second, the log-normal fits
to the distribution required two coarse mode distributions. Both the OPC and the APS
recorded particle number at diameters well above the UH inlet's 50% passing efficiency
(3.5 μm) for particles with a density of 2.06 g cm⁻³. In fact the NMD for the second
coarse mode fit (Coarse 2 in Table 3.8) of the Sierra Madre and Mexico City distributions
are above the inlet's 50% efficiency diameter. These fits also have unrealistically narrow
σₚ's. There can be no doubt that the concentration of these supermicrometer aerosols are
being undersampled aboard the DC-8.
Table 3.8 – Summary of unheated (top) and refractory (bottom) aerosol statistics for the log-normal fits displayed in Figure 3.29.

<table>
<thead>
<tr>
<th>Leg</th>
<th>Mode</th>
<th>N (# cm⁻³)</th>
<th>V (mm³ cm⁻³)</th>
<th>NMD (µm)</th>
<th>VMD (µm)</th>
<th>σvg (⁻)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gulf of Mexico</td>
<td>Aitken</td>
<td>5.5E+02</td>
<td>9.9E-03</td>
<td>0.023</td>
<td>0.045</td>
<td>1.60</td>
</tr>
<tr>
<td></td>
<td>Acc.</td>
<td>1.5E+03</td>
<td>5.2E+00</td>
<td>0.12</td>
<td>0.29</td>
<td>1.74</td>
</tr>
<tr>
<td></td>
<td>Coarse 1</td>
<td>1.6E-02</td>
<td>1.7E-01</td>
<td>1.5</td>
<td>5.1</td>
<td>1.89</td>
</tr>
<tr>
<td></td>
<td>Coarse 2</td>
<td>2.4E-01</td>
<td>1.2E+01</td>
<td>2.9</td>
<td>7.2</td>
<td>1.73</td>
</tr>
<tr>
<td>Sierra Madre Oriental</td>
<td>Aitken</td>
<td>4.4E+03</td>
<td>9.7E-02</td>
<td>0.029</td>
<td>0.042</td>
<td>1.41</td>
</tr>
<tr>
<td></td>
<td>Acc.</td>
<td>1.4E+03</td>
<td>4.7E+00</td>
<td>0.13</td>
<td>0.27</td>
<td>1.66</td>
</tr>
<tr>
<td></td>
<td>Coarse 1</td>
<td>4.3E-01</td>
<td>2.8E+00</td>
<td>1.6</td>
<td>3.4</td>
<td>1.67</td>
</tr>
<tr>
<td></td>
<td>Coarse 2</td>
<td>1.4E-02</td>
<td>2.8E+00</td>
<td>6.2</td>
<td>8.3</td>
<td>1.36</td>
</tr>
<tr>
<td>Mexico City</td>
<td>Aitken</td>
<td>4.8E+03</td>
<td>8.3E-02</td>
<td>0.024</td>
<td>0.043</td>
<td>1.56</td>
</tr>
<tr>
<td></td>
<td>Acc.</td>
<td>1.5E+03</td>
<td>4.5E+00</td>
<td>0.10</td>
<td>0.34</td>
<td>1.92</td>
</tr>
<tr>
<td></td>
<td>Coarse 1</td>
<td>4.9E+00</td>
<td>4.9E+01</td>
<td>1.7</td>
<td>4.1</td>
<td>1.71</td>
</tr>
<tr>
<td></td>
<td>Coarse 2</td>
<td>2.5E-01</td>
<td>5.9E+01</td>
<td>6.9</td>
<td>8.5</td>
<td>1.30</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Leg</th>
<th>Mode</th>
<th>N (# cm⁻³)</th>
<th>V (mm³ cm⁻³)</th>
<th>NMD (µm)</th>
<th>VMD (µm)</th>
<th>σvg (⁻)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gulf of Mexico</td>
<td>Aitken</td>
<td>1.2E+03</td>
<td>1.1E+00</td>
<td>0.063</td>
<td>0.23</td>
<td>1.93</td>
</tr>
<tr>
<td></td>
<td>Acc.</td>
<td>5.7E-01</td>
<td>3.7E+00</td>
<td>1.6</td>
<td>3.3</td>
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<td>6.9E+00</td>
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<td>8.0</td>
<td>1.30</td>
</tr>
<tr>
<td>Sierra Madre Oriental</td>
<td>Aitken</td>
<td>1.8E+03</td>
<td>1.2E-02</td>
<td>0.020</td>
<td>0.028</td>
<td>1.42</td>
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<td></td>
<td>Acc.</td>
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<td>8.2E-01</td>
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<tr>
<td></td>
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<td>6.1E-01</td>
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<td>1.3</td>
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<tr>
<td></td>
<td>Coarse 2</td>
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<tr>
<td>Mexico City</td>
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<td>6.7E-03</td>
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<td>0.022</td>
<td>1.42</td>
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<td></td>
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<tr>
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<td>4.5E+01</td>
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<td>3.9</td>
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<tr>
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<td>5.4E+01</td>
<td>6.8</td>
<td>8.4</td>
<td>1.30</td>
</tr>
</tbody>
</table>

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Figure 3.28 – DC-8 flight path from 17:00 to 20:00 UTC on March 19th. Symbols are coloured by scattering angstrom exponent. Marker size is proportional to total aerosol light scattering. MBL seasalt and FT pollution have values in the 1.5-2.0 range while dust in Mexico City results in values near 0.0.
Figure 3.29 – Same as Figure 3.28 but coloured by angstrom exponent of absorption. Pollution mixed with dust have intermediate values 1.5-2.5 while the dust near Mexico City has values as high as 3.5-4.0.
Figure 3.30 – Same as Figure 3.28 but coloured by submicrometer gamma, $\gamma_s$. MBL aerosol have high values (0.6-0.7) due to the presence of seasalt, polluted values are intermediate 0.4-0.5 while the presence of submicrometer mineral dust is suppressing $\gamma_s$ (0.2-0.3) in the measurements at Mexico City.
Figure 3.31 — Size distributions and log-normal fits for the Mexico City urban/industrial plume mixed with mineral dust from the Central Highlands. Dust in the Mexico City CBL exceeds 250 μg std m⁻³ but is ~1 order of magnitude less over the Sierra Madre Oriental Mountains and the Gulf of Mexico. This accounts for the differences in scattering and absorption angstrom exponent as well as γ, plotted in Figures 3.28 – 3.30.
3.4 Discussion

Climate models which do not simulate the aerosol size distribution using a modal or a sectional approach must rely on bulk parameterizations. The most common parameterization used is the FORTRAN based optical properties of aerosols and clouds program (OPAC), [Hess et al., 1998]. GCM's participating in the AEROCOM project rely on various parameterizations for the mass median diameters of aerosol within their model (Table 4, [Textor et al., 2006]). GCM's use various approaches to alter the properties of the aerosol components and their size distribution depending on the complexity of the aerosol dynamics that are represented within the model. Aerosol models that can dynamically alter the number and mass median diameter as well as the width of the aerosol size distribution \(\sigma_d\) are needed in order to accurately simulate the aerosol field in the ambient atmospheric environment. The simplest demonstration of this need is the behavior of aging pollution within the CBL of Eastern North America. Figure 3.21 demonstrates that even when evaluated broadly using campaign averages, coagulation and condensation significantly alter the aerosol size distribution, and therefore optical properties, as the airmasses ages.

In this section I evaluate the 60-km STEM-2K3 simulations of atmospheric physics, thermodynamics, trace gases and aerosols using the DC-8 measurements over Mexico and the Gulf of Mexico. I then evaluate how OPAC parameterizations of accumulation mode size distributions, refractory soot and mineral dust against the fits generated from in-situ airborne measurements. Finally, I briefly discuss the f(RH) measurements and the wavelength dependence of light scattering and absorption. These
later two topics, f(RH) and wavelength dependence, depend on the aerosol size
distribution but are measured using separate instrumentation. Model calculations of
aerosol optical properties based on simulated size distributions will necessarily need to
replicate the trends that we observe in these data.

3.4.1 Evaluating STEM 2K3 thermodynamic variables and their influence on
aerosol optical properties over the Mexican Highlands and the Gulf of Mexico

Perhaps the greatest challenge to modeling the global aerosol field is the scaling
problem. In-situ measurements are precise, measuring particle diameters to within ~10%
at sizes as small as 50 nm for concentrations as low as 200 cm⁻³. However, the spatial
and temporal scales over which these measurements are made are small compared to the
synoptic scale of the air masses in which these aerosol reside. The result is that it is
nearly impossible to determine the accuracy of estimates for observed variability
compared to the actual airmass variability itself.

Additionally, computational limits hamper our efforts to model the global aerosol
field. Global models typically have coarse horizontal (10-100’s of km’s) and vertical
(100’s of meters to kilometers) resolution and use parameterizations based on higher-
resolution models to describe subgrid-scale thermodynamic and aerosol related processes.
Varying the dimensionality, domain size, and spatial resolution of the more detailed
models can significantly alter the parameterizations derived for use in the global models
[Petch and Gray, 2001]. Thus, even if the spatially and temporally varying global
aerosol field could be simulated with perfection, sub-grid scale variations in relative
humidity alone could result in 10-80% errors in aerosol direct radiative forcing [Haywood
et al., 1997; Petch, 2001]. This source of error is often not considered in studies focused
on determining the global annual average values of aerosol direct and indirect effects. When combined with the considerable uncertainty associated with simulating aerosol sources, sinks and the atmospheric process which govern their residence times it is no surprise that observational atmospheric scientists view the results of some of these simulations with considerable skepticism [Huebert, 2007].

In this section I compare in-situ observations over Mexico and the Gulf of Mexico during INTEX-B to the output from the 60 km resolution regional chemical transport model, STEM 2K3. This analysis highlights the need for the modeling community to assess the fidelity with which they can reproduce not only the spatial and temporal locality of trace gas and aerosols but also the critical role the relative humidity field plays in determining estimates of aerosol optical properties. The meteorological “driver-model” for the STEM 2K3 regional chemical transport model is the Weather Research & Forecasting model (WRF). Figure 3.32 compares the temperatures and pressures simulated by WRF to those measured by the DC-8 over Mexico and the Gulf of Mexico during INTEX-B. These two state variables are well simulated with a mean ratio of simulated to observed values of 0.9997 for temperature and 1.003 for pressure. Highlighted in red are data points lying beyond two standard deviations for each ratio. Here I assumed that these data points represent spatial and/or temporal dislocations between the airmass simulated and airmass sampled. The two panels below the temperature and pressure comparisons in Figure 3.32 are the comparisons of relative humidity and include the poorly simulated values highlighted in red. For T and P, it is predominantly poor simulations of ambient temperature that results in poor simulation of the ambient RH field.
Figure 3.32 – Comparison of STEM 2K3 simulations of atmospheric temperature, pressure and water vapour mixing ratio compared to in-situ measurements aboard the NASA DC-8 over Mexico and the Gulf of Mexico during INTEX-B (top row). Influence of temperature, pressure and water vapour mixing ratio outlier values (in red) on the STEM 2K3 simulation of relative humidity (bottom row).

The upper-right panel of Figure 3.32 compares water vapour mixing ratio ($w$) computed from model RH, T and P fields. The model tends to over predict $w$ at low values and under predicts $w$ by about 10% in the MBL. The simulated values range from as low as $1/10^{th}$ the observed values and as much as 25 times the observed values. Some of this error relates directly to spatial and temporal inaccuracy in the model but they also include the effects of subgrid-scale variability (e.g. two very high DC-8, very low STEM RH points in lower right panel). Logarithms of the water vapour mixing ratio were fit
using a robust linear regression (underweights outliers). This fit is shown as the red line in the upper-right panel of Figure 3.32. Arbitrarily, data greater than +/-10% of the fit were flagged for elimination. These data are highlighted in red in the RH comparison shown in the bottom-right panel of figure 3.32. Combining the T, P and w exclusion criteria and eliminating the poorly simulated data from the RH field results in a reduction in the mean ratio of simulated to observed RH values from 1.35 with a standard deviation of 1.52 to a mean of 1.03 with a standard deviation of 0.35. The RH comparison before and after applying the T, P and w exclusion criteria is summarized in Figure 3.33.

Figure 3.33 – Raw comparison of STEM 2K3 relative humidity compared to DC-8 observations over Mexico and the Gulf of Mexico during INTEX-B (left). Comparison after eliminating data where ambient temperature, pressure or water vapour mixing ratio indicate poor simulation of the underlying atmospheric thermodynamics (right). Error bars at 80% and 90% RH indicate the uncertainty in simulated RH which would be comparable to the observed variability in f(RH) measurements for a broad group of aerosols of anthropogenic origin.
Notably much of the data below the deliquescence point of most ionic aerosol salts (~40% RH) are eliminated. Where RH is poorly simulated but still below 40% we could retain these data without introducing substantial error to optical depth calculations. However, here I assume that the error associated with these data are the result of poor simulation of the spatial and/or temporal location of the airmasses sampled and not simply the result of incorrectly assigning water vapour mixing ratio to a well simulated meteorological or aerosol field. In order to retain more data we might relax our w selection criteria when both observed and simulated RH are below 40% and where T and P appear to be well simulated.

HiGEGAR [Howell et al., 2006] and other measurements of f(RH) [Anderson et al., 2003; Carrico et al., 2003] indicate that urban/industrial aerosol $\gamma_T$ is ~0.5 with a typical variability due to composition of +/-0.1. This value is comparable to the accuracy of the airborne f(RH) measurement itself (see section 2.3.4), however trends in f(RH) can largely be explained not by the measurement uncertainty but rather by their source and the ratio of inorganic to organic aerosol components [Clarke et al., 2007; Quinn et al., 2005; Quinn et al., 2006].

At 80% RH, variation in $\gamma_T$ of 0.5 +/-0.1 corresponds to an increase in light scattering by a factor of between 1.5 and 1.9 compared to aerosol light scattering at 40% RH. Using a fixed $\gamma_T$ of 0.5 we might ask, “what range of error in the simulation of the ambient RH values could be tolerated so that the simulated f(RH) values do not exceed values of 1.7 +/-0.2, values which correspond to a 12% uncertainty in ambient extinction”. The corresponding range of RH values is 80% +/-5%. At 90% RH and $\gamma_T$ of 0.5, the acceptable uncertainty in RH values narrows to 86-93% RH. Compare these
ranges, shown as red data points with error bars in Figure 3.33 to the range of STEM 2K3 values simulated over Mexico and the Gulf of Mexico during INTEX-B. DC-8 measurements between 80% and 95% RH average 87% whereas the STEM 2K3 values at these same locations average just 75%. The point-by-point low bias in the simulated RH values are, on average, 15% lower than the observed values over this RH range. This appears to be due to the underestimate of atmospheric water vapour mixing ratios, particularly for high values in the MBL, which average about 10% below the observed values. For anthropogenic pollution with a $\gamma_T$ range, 0.4-0.6, the 80%:40% $f$(RH) factors based on the observations range from 1.9-2.6. The values based on the simulation would only be 1.4-1.7. The result is an average underestimate of ambient aerosol light scattering of ~30%.

Due to the non-linear nature of the $f$(RH) relation, accurately simulating high relative humidity environments becomes increasingly important for simulating ambient aerosol optical properties. Subgrid-scale processes and variability also confound model reliability on regional to global scales. Poor simulation of high RH environments can also affect the aerosol number distribution. Failure to accurately simulate coagulation and scavenging of nucleation or Aitken mode particles by activated or nearly activated aerosol will enhance their survivorship. This allows them to participate as CCN in the next model cloud cycle when in reality these particles should have been removed.
3.4.2 Evaluating STEM-2K3 profiles over the Mexican Highlands and the Gulf of Mexico

Here I evaluate vertical profiles of aerosol mass and extinction over Mexico and the Gulf using the 60-km resolution STEM-2K3 CTM (STEM) simulation for INTEX-B [Carmichael et al., 2003a; Carmichael et al., 2003b; Tang et al., 2004a]. The STEM data were generated along the DC-8 flight path at 60-second resolution. DC-8 true airspeed is 150 – 220 m s\(^{-1}\) which corresponds to a linear sampling resolution of 9-14 km meaning each STEM data point is a sub-grid scale interpolation from its nearest neighbours. To compare the observations to the simulation, the STEM data is processed identically to the vertical profiles shown in section 3.2.2. As discussed in the previous section, data points where WRF poorly simulated the observed temperature (T), pressure (P) or water vapour mixing ratio (\(w\)) have been eliminated from the analysis in order to evaluate the fidelity of the model’s prediction of the aerosol over Mexico and the Gulf.

Figure 3.34 compares the vertical profiles of CO, submicrometer sulfate, organic carbon and black carbon mass over the Central Highlands of Mexico. The DC-8 submicrometer OC mass is the sum of volatile and refractory mass. DC-8 black carbon mass is calculated from submicrometer PSAP absorption at 530 nm assuming a mass absorption efficiency of 10 m\(^2\) g\(^{-1}\). The CO profile in Figure 3.34 shows good agreement simulating the column burden to within 5% after correcting for an 18 ppbv CO bias in STEM. Sulfate is predicted to within 5% over the entire CBL whereas organic carbon mass is over predicted by 11%. But since a fraction of the operationally defined RefOC is non-carbon refractory mass the STEM over prediction must be greater than 11%.
vertical profile of black carbon is well simulated with an overestimate of the column burden of only 8%, and within measurement uncertainty.

In figure 3.35 the vertical profiles of total and submicrometer scattering, dust mass and submicrometer absorption are compared. The STEM simulation of total and submicrometer scattering underestimate the column burden by 48% and 30% respectively. This discrepancy is largest near the surface and become less significant with height. The simulation of dust predicts a column burden 42% less than the observations and indicates that the vertical transport is too effective, showing little variation with height (3rd panel of Figure 3.35). Based on the shape of the dust mass profile, the total scattering profile should show a systematic increase above the submicrometer values. Since there is no apparent difference between STEM predictions of total and submicrometer scattering this indicates a problem with the model treatment of scattering by supermicrometer dust. A closer examination of the data revealed that the dust mass is classified as “Fine”. Coarse mode dust mass is negligible which accounts for the negligible difference between total and submicrometer scattering. Relocating the “Fine” dust to the “Coarse” mode and using size distributions summarized in this dissertation would likely improve the model’s simulation of dust optical properties over Mexico and the Gulf. The mass scattering efficiency ($\lambda$=550 nm) for all coarse mode mass measured over the Central Highlands averages 2.2 m$^2$ g$^{-1}$. I correct the STEM total scattering plotted in Figure 3.35 by applying this MSE to the observed profile of dust over Mexico. The new profile (green) shows an increase over the original STEM simulation of dust mass but still has an AOD 20% lower than the observations, a difference that can be explained by the 30%

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3 Computed from TSI Neph impactor efficiency curve and using a bulk density of 2.0 g cm$^{-3}$.  
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underestimate for submicrometer scattering. Simulated submicrometer absorption in Figure 3.35 is within 10% of the observations. This is expected since the mass absorption efficiency of BC used by STEM is the same as that used to derive BC from the observations \((10 \text{ m}^2 \text{ g}^{-1})\). Recall that the column burden of BC simulated (Figure 3.34) was within 8% of the observations.

Figures 3.36 and 3.37 are the same analysis but for the anthropogenically influenced FT over the Gulf of Mexico. CO is underestimated in the UT and overestimated near the surface. Sulfate is consistently underestimated resulting in a column burden value 32% below the observations. The shape of the vertical distributions of OC and BC are relatively well simulated. However, the column burden of OC is over-predicted by \(-63\%\) while BC is over predicted by 33%. Total scattering over the Gulf (Figure 3.37) is not well simulated, under predicting the column burden by 28%. Once again this is the result of dust being tagged as “fine” rather than “coarse” in the simulation. Submicrometer scattering is predicted well but its variability near the surface is lower than the observations. The column burden is within just 2% of the measured column burden.

Figure 3.37 also shows that too much dust is being transported vertically and that the total column burden is over predicted by a factor of two. As we did for the Central Highlands we can correct the simulation of total scattering by using the simulated submicrometer scattering and the observed column burden of dust. The calculated total scattering is plotted as the green line in Figure 3.37 and results in an AOD within 3% of the observed value and well within uncertainties in the measurements. The shape of the
vertical profile for submicrometer absorption is well simulated but tends to over predict BC throughout the column resulting in a column burden 50% larger than that observed.

Because of its significance to direct radiative forcing I look closer at the agreement between the DC-8 black carbon estimates and those simulated by STEM. STEM CO values in the clean FT (CO < 90 ppbv; O₃ < 40 ppbv) over Mexico (Highlands and Gulf) have a median bias of 18 ppbv. This value is subtracted from the simulated STEM CO which is then plotted versus the DC-8 measurements of CO in the top two panels Figure 3.38. The data for the Central Highlands is in the upper-left panel while the Gulf of Mexico FT is on the upper-right panel of the figure. Except for the large CO excursions during the missed approach at Mexico City the point-by-point comparison between STEM and the DC-8 data are favourable, resulting in a correlation coefficient of 0.62 over the Central Highlands and 0.73 in the FT over the Gulf of Mexico. The same analysis but for BC is shown in the bottom panels of Figure 3.38 and demonstrates the difficulty in modeling both the near-source concentrations of BC (correlation coefficient of 0.53) and the BC concentration in the FT over the Gulf (correlation coefficient of 0.61). Thus even though the campaign average column burden of BC for the two regions were simulated to within ~10% and ~35%, the median ratio of the simulated to the observed values are 1.5 with a range of 0.25 to ~50 over the Central Highlands and 1.5 with a range of 0.20 to ~100 in the FT over the Gulf.

The central highlands of Mexico are relatively arid and airmasses from the region have corresponding low RH. Seasonally, aerosol removal via wet deposition and scavenging is relatively weak compared to other locations. We can evaluate the validity of this claim by plotting regressions of the DC-8 observations of BC mass (derived from
absorption) versus CO for both the Mexican Highlands and FT over the Gulf of Mexico. This is shown Figure 3.39. The DC-8 data from both regions show a tight relationship (R² = 0.816 and R² = 0.843) of the form:

\[ BC = -0.30 + 0.0040 \cdot CO \]  

(3.4)

where CO is in ppbv and BC is µg std m⁻³. The bottom two panels of Figure 3.39 show that the STEM simulation replicates the observed BC:CO relation well. Although the STEM values of BC for a given concentration of CO replicate the observations, there are still inaccuracies with regard to modeling the concentration of BC at a particular location in space and time. Part of this error relates to the CO bias of 18 ppbv, while spatial and temporal dislocation of the plumes will also influence this comparison. Finally, wet and dry removal processes are also a factor as they will invalidate the BC:CO relation in equation 3.4.

Because model BC is related to CO, in the absence of wet removal, errors in BC are linearly related to errors in simulating CO. Both the systematic bias and spatial and temporal inaccuracies can be condensed to a 1:1 relation by plotting the BC ratios vs. CO ratios, i.e. BC\textsubscript{STEM}:BC\textsubscript{DC-8} versus CO\textsubscript{STEM}:CO\textsubscript{DC-8}. This is shown for the Central Highlands in figure 3.40 where the left hand panel includes all data and the right hand panel includes only the data where T, P and w were well simulated. The data points are colour coded by the observed ratio of aerosol scattering at 550 nm versus measured CO. Wet and dry removal reduces the Scat:CO ratio because CO is a conservative tracer compared to aerosol scattering. After excluding STEM data where T, P and w were poorly simulated, the large overestimates in STEM black carbon concentrations are
largely eliminated. This indicates that many of these data were simply locations where
the meteorology and/or plume location were not well simulated and highlights the need to
stratify model output prior to conducting comparisons between models and observations.
Where STEM over predicts CO there is a larger over prediction of BC concentrations.
These data are where the observed BC concentrations are less than $0.5 \, \mu g \, m^{-3}$ (not
shown). Since dilution will only shift the relation along the 1:1 line these errors must be
associated with removal process. There are two possibilities. First, higher than observed
CO could be transported into the model domain at the domain boundary. If the model
assumes some background concentration of BC is associated with the imported CO, but
the BC was previously removed by wet or dry deposition, this would result in a larger
overestimate in BC mass compared to CO. Second, STEM may over predict CO
emissions within the domain. As the real airmass ages, and due to the very dry nature of
the CBL, poor simulation of the dry deposition of the BC containing aerosol will result in
larger and larger errors in the simulated BC concentrations compared to CO errors over
time. This trend is more clearly illustrated in the data from the FT over the Gulf Figure
3.41.

The data collected over the Gulf of Mexico are plotted in Figure 3.41 in the same
fashion as Figure 3.40. Over the Gulf we expect some removal of aerosol due to wet
deposition. After eliminating the poorly simulated data we retain a group of data where
errors in the simulated BC mass are much greater than the CO error. Once again some of
the data predict BC concentrations 2-4 times that observed and have low Scat:CO ratios,
$-0.1-0.2$. There is also a second group of outliers where CO was simulated to within
$-25\%$ of the observations but BC concentrations are factors of 5-30 times higher than the
observations. These outliers all have Scat:CO ratios below 0.1 and observed BC concentrations less than 0.1 µg m⁻³, values at or near the detection limit of the PSAP instrument (1 Mm⁻¹ divided by BC MAE of 10 m² g⁻¹). I interpret these data points as locations where the STEM 2K3 model accurately predicted the location of the airmass being sampled but that poor cloud scavenging (perhaps at the sub-grid scale) results in inadequate removal of BC and other aerosol species. This would ultimately lead to an overestimate of aerosol optical properties at these locations and is a potential topic for future model improvement.

As shown here, total aerosol scattering over Mexico and the Gulf can likely be improved with more accurate simulation of the vertical distribution and size distribution of the coarse-mode dust. However, removal processes for primary BC aerosol may be poorly simulated, particularly as we move away from the source region. This leads to a greater overestimate in submicrometer absorption over the Gulf (33%) affecting the simulated values of aerosol single scatter albedo. Since primary aerosol are internally mixed with volatile material at sizes that are effective as CCN, improving wet deposition in STEM would improve any future estimates of the indirect effects derived from STEM-2K3 simulations. Other models with more dynamic simulations of the aerosol size distribution should perform similar analysis to those presented here to verify their own removal of BC mass and the fidelity with which they simulate CO and BC in the Valley of Mexico and over the Gulf.
Figure 3.34 – Comparison between vertical profiles of CO, submicrometer SO$_4^{2-}$, organic carbon and black carbon measured aboard the DC-8 and simulated by STEM-2K3 CTM over the Central Highlands of Mexico.
Figure 3.35 – Comparison between vertical profiles of total and submicrometer scattering, supermicrometer dust mass and submicrometer aerosol absorption measured aboard the DC-8 and simulated by STEM-2K3 CTM over the Central Highlands of Mexico.
Figure 3.36 – Comparison between vertical profiles of total and submicrometer scattering, supermicrometer dust mass and submicrometer aerosol absorption measured aboard the DC-8 and simulated by STEM-2K3 CTM in the FT over the Gulf of Mexico.
Figure 3.37 – Comparison between vertical profiles of total and submicrometer scattering, supermicrometer dust mass and submicrometer aerosol absorption measured aboard the DC-8 and simulated by STEM-2K3 CTM in the FT over the Gulf of Mexico.
Figure 3.38 – STEM CO (top) and BC (bottom) versus DC-8 observations in the polluted CBL of the Central Highlands of Mexico (left) and the polluted FT over the Gulf of Mexico (right) during INTEX-B. STEM CO data have been corrected for a clean FT CO bias of 19 ppbv and exclude data where T, P and w are poorly simulated.

Figure 3.39 – Regressions of BC versus CO from the DC-8 observations (top) and for the STEM-2K3 model. Data from the Central Highlands is on the left while data from the FT over the Gulf of Mexico are on the right. CO data have been corrected for a clean FT CO bias of 18 ppbv and exclude data where T, P and w are poorly simulated.
Figure 3.40 – Ratio of simulated BC to observed BC plotted versus the ratios of CO for the Central Highlands of Mexico. The left panel includes all data whereas the right panel excludes points where T, P and w were poorly simulated. Data are colour coded by the ratio of scattering at 550 nm to CO. Low values are indicative of aerosol removal by wet deposition. Data along the 1:1 line indicate model error associated with simulating the intensity of urban plumes. Data above the 1:1 line in the left panel indicate poor simulation of the location of urban plume and/or poor simulation of BC removal by wet deposition. By excluding data based on poorly simulated thermodynamics (right panel) we infer that STEM is over predicting CO by 25-50% and that the BC is not being removed effectively resulting in overestimates of BC mass by a factor of ~2-5.
Figure 3.41 – Same as figure 3.40 but for the FT (alt > 1.5 km) over the Gulf of Mexico. The left panel shows all data from the STEM 2K3 simulation whereas the right panel shows only data where T, P and w were well simulated along the DC-8 flight path. STEM’s over prediction of BC mass, particularly near a CO\textsubscript{STEM}/CO\textsubscript{DC-8} ratio of 1.0 +/- 0.25, and at low ratios of aerosol scattering to CO (blue colour shading) indicate poor simulation of BC removal by wet deposition.
3.4.3 Comparison of airborne measurements to the OPAC Parameterization

In this section I highlight the error inherent to models which use the OPAC parameterization for aerosol size distribution. Error is evaluated as the ratio between the integral number, volume, scattering or absorption using the parameterizations divided by the integrals from the mean distribution of the observations. These are referred to as, number ratio, scattering ratio, absorption ratio etc. In the comparisons aerosol volumes are used to normalize the comparison based on the assumption that a model using the OPAC parameterizations has accurately simulated total aerosol mass. Certainly errors in simulating thermodynamic parameters (P, T, RH), total aerosol mass, mass fractions of hydrophobic versus hydrophilic aerosol components, etc. will compound error between observations and simulations. The goal here is simply to evaluate how errors in parameterizations of the aerosol size distribution propagate into errors into the aerosol direct effect when all other factors are held constant.

Figure 3.42 compares the OPAC “Water Soluble” aerosol size distribution to the total aerosol size distribution measured for the three “ages” of anthropogenic pollution measured in the continental boundary layer of Eastern North America during INTEX-NA. Accumulation mode aerosol composition is assumed to be \((\text{NH}_4)_2\text{SO}_4\) with 550 nm wavelength refractive indices of 1.44-0.0i and 1.40-0.0i at relative humidities of 40% and 80% and a hygroscopic growth factor \(g(80\%:40\% \text{ RH})=1.27\) [Tang, 1997]. Accumulation mode aerosol mass is set to 12.6 \(\mu\text{g std m}^{-3}\) and assumes a density of 1.8 g cm\(^{-3}\) resulting in an accumulation mode volume of 7 \(\mu\text{m}^3\) cm\(^{-3}\), approximately the average value of the “Aged” aerosol in the ENA CBL.
Table 3.9 summarizes the ratio of OPAC number, CCN number (Dp > 0.070 μm), volume and scattering to the values computed for each of the three ages of anthropogenic pollution in the ENA CBL. For light scattering at 40% and 80% RH the OPAC parameterization is indistinguishable from the “Aged” CBL pollution aerosol. Even for the “Fresh” pollution aerosol scattering is at most overestimated by only ~30%.

Table 3.9 – Ratio of OPAC “Water Soluble” distribution integrals to integrals computed from in-situ airborne observations.

<table>
<thead>
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<th>Observations</th>
<th>OPAC – Water Soluble</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Number Ratio</td>
<td>CCN Ratio</td>
</tr>
<tr>
<td>Fresh</td>
<td>0.76</td>
<td>0.65</td>
</tr>
<tr>
<td>Intermediate</td>
<td>1.38</td>
<td>0.77</td>
</tr>
<tr>
<td>Aged</td>
<td>3.02</td>
<td>1.14</td>
</tr>
</tbody>
</table>

Since the OPAC parameterization is static, we expect large discrepancies in aerosol number as the aerosol ages. Under/overestimates range from 0.76 to a factor of 3.0. When only CCN are considered (defined here as particles larger than 0.07 μm) the OPAC parameterization is too low by 25-35% for the fresh and intermediate ages and then overestimates number by 15% after aging (Table 3.9). This range of potential error highlights the need for dynamic aerosol representations in global climate models which are intended to predict CCN.
Figure 3.42 – Comparison of number, volume and scattering size distributions for aging anthropogenic aerosol in the North American boundary layer compared to the OPAC parameterization for water soluble aerosol.

Figure 3.43 and Table 3.10 evaluate the agreement between the OPAC “Soot” and the refractory aerosol distribution observed in the ENA CBL. When modeled as an externally mixed component, aerosol absorption \( m=1.44-0.1i \) is in good agreement with the observations. Note however that the geometric mean diameter of the absorption distribution is \( \sim 1/2 \) the observed value for refractory aerosol. When optical properties are computed assuming internal mixing this will significantly alter the composite particle absorption enhancement as it is critically dependent on the ratio of core:shell diameters [Fuller et al., 1999; Schnaiter et al., 2005].

The OPAC “soot” distribution predicts refractory aerosol number a factor of 2-5 higher than that observed (Table 3.10). In the ambient environment these primary aerosols serve as condensation nuclei for volatile ionic and organic species creating
internally mixed aerosol which potentially become CCN. In my analysis the ratio of refractory aerosol volume to total accumulation mode refractory volume is fixed at 0.09 or 9%. RCN ratios of the aging BL pollution increase from 0.5 to 0.7 using the fits to the North American observations. However the RCN calculated using the OPAC parameterization results in a ratio of 1.1, i.e. there are 10% more refractory number than total number, an unphysical result.

![INTEX-A Anthro - CBL](image)

**Figure 3.43** – Same as figure 3.42 but comparing OPAC “Soot” to refractory aerosol.
Table 3.10 – Same as table 3.9 but comparing OPAC “Soot” to refractory aerosol number, volume and absorption.

<table>
<thead>
<tr>
<th>Observations</th>
<th>Number Ratio</th>
<th>Volume Ratio</th>
<th>Absorption Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh</td>
<td>1.71</td>
<td>1.00</td>
<td>0.94</td>
</tr>
<tr>
<td>Intermediate</td>
<td>3.03</td>
<td>1.00</td>
<td>0.93</td>
</tr>
<tr>
<td>Aged</td>
<td>4.75</td>
<td>1.00</td>
<td>0.92</td>
</tr>
</tbody>
</table>

Figure 3.44 and Table 3.11 evaluate three separate parameterizations for mineral dust available in the OPAC inventory. The types are insoluble mass, “Insoluble”, accumulation mode mineral dust “Mineral Acc.” and mineral dust after long-range transport, “Mineral Trans.” In this case the integral volumes for Mineral Acc. and Mineral Trans. do not equal the observed values, (5 μg std m⁻³ divided by 2.0 g cm⁻³) as the OPAC parameterization specifies a particle density of 2.6 g cm⁻³ for these two components. In Table 3.11 the distributions listed in the left hand column are divided by the urban dust measured in the North American CBL. The ratios of scattering and absorption are computed using a refractive index of 1.56-0.006i. Scattering calculated from the two sets of observations are identical whereas using any of the OPAC parameterizations will result in an underestimate for both scattering and absorption.

The average distributions for urban North American dust and the Asian Dust in Figure 3.44 show a remarkable similarity even though they were measured on two separate campaigns using different OPC and APS instruments. The 50% passing efficiency diameter of the UH solid diffuser inlet for a particle density of 2.06 g cm⁻³ is no less than 3.5 μm [McNaughton et al., 2007], ignoring possible influences of the shape factor. The fact that the VMD for both the IA and the IB supermicrometer dust distributions are both 3.1 μm is strong evidence that inlet passing efficiency is controlling
the shape of the aerosol size distribution. The fact that significant numbers of particles up to \( \sim 8.0 \, \mu m \) are being sampled indicates that undersampling above 3.5 \( \mu m \) is almost certainly occurring. This result is consistent with the inlet’s comparisons against the University of Denver Low-turbulence inlet [Huebert et al., 2004; Wilson et al., 2004]. Note however that the passing efficiency of the UNH inlet, used for sampling aerosol chemistry, is comparable to the UH inlet [McNaughton et al., 2007] and thus undersampling should not adversely affect comparisons using both data sets.

Figure 3.44 – Urban Dust in the North American boundary layer and Asian Dust in the North Pacific FT compared to three parameterizations from OPAC.
Table 3.11 – Ratio of Asian Dust and OPAC parameterizations of dust compared to the observations of urban/industrial dust in the North American continental boundary layer.

<table>
<thead>
<tr>
<th>Distribution</th>
<th>INTEX-NA - Urban Dust</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Number Ratio</td>
</tr>
<tr>
<td>IB Asian Dust</td>
<td>0.74</td>
</tr>
<tr>
<td>Insoluble</td>
<td>0.05</td>
</tr>
<tr>
<td>IA Mineral Acc.</td>
<td>0.41</td>
</tr>
<tr>
<td>Mineral Trans.</td>
<td>0.12</td>
</tr>
</tbody>
</table>

3.4.4 \( f(RH) \) and campaign average ambient aerosol optical depth

Satellite remote sensing is better suited to determining average aerosol optical depth (AOD) at regional to global scales than in-situ airborne measurements. On the other hand, in-situ measurements are more precise and can be directly related to the aerosol microphysics and chemistry. Thus our in-situ measurements have been used to calibrate/validate both satellite [Kahn et al., 2004] and airborne remote-sensor retrievals.

HiGEAR measurements of aerosol light scattering and absorption are measured below 40% RH, i.e. “dry”. For comparison purposes these dry profiles of extinction have to be converted to ambient extinction values based on ambient RH and the \( f(RH) \) equation:

\[
\sigma_{sp,amb} = \sigma_{sp,dry} \left( \frac{RH_{dry}}{100} \right)^{y} \left( 1 - \frac{RH_{amb}}{100} \right)
\]  

(3.5)

Light scattering measured by the wet and dry RRNephps used to calculate \( f(RH) \) can potentially over/underestimate \( f(RH) \) by a factor of 0.67-1.5 (see discussion in 2.3.4). Intercomparisons with independent measurements of ambient light extinction during the
field campaigns allow us to assess closure between our dry measurements after conversion to ambient conditions. Figures 3.45 and 3.46 compare our in-situ ambient extinction measurements with an airborne high spectral resolution LIDAR (HSRL) aboard a separate airborne platform (NASA B200) but while flying in formation during MIRAGE [Rogers et al., 2007]. Linear regressions of the data indicate a high degree of correlation and a discrepancy of just 15%.

Figure 3.45 – Comparison ambient extinction from four vertical profiles during MIRAGE. HiGEAR aerosol data collected aboard the NSF/NCAR C-130 is shown in green. High spectral resolution LIDAR measurements from the NASA King Air B200 aircraft are shown in black; ambient RH in red.
Figure 3.46 – Linear regression of HiGEAR ambient aerosol extinction compared to HSRL extinction. After correcting the HiGEAR dry extinction values to ambient conditions, the measurements agree to within 15% despite being measured on separate airborne platforms.

GCM’s simulating ambient extinction will need to apply appropriate humidity dependent growth curves to their aerosol populations and should account for the suppression of hygroscopic growth by organic aerosol and mineral dusts. Table 3.12 summarizes $\gamma_T$ for each of the major airmass types which contribute to tropospheric light extinction. $f$(RH) is also a function of particle size [Howell et al., 2006] so I have included NMD’s for these distributions. I also tabulate dry single scatter albedo which will increase with humidification. Ambient aerosol optical depth refers to the integral of light extinction for the profiles shown earlier.

Quinn et al. [2005], derived parameterizations for $\gamma_T$ as a function of particulate organic matter mass (POM) and sulfate mass which I briefly compare to the range of $\gamma_T$
values observed aboard the aircraft. For pollution dominated North America airmasses
that are not influenced by seasalt the $\gamma_T$ values are $\sim 0.5 \pm 0.1$. Using the Quinn et al.,
INTEX-NA/ICARTT parameterization this implies a ratio of $\text{POM}:(\text{POM} + \text{sulfate})$ of
between 0.8 and 0.4. When seasalt is present $\gamma_T$ is enhanced and has a value of $\sim 0.55 \pm 0.1$ implying a $\text{POM}:(\text{POM} + \text{sulfate})$ ratio of 0.7 to 0.3. FT measurements of biomass
burning aerosol show the lowest $\gamma_T$ values, 0.22 $\pm 0.07$. These aerosol also contained
the highest fractions of both volatile and refractory OC [Clarke et al., 2007]. These low $\gamma_T$
values correspond to a Quinn et al. POM ratio of between 1.3 and 1.0, i.e. there is
more POM than sulfates, a result consistent with our own observations. In summary the
aircraft range of $\text{POM}:(\text{POM} + \text{sulfate})$ values derived from the Quinn et al.
parameterization ($0.3 - 1.3$) is comparable to the range of values measured aboard the
R/V Ron Brown during INTEX-NA/ICARTT ($0.2 - 1.0$). The exception is the low $\gamma_T$
biomass burning aerosol which was more extensively sampled by the DC-8 in the seasalt-
free FT.

In the absence of explicit calculations of aerosol hygroscopicity based on aerosol
chemistry, GCM's would be well advised to incorporate parameterizations such as Quinn
et al., for computing ambient extinction in both the BL and the FT. Note however that
accurately simulating and/or comparing differences in simulated ambient AOD as a
function of composition will require modelers to demonstrate that differences are not
being driven by errors associated with simulating the state variables, T, P and $w$. As
shown in Figure 3.33 of section 3.4.1, errors associated with simulating relative humidity
can overwhelm composition-driven differences in aerosol f(RH) even if aerosol
composition is well simulated by the model.
Table 3.12 – Summary of aerosol optical properties for selected atmospheric regimes, airmass types. Number mean diameter is the average value from the log-normal fitting process, dry SSA and $\gamma_T$ are campaign averages for the airmass type. Ambient AOD is extinction calculated at the average value of $\gamma_T$ and integrated over the atmospheric compartment within which the airmass resides. These integrals correspond to the profiles of ambient extinction in Appendix A.

<table>
<thead>
<tr>
<th>Eastern North America</th>
<th>Regime</th>
<th>Type</th>
<th>NMD (µm)</th>
<th>Dry SSA</th>
<th>$\gamma_T$</th>
<th>Ambient AOD</th>
</tr>
</thead>
<tbody>
<tr>
<td>FT</td>
<td>Clean</td>
<td>0.02</td>
<td>1.00</td>
<td>LOD</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Anthro</td>
<td>0.06</td>
<td>0.947 (0.042)</td>
<td>0.49 (0.10)</td>
<td>0.07</td>
<td></td>
</tr>
<tr>
<td></td>
<td>BB</td>
<td>0.25</td>
<td>0.952 (0.033)</td>
<td>0.22 (0.07)</td>
<td>0.30</td>
<td></td>
</tr>
<tr>
<td>CBL</td>
<td>Fresh</td>
<td>0.04</td>
<td>0.981 (0.029)</td>
<td>0.44 (0.10)</td>
<td>0.08</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Intermediate</td>
<td>0.07</td>
<td>0.986 (0.024)</td>
<td>0.45 (0.08)</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Agad</td>
<td>0.10</td>
<td>0.973 (0.023)</td>
<td>0.48 (0.08)</td>
<td>0.16</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Mexico</th>
<th>Regime</th>
<th>Type</th>
<th>NMD (µm)</th>
<th>Dry SSA</th>
<th>$\gamma_T$</th>
<th>Ambient AOD</th>
</tr>
</thead>
<tbody>
<tr>
<td>FT</td>
<td>Clean</td>
<td>0.04</td>
<td>1.00</td>
<td>LOD</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Anthro</td>
<td>0.11</td>
<td>0.948 (0.015)</td>
<td>0.48 (0.01)</td>
<td>0.15</td>
<td></td>
</tr>
<tr>
<td>CBL</td>
<td>Anthro</td>
<td>0.13</td>
<td>0.934 (0.018)</td>
<td>0.32 (0.09)</td>
<td>0.19</td>
<td></td>
</tr>
<tr>
<td>MBL</td>
<td>Anthro</td>
<td>0.11</td>
<td>0.962 (0.019)</td>
<td>0.65 (0.04)</td>
<td>0.17</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Hawaii</th>
<th>Regime</th>
<th>Type</th>
<th>NMD (µm)</th>
<th>Dry SSA</th>
<th>$\gamma_T$</th>
<th>Ambient AOD</th>
</tr>
</thead>
<tbody>
<tr>
<td>FT</td>
<td>Clean</td>
<td>0.04</td>
<td>1.00</td>
<td>LOD</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mixed</td>
<td>0.075</td>
<td>0.979 (0.010)</td>
<td>0.39 (0.07)</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td>MBL</td>
<td>Anthro</td>
<td>0.14</td>
<td>0.983 (0.010)</td>
<td>0.55 (0.05)</td>
<td>0.07</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Background</td>
<td>0.15</td>
<td>1.002 (0.008)</td>
<td>0.55 (0.04)</td>
<td>0.07</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Alaska</th>
<th>Regime</th>
<th>Type</th>
<th>NMD (µm)</th>
<th>Dry SSA</th>
<th>$\gamma_T$</th>
<th>Ambient AOD</th>
</tr>
</thead>
<tbody>
<tr>
<td>FT</td>
<td>Clean</td>
<td>0.04</td>
<td>1.00</td>
<td>LOD</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mixed</td>
<td>0.074</td>
<td>0.983 (0.015)</td>
<td>0.32 (0.11)</td>
<td>0.09</td>
<td></td>
</tr>
<tr>
<td>MBL</td>
<td>Anthro</td>
<td>0.14</td>
<td>0.984 (0.021)</td>
<td>0.62 (0.15)</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Background</td>
<td>0.14</td>
<td>0.993 (0.029)</td>
<td>0.55 (0.13)</td>
<td>0.06</td>
<td></td>
</tr>
</tbody>
</table>
Over the Central Highlands of Mexico and in the FT over the Eastern North Pacific $\gamma_T$ is typically suppressed in the presence of mineral dust. The average value over the central highlands is 0.32 whereas when the FMF$_{scat}$ is below 0.6 the ENP $\gamma_T$ values are 0.32-0.39 +/- 0.1. This does not imply that dust is suppressing accumulation mode aerosol hygroscopicity but that the increase in light scattering from the accumulation mode aerosol is small compared to the scattering by the relatively hydrophobic mineral dust [Howell et al., 2006]. Anderson et al. [2005] previously evaluated the dependency of the fine mode fraction of scattering on scattering Angstrom exponent. Figure 3.47 plots their relationship with data from the FT during ACE-Asia, INTEX-NA and INTEX-B. It is important to note that when using this relation in remote sensing applications the ambient Angstrom exponent will differ from the dry Angstrom value. However, Redemann et al. [2003] noted that this difference is small (<5%) below 90% RH.

To evaluate the effect of mineral dust on $\gamma_T$ I plot $\gamma_T$ versus dry aerosol scattering Angstrom exponent (450/700) in Figure 3.48. Symbols are scaled by total aerosol scattering at 550 nm and shaded by FMF$_{scat}$. FT data from ACE-Asia are solid squares; INTEX-NA data are circles; INTEX-B data are triangles and include all data not collected in the MBL near MEX, HI and AK. As discussed, the mass fraction of organic carbon, affects $\gamma_T$ [Clarke et al., 2007; Quinn et al., 2005] and is responsible for the variability in $\gamma_T$ for Angstrom exponents greater than 1.0. As FMF$_{scat}$ becomes smaller the scattering Angstrom exponent decreases (Figure 3.47). Figure 3.48 shows that as the scattering Angstrom exponent drops below 1.0 the $\gamma_T$ values generally do not exceed 0.3. Recall that earlier in my analysis, biomass burning aerosol were separated from pollution using a threshold $\gamma_T$ of 0.3. These data have been removed from Figure 3.48 but account...
for the sharp cutoff in INTEX-NA data points at $\gamma_T < 0.3$. The scattering Angstrom exponents of the biomass burning aerosol ($\sim 1.0$) are above dust values ($\sim < 1.0$) providing a means of separating the two aerosol types.

For satellite retrievals over land, where marine aerosol influences are negligible, and where scattering Angstrom exponents are below 1.0, $f(RH)$ gamma values can to some extent be inverted from Angstrom exponents. With estimates of the ambient RH field the dry $FMF_{sent}$ can then be estimated. This can be used to estimate the relative contribution of anthropogenic pollution and urban/industrial or “natural” mineral dusts to column AOD. This relationship should be most useful for MISR and CALIPSO, where multi-angle imaging and LIDAR can resolve aerosol height and thus separate the wavelength dependence of aerosol scattering in the FT from scattering in the MBL.
Figure 3.47 – Submicrometer fraction of scattering SMF\textsubscript{scat} versus total, dry aerosol scattering Angstrom exponent for ACE-Asia (red squares), INTEX-NA (blue circles), and INTEX-B (green triangles). Note that for ACE-Asia and INTEX-B the SMF\textsubscript{scat} was measured using two TSI nephelometer while submicrometer scattering during INTEX-B used an RRNeph corrected according to the empirical formulation of Anderson \textit{et al.} [2003].
Figure 3.48 – Total aerosol gamma, $\gamma_T$, versus dry aerosol angstrom exponent. Aerosol composition influences $\gamma_T$ variability but as hydrophobic mineral dust begins to dominate aerosol extinction the increase in light scattering as a function of relative humidity $f(RH)$ is negligible.

Table 3.12 also summarizes ambient AOD computed from the campaign average RH profile and the average $\gamma_T$ for the airmasses indicated. The highest AOD are for biomass burning plumes over North America. However, the magnitude of this AOD is misleading due to the episodic nature of biomass burning. It is unlikely that a high BB extinction value will be integrated over the entire FT column. Rather figures 3.15 and 3.16 show that these BB plumes are thin filaments or plumes a few 100 meters thick to 1-2 km in vertical extent. Anthropogenic plumes are ubiquitous in the North American FT and dominate the FT over the North Pacific. And while these layers are often interspersed with cleaner layers, the contribution of the clean layers to AOD is negligible.
(< 0.01 for 10 km integral). Thus the range (0.07-0.10) of campaign average AOD's for FT airmasses of anthropogenic origin are probably more representative of global annually averaged values observed by satellite or simulated by climate models for these regions.

AOD in the boundary layer can be driven as much by the strength of the emissions as it can by the average ambient relative humidity [Shinozuka et al., 2007].

The data presented here support this important consideration. Over the heavily perturbed but arid Central Highlands of Mexico ambient AOD is 0.19 when integrated over 2 km. The Gulf of Mexico MBL (alt < 1.5 km) was less polluted than the near-source highlands region but the high relative humidity results in a comparable ambient AOD, 0.17. Over continental North America the evolution of the boundary layer aerosol size distribution exerts a large influence on AOD. When stratified by the age groupings the AOD in the CBL nearly triples using the same relative humidity profile (Table 3.12).

3.4.5 Wavelength dependence of light scattering and absorption

_in-situ_ airborne measurements of $3\lambda$ (470, 530, 660 nm) aerosol light absorption were made for the first time aboard the NASA DC-8 and the NSF/NCAR C-130 during INTEX-NA & B, MIRAGE and IMPEX. Each data point in the figures is an average value for 5-10 minute level leg averages. Three wavelength (450, 550, 700 nm) measurements of light scattering are also obtained using the TSI $3\lambda$ nephelometer. TSI nephelometer data is corrected according to [Anderson and Ogren, 1998]. PSAP measurements are corrected according to [Virkkula et al., 2005] which is considered an update to the corrections applied to the single wavelength PSAP measurements of aerosol absorption [Bond et al., 1999]. PSAP instrument noise may affect absorption accuracy at

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low signal (< 1.0 Mm\(^{-1}\)). Instrument noise levels were not higher (See Chapter 2) than noise in the single-wavelength PSAPs evaluated by Anderson et al. [2003].

Angstrom exponent of scattering is controlled by particle diameter. Aerosol populations with small diameters, such as fresh pollution, have steep wavelength dependencies and a large Angstrom exponent. Large aerosols such as dust and seasalt have small wavelength dependencies and small, even slightly negative Angstrom exponents. The Angstrom exponent of absorption is not a function of size but rather a function of composition. Light absorbing carbon or “black carbon”, BC, has relatively weak wavelength dependence and therefore a low angstrom exponent \(\approx 1.0\). Refractory organic carbon and humic-like substances associated with BC can enhance the wavelength dependence of aerosol absorption [Graber and Rudich, 2006; Kirchstetter et al., 2004]. We first reported measurements of enhanced short-wave absorption by refractory material in biomass burning plumes in Clarke et al. [2007]. In addition to their optical properties these relatively hydrophobic organic species also suppress f(RH) [Quinn et al., 2005].

In figure 3.49-3.52 I plot the Angstrom exponent of aerosol absorption versus the scattering Angstrom exponent for the campaign specific 300- to 600- second level leg averages. In the figures marker size is scaled according to the intensity of total light scattering at 550 nm; a measure of the strength of the signal used to determine both Angstrom exponents. Finally, the data are shaded according to \(\gamma_T\), an independent assessment of the aerosols composition based on hygroscopicity. In figure 3.49 the biomass burning aerosols separate from the anthropogenic pollution in the North American FT relatively well. Compared to Anthro aerosols, BB aerosols have larger
NMD's, have lower scattering Angstrom exponent, and contain higher mass fractions of volatile and refractory OC. As discussed in Clarke et al. [2007], this results in higher absorption Angstrom exponent and low $\gamma_T$.

In figure 3.50 I plot the same relation but for the polluted CBL of the Mexican Highlands and the FT over the Gulf of Mexico. Because seasalt aerosol is non-absorbing at visible wavelengths no MBL data is included in the analysis. For the Mexico region most data show a composition somewhere between a BB and a Pollution type composition. This is in agreement with preliminary findings of high ammonium nitrate, K$^+$, and organic mass fractions in these near-source emissions. Additionally, samples from the March 19$^{th}$ flight are dominated by supermicrometer dust which has a steeper wavelength dependence of absorption than all other aerosol types [Sokolik and Toon, 1999]. The data from Mexico indicate dust absorption Angstrom exponents as high as 3.0 to 4.0.

The FT data collected near Hawai'i and Alaska contain all three aerosol types, anthropogenic pollution, biomass burning and dust. These are presented in Figures 3.51 and 3.49. For the dust dominated samples (scattering angstrom < 0.75) absorption angstrom exponents exceed 4.0 a value that may be unrealistically high. The reason for these high values has not been determined and may be linked to PSAP performance and/or the Virkkula et al. [2005], correction applied to the PSAP data. When attempting to simulate ambient aerosol absorption the trends in wavelength dependence such as those presented here should be replicated by the model. This can be accomplished by using size distribution measurements and wavelength specific refractive indices to
calculate the observed absorption values. This has not been performed using the available data but could form the basis of future work.
Figure 3.49 – Absorption angstrom versus scattering angstrom for FT measurements during INTEX-NA. When scaled by total light scattering and coloured by $\gamma_T$ the unique optical properties of BB and Pollution aerosol are clear.

Figure 3.50 – Same as figure 3.49 but for aerosol measured in the CBL of the Mexican Highlands and in the FT (alt > 1.5 km) over the Gulf of Mexico.
Figure 3.51 – Same as figure 3.49 but for aerosol measured in the FT (alt > 1.5 km) near Hawai‘i.

Figure 3.52 - Same as figure 3.49 but for aerosol measured in the FT (alt > 1.5 km) near Alaska.
3.5 References


Feichter, J., E. Kjellstrom, H. Rodhe, F. Dentener, J. Lelieveld, and G.J. Roelofs, Simulation of the tropospheric sulfur cycle in a global climate model,


Newman, L., Atmospheric oxidation of sulfur dioxide: A review as viewed from power plant and smelter plume studies, Atmospheric Environment, 15, 2231, 1981.


4.0 Size distributions and the aerosol indirect effect

Altering the concentration of aerosol number in the ambient atmosphere can potentially alter the number of cloud condensation nuclei (CCN) activating to form clouds and thereby alter cloud optical properties and their radiative effects [Albrecht, 1989; Twomey, 1974]. Depending on local meteorological conditions, altering the number and the size of cloud droplets may also modify cloud liquid water content, cloud lifetime and precipitation patterns [Ackerman et al., 2004; Rosenfeld, 2000]. AeroCom designed and carried out a preliminary model comparison designed to test model diversity with respect to simulating the indirect effect of aerosols on climate [Penner et al., 2006]. One of the conclusions reached during this assessment was, “[prediction aerosol number] requires significant improvement in order to improve the prediction of aerosol indirect effects.”

Vertical profiles of aerosol number and mass were discussed in section 3.2 and will be of use to the AeroCom community when assessing the accuracy of their aerosol number simulations. In this chapter I summarize observations of clean background conditions in the remote marine environment and the free troposphere. I also provide a brief analysis of the evolution of aerosols in airmasses recently lofted to the upper troposphere. At the end of the chapter I assess the relative increase in remote MBL CCN concentrations as a result of the entrainment of FT biomass burning and anthropogenic aerosols which were discussed in conjunction with their direct effects in Chapter 3.
4.1 Aerosol in the remote Eastern North Pacific marine boundary layer

4.1.1 Identifying clean MBL conditions using sea salt aerosol composition

Reference seawater has a salinity of exactly $S_R = 35.16504 \text{ g kg}^{-1}$ [SCOR/IAPSO, 2008]. Open ocean salinity is controlled by the balance between evaporation and precipitation and varies between 33%0 and 36%0. Even though salinity varies, Marcet's Principle or the Rule of Constant Proportions states that “regardless of how the salinity may vary, the ratio between the major ions in open ocean seawater is nearly constant.” This principle is valid over the open ocean because the time scales for chemical processes that affect the concentrations of these major ions are typically much longer than mixing processes such as advection, dispersion and diffusion [Libes, 1992]. In coastal regions salinity is more variable due to river and groundwater inputs and Marcet's Principle is not necessarily valid.

Using Marcet's Principle and assuming that sea salt aerosol have the same bulk composition as seawater at the time of their formation we can calculate several molar ratios that serve as conservative tracers for sea salt aerosol over the remote ocean. The most common use of this technique is the separation of primarily produced sea salt sulfate (ssSO$_4^{2-}$) compared to non-sea salt sulfate (nssSO$_4^{2-}$). The ratio of primarily produced sea salt sulfate (ssSO$_4^{2-}$) to the conservative tracer sodium, Na$^+$, is 0.060 mol mol$^{-1}$ (0.252 g g$^{-1}$). Two secondary semi-conservative tracers for sea salt aerosol are the ratios of Ca$^{2+}$:Na$^+$ and Ca$^{2+}$:Mg$^{2+}$. While sodium and magnesium are conservative tracers, calcium concentrations vary with seawater alkalinity due to biogeochemical processes associated with photosynthesis and remineralization [Libes, 1992]. Nominally these two molar ratios are Ca:Na = 0.020 and Ca:Mg = 0.19.
While salinity, or alternatively chlorinity, is a conservative seawater tracer, the chloride ion, Cl\(^-\), is not a conservative sea salt aerosol tracer. Chloride, present in sea salt aerosols at the time of their formation, can be lost according to one or more of the following reactions:

\[
NaCl(s) + HNO_3(g) \rightarrow NaNO_3(s) + HCl(g)
\]

\[
2NaCl(s) + H_2SO_4(g) \rightarrow Na_2SO_4(s) + 2HCl(g)
\] (4.1)

\[
NaCl(s) + H_2SO_4(g) \rightarrow NaHSO_4(s) + HCl(g)
\]

Thus it can be shown that while sodium remains a conservative tracer for refractory sea salt aerosol, aged sea salt aerosol typically exhibits a “chloride deficit” [Seinfeld and Pandis, 1998].

Seawater is also a source of primary organic aerosol [Middlebrook et al., 1998]. Based on ocean productivity we expect a pronounced seasonal variability of oceanic organic aerosol concentrations and composition within each biogeochemical province. Aerosol produced from biologically rich waters, such as those in upwelling regions; probably have much higher concentrations than in more oligotrophic waters. Still, in a careful analysis employing aerosol size distributions, ion chromatography and gravimetrically determined aerosol mass, Quinn and Coffman [1998] determined that aerosols over the Southern Ocean with Dp < 0.45 \(\mu\)m where composed primarily (100% +/- 10%) of nssSO\(_4^{2-}\), ammonium, secondarily produced methanesulfonate (MSA) and sea salt.
No measurements of organic aerosol are available aboard the DC-8 for INTEX-NA & B nor can the contribution of organic aerosol be inferred, as per [Clarke et al., 2007], at the level of precision presented in Quinn and Coffman [1998] or Middlebrook et al. [1998]. However, concentrations of primary organic aerosol produced from the oligotrophic waters of the North Pacific Subtropical Gyre and the HNLC\(^1\) waters of the North Pacific Subpolar Gyre are probably low, similar to the Southern Ocean, and are not considered further.

I classify North Pacific MBL airmasses as “clean background” when the ratio of Ca:Na and Ca:Mg are below 0.04 and 0.4 allowing for a factor of 2 variation seawater alkalinity. The remainder of the data is classified as anthropogenically influenced because its composition is being influenced by material of crustal rather than oceanic origin.

The validity of this approach is evaluated in Figure 4.1. Here University of New Hampshire, filter-based chemistry measurements of the molar concentrations of Cl\(^-\), Na\(^+\), Ca\(^{2+}\) and Mg\(^{2+}\) are each divided by their seawater molar concentrations in order to calculate sea salt aerosol mass. These mass estimates are then regressed against total aerosol mass from HiGEAR aerosol size distributions using a sea salt density of \(\rho=2.2\) g cm\(^{-3}\). Data include only samples labeled as “clean background”, i.e. when aerosol composition is not significantly different than the bulk composition of seawater.

Note the 35% Cl\(^-\) deficit in the upper left panel of Figure 4.1. The \(\sim 15\%\) discrepancies between the total seasalt mass estimates of Na\(^+\) and Mg\(^{2+}\) is consistent with a slightly lower 50% passing efficiency for the UNH inlet compared to the UH

\(^1\) High nutrient (nitrate), low chlorophyll
sample inlet [McNaughton et al., 2007]. \( \text{Ca}^{2+} \), the more variable semi-conservative tracer, is also within \( \sim 15\% \). This assessment of mass closure between the two independent measurements of sea salt aerosol mass lends confidence to later analysis for aerosols whose composition is poorly constrained.

![Graphs showing mass closure between University of New Hampshire (SAGA) sea salt aerosol mass (derived from molar ratios of major seawater ions) and the integral of University Hawai‘i aerosol volume distributions multiplied by a sea salt density of 2.2 g cm\(^{-3}\). Closure within 15\% for the conservative and semiconservative tracers, sodium, magnesium and calcium are within uncertainties between the differing airborne inlet sampling systems. Chloride is not conserved due to reactions with acid atmospheric gases.](image)

**Figure 4.1** — Mass closure between University of New Hampshire (SAGA) sea salt aerosol mass (derived from molar ratios of major seawater ions) and the integral of University Hawai‘i aerosol volume distributions multiplied by a sea salt density of 2.2 g cm\(^{-3}\). Closure within 15\% for the conservative and semiconservative tracers, sodium, magnesium and calcium are within uncertainties between the differing airborne inlet sampling systems. Chloride is not conserved due to reactions with acid atmospheric gases.

4.1.2 Clean background versus anthropogenically influenced aerosol size distributions in the remote marine boundary layer of the Eastern North Pacific

Few size distributions met the “clean background” criteria while sampling over the North Atlantic and the Gulf of Mexico study regions; an indication of the magnitude and persistence of anthropogenic emissions. In the Gulf of Mexico I analyzed fifty-six,
300-second level leg averages of anthropogenically influenced MBL air. The average log-normal fits statistics for these distributions is contained in Appendix C - Table C.2. Over the remote Eastern North Pacific, distributions were divided into those collected near Hawai‘i (Latitude < 40°N) and those collected near Alaska (Latitude > 40°N). Near Hawai‘i, 14 level legs met “clean background” conditions while 25 samples were anthropogenically influenced. Near Alaska there were 26 “clean background” samples and 28 anthropogenically influenced airmass sampled. Figure 4.2 plots the unheated (top) and refractory (bottom) number (left) and volume (right) aerosol size distributions for “clean background” aerosol near Hawai‘i. Figure 4.3 plots the distributions measured near Alaska (North of 40°N).

In both regions the “clean” unheated aerosol requires a three mode fit while the refractory distribution only requires two modes. Both the Hawai‘i and the Alaskan “clean” unheated size distributions display a pronounced Hoppel minimum at ~0.060-0.090 μm separating aerosols which have been cloud processed (Dp ~ 0.070 μm) from those which have not been activated in cloud (Dp < 0.070 μm) [Hoppel et al., 1994; Hoppel et al., 1986]. The refractory distributions contain both the supermicrometer dominated seasalt aerosol as well as an “ultrafine” sea salt mode [Clarke et al., 2006; Martensson et al., 2003].

In the first column of figure 4.4 and 4.5 I assess optical closure between aerosol light scattering calculated using the distribution in figures 4.2 and 4.3 comparing them to the corrected [Anderson and Ogren, 1998] scattering values measured using the TSI 3λ nephelometer. Scattering values calculated based on the fits to each size distributions are within 25% of those measured directly. In the second column of figures 4.4 and 4.5 I
calculate wavelength dependent dry aerosol mass scattering efficiencies ($\sigma_{sp, \lambda}$) as a function of relative humidity. $\sigma_{sp}$ for the Aitken and accumulation mode ($m_{12}$) aerosol is calculated assuming an ammonium sulfate composition with a dry aerosol density of 1.8 g cm$^{-3}$. Sea salt aerosol $\sigma_{sp}$ (labeled $m_3$ in Figure 4.5) is assigned a dry density of 2.2 g cm$^{-3}$. Ambient refractive indices and densities are calculated using their RH dependent values [Tang and Munkelwitz, 1994; Tang et al., 1997].
Figure 4.2 – Total (top) and refractory (bottom) aerosol number (left) and volume (right) distributions measured in the Hawaiian trade wind regime. Distributions represent clean background conditions where aerosol composition is not significantly different than seawater.

Figure 4.3 – Same as figure 4.2 but for the Alaskan Low of the Eastern North Pacific.
Figure 4.4 – Optical closure between calculated and measured aerosol scattering at three wavelengths using individual, 3-mode, log-normal fits to the remote marine aerosol size distribution (first column). Mass scattering efficiency as a function of relative humidity for the size distribution in Figure 4.2 (second column) assuming an ammonium sulfate composition in the Aitken and Accumulation modes ($m_{12}$) and sea salt in the supermicrometer mode, $m_3$.

Figure 4.5 – Same as Figure 4.4 but for the Alaskan Low.
Figures 4.6 and 4.7 summarize aerosol size distributions in the remote MBL when the aerosol composition differs from that of seawater. Qualitatively the distribution’s shapes do not differ from those under clean conditions. Each distribution requires 3 unheated and 2 refractory lognormal fits and has a distinct *Hoppel minimum* in the 60-90 nm size range. The gas phase tracers CO and O\textsubscript{3} are elevated with respect to background values over the remote ocean (< 90 ppbv; < 40 ppbv). Additionally, the concentrations do not differ (\(\alpha=0.05\)) between the clean and polluted cases for either Hawai‘i (CO = 138 & 144 ppbv; O\textsubscript{3} = 44 & 47 ppbv) or Alaska (CO = 156 & 158 ppbv; O\textsubscript{3} = 49 ppbv). The “clean background” aerosol selection criterion is based on sea salt aerosol molar ratios and weights the classification by aerosol mass, i.e. seasalt. Refractory aerosol number of anthropogenic origin is dominated by Aitken mode sizes (0.01-0.10 \(\mu\text{m}\)) and can contribute negligibly to mass.

Thus some distributions labeled as “clean” may in fact contain aerosol of anthropogenic origin. If however I compare the statistics of anthropogenic gas and aerosol phase tracers with lifetimes shorter than CO and O\textsubscript{3} there are some quantitative differences. For example, near Hawai‘i and Alaska HNO\textsubscript{3} (g) are higher in the polluted airmasses than for the clean conditions. Wind speeds are not higher (\(\alpha=0.05\)) in polluted airmasses compared to clean airmasses yet refractory CN are 2-3 times higher in polluted airmasses, the difference being significant (\(\alpha=0.05\)) near Hawai‘i. Finally, for clean cases near Hawai‘i and Alaska, aerosol absorption is not significantly different from zero using a 1-tailed Student’s t-test (\(\alpha=0.05\)). But for polluted cases in each region absorption is greater than zero with mean values of 0.4 and 0.2 Mm\(^{-1}\). Thus the elevated
refractory CN in the polluted airmasses must contain absorbing material presumably of anthropogenic origin.

SO₂ and UCN are more variable between the Hawaiian and Alaskan regions. SO₂ is particularly high in clean airmasses near Hawai‘i where volcanic emissions lead to an average value of 1500 pptv. Polluted air near Hawai‘i is also high in SO₂ with an average concentration of 750 pptv. The likely source of this “polluted MBL” SO₂ is also Kilauea volcano and/or a biogenic source because the polluted FT average near Hawai‘i is < 100 pptv. Near Alaska mean SO₂ and UCN in the polluted airmasses are double the background values of 60 pptv and 1300 cm⁻³ but this difference is not significant due to the high variability.

Overall this data, which is summarized in tabular format in Appendix-B, tend to support the hypothesis that I have effectively separated relatively clean background aerosol from airmasses containing anthropogenic aerosol. So that while the gas phase tracers (e.g. CO and O₃) are elevated compared to background values, the short atmospheric residence times of aerosols in the MBL [Raes et al., 2000] mean the “clean background” distributions are suitable for comparison to aerosols in pre-industrial (<1750) climate model simulations [Schulz et al., 2006]. Later in the chapter these distributions are compared to other observations [Heintzenberg et al., 2000], parameterizations [Hess et al., 1998; Porter and Clarke, 1997] and model simulations [Caffrey et al., 2006] and include a comparison to wind speed dependent parameterizations of sea salt size distributions [Lewis and Schwartz, 2004].
Figure 4.6 - Total (top) and refractory (bottom) aerosol number (left) and volume (right) distributions for anthropogenically influenced airmasses measured in the Hawaiian trade wind regime.

Figure 4.7 – Same as Figure 4.7 but for the anthropogenic pollution in the MBL of the Alaskan Low.
4.2 Background aerosol in the North Pacific and North American free troposphere

4.2.1 Clean background conditions in the free troposphere over the North Pacific and North America

For this dissertation clean background conditions in the FT are defined as airmasses with a carbon monoxide concentration less than 90 ppbv and ozone concentration less than 40 ppbv. These Northern Hemisphere background values [Seinfeld and Pandis, 1998] are chosen so that they might be compared to “Pre-Industrial” climate model simulations [Schulz et al., 2006]. Just 1.7% of the FT INTEX-NA data meets these criteria. Over Mexico 16% of the data meet these criteria while just 0.5% of the data collected over the Eastern North Pacific can be considered “clean” using the CO and O₃ criteria.

When stratified only by CO and O₃ the concentrations of other anthropogenic tracers in the clean FT airmasses are also minimized (see Appendix – B). The one notable exception is CO₂ over North America in summer 2004. There, CO₂ in the UT and LT have the highest values, 378.3 and 377.8 ppmv, compared to Anthro and BB values of 374 in the FT and 368 in the polluted BL. This presumably relates to the fact that these “clean” FT airmasses are well aged and may not have been in contact with the surface, and/or diluted by surface air since the onset of summertime CO₂ drawdown in the Northern Hemisphere (NH). Over Mexico in spring 2006 the CO₂ profile is reversed. Low “clean” FT values average 381.5 ppmv and showed evidence of dilution by interhemispheric exchange (see trajectories in Figure 3.6). Average MBL CO₂ concentrations over the Gulf of Mexico during INTEX-B averaged 385.6 ppmv (Appendix – B).
Attempting to fit multiple “clean” FT distributions is complicated by low sample number and concentrations at or near the detection limits of some instruments. Therefore the distributions are pooled prior to computing a single lognormal fit. Figure 4.8 summarizes the mono-modal lognormal fit for the unheated and refractory size distributions measured over ENA and MEX during INTEX-NA & B. I also include the distributions used by Caffrey et al. [2006] when simulating the entrainment of background FT air into the MBL near Hawai‘i. The Caffrey et al. distribution is based on earlier measurements of background FT air at the Mauna Loa Observatory (MLO) [Clarke et al., 1996; Weber and McMurry, 1996]. Qualitatively the number distributions in Figure 4.8 are nearly identical in shape. The ENA distribution has the most number and contains a larger peak at 10-20 nm. This is similar to the Weber and McMurray MLO distributions (not shown).

Because there are few samples measuring the size distribution it is important to compare the integral numbers produced from the log normal fits to the median concentrations measured at 1-Hz. At SATP the median of 1-Hz cold CN for the ENA and MEX lower troposphere (2-6 km) are 500 cm$^{-3}$ and 1000 cm$^{-3}$, values that bracket previous measurements over the remote North Pacific [Clarke et al., 1999; Clarke and Kapustin, 2002; Moore et al., 2003]. The unheated integral numbers generated from the ENA and MEX fits are 1100 cm$^{-3}$ and 500 cm$^{-3}$. The ENA refractory size distribution integral number is higher (500 cm$^{-3}$) than the median of the 1-Hz, hot CN values, 170-330 cm$^{-3}$. This results in an RCN ratio for the fit which is double the median RCN ratio based on the averaged 1-Hz data. The integral number for the MEX refractory number fit is lower (150 cm$^{-3}$) than the averaged 1-Hz value, 250 cm$^{-3}$, but results in an RCN
estimate (0.31) close to the ENA and MEX averaged 1-Hz values (0.25). Integrals of unheated aerosol volume multiplied by an ammonium sulfate density of 1.8 g cm\(^{-3}\) results in mass estimates of 0.37, 0.20 and 0.11 \(\mu g\) m\(^{-3}\) for the Caffrey \textit{et al.}, ENA and MEX distributions. At MLO the 1996-2006 mode value (i.e. most commonly observed) for the sum of aerosol \(SO_4^{2-}\), \(NO_3^-\) and \(NH_4^+\) is 0.26 \(\mu g\) m\(^{-3}\). Thus aerosol volume from the Caffrey \textit{et al.} and ENA distributions better replicate the mode value of the long-term MLO data. Based on this comparison the best lognormal fit parameters for clean FT aerosol in the Northern Hemisphere are, \(N=500\) cm\(^{-3}\), \(NMD=0.040\) \(\mu m\), and \(\sigma_g=2.00\). For the refractory aerosol internally mixed with volatile aerosol the fit parameters are; \(N=125\) cm\(^{-3}\), \(NMD=0.025\) \(\mu m\) and \(\sigma_g=1.60\). These values result in total and refractory masses of 0.26 \(\mu g\) m\(^{-3}\) and 5.0\(\times\)10\(^{-3}\) \(\mu g\) m\(^{-3}\), an RCN ratio of 0.25, and a refractory volume fraction of just 2%.

These fit parameters are compared to the OPAC parameterizations of “Water Soluble” aerosol and “Soot” in figure 4.9. The OPAC parameterization under predicts number by a factor of 2.5 when aerosol volumes are set equal (0.26 \(\mu g\) m\(^{-3}\) divided by 1.8 g cm\(^{-3}\)). OPAC dry light scattering at 550 nm and 10% RH (Figure 4.10) is a factor of 1.6 higher than the HiGEAR value. At 80% RH OPAC light scattering is higher by a factor of 1.4. Thus FT aerosol optical depths for “pre-industrial” simulations may be over estimated by about half when the clean FT aerosol is parameterized using the OPAC water-soluble distribution. Conversely, when entraining aerosol from the clean FT, GCM’s using the OPAC size distributions will under predict potential MBL CCN number by about a factor of 2.5 even when the simulation of aerosol mass matches the long-term record at MLO.
Figure 4.8 – Lognormal fits of unheated (top) and refractory (bottom) aerosol number (left) and volume (right) distributions for the clean FT. The Caffrey et al. [2006] distribution is shown for comparison and is based on previous measurements at the Mauna Loa Observatory [Clarke et al., 1996; Weber and McMurry, 1996].
Figure 4.9 – Comparison of OPAC [Hess et al., 1998] versus HiGEAR unheated (top) and refractory (bottom) aerosol number (left) and volume (right) distributions for the clean free troposphere. Aerosol volumes are equivalent and use a value of 0.26 μg m$^{-3}$, the mode value for the sum of SO$_4^{2-}$, NO$_3^-$ and NH$_4^+$ based on the 1996-2006 MLO record and assuming a density of 1.8 g cm$^{-3}$.

Figure 4.10 – Comparison of OPAC [Hess et al., 1998] versus HiGEAR aerosol scattering distributions for the clean FT. Distributions are computed for dry conditions (RH=10%) and at 80% relative humidity, the average value in the MBL. Scattering is over predicted by OPAC by a factor of 1.6 at 10% RH and by a factor of 1.4 at 80% RH.
4.2.2 Airmasses influenced by deep convection over continental North America in summertime

Boundary layer airmasses over the remote ocean can become enriched in SO\textsubscript{2} and aerosol sulfate from volcanic and biogenic emissions of sulfur. Anthropogenically impacted boundary layer air is enriched in aerosol precursors such as SO\textsubscript{2}, NH\textsubscript{3} and volatile organic compounds as well as primary aerosol soot [McNaughton et al., 2004]. When these airmasses are entrained into convective cloud cells the majority of the soluble gases (SO\textsubscript{2}, NH\textsubscript{3}, HNO\textsubscript{3}) and aerosols (SO\textsubscript{4}, NO\textsubscript{3}) are removed from the atmospheric column by wet deposition and scavenging. A small fraction however, survive convection and are detrained into the upper troposphere where, in the absence of pre-existing aerosol surface area, new particle number are formed through gas-to-particle conversion [Clarke et al., 1999; Clarke et al., 1998]. Here we examine the evolution of these particles after convection over North America.

Deep convection and extensive thunderstorm activity is common over continental North America during the summer and was extensively sampled during INTEX-NA [Hudman et al., 2007; Singh et al., 2007a]. Using fast measurements of NO\textsubscript{x}, OH and \textit{J}\textsubscript{HNO\textsubscript{3}} Bertram et al. [2007], determined that the NO\textsubscript{x}:HNO\textsubscript{3} ratios throughout much of the upper troposphere (alt > 6 km) were 2-6 times the steady state values. Based on the kinetics of the conversion of anthropogenic and lightning NO\textsubscript{x} \rightarrow HNO\textsubscript{3} in the upper troposphere, Bertram et al. developed an airmass age index, or, "days since convection" variable for the INTEX-NA dataset. The main assumption in the approach is that all nitric acid is removed from the atmospheric column during convection, i.e. \([\text{HNO}_3] = 0\) at \(t = 0\). Additionally the technique is not valid below 6 km as reservoir nitrogen species...
such as PAN begin to thermally decompose producing nitric acid via a second chemical pathway [Singh et al., 2007b].

Using the Bertram et al., “time since convection” index, 1544 data points are pooled into geometrically increasing time intervals; 0-3 hrs, 3-6 hrs, 6-12 hrs, 12-24 hrs, 24-48 hrs and 48-120 hrs. These 1544 data points represent 36% of all data collected in the upper troposphere (alt > 6.0 km) during INTEX-NA and are not mutually exclusive to those considered in our previous analysis (e.g. Section 3.3.2). The top panel of Figure 4.11 shows the rapid photolysis of UT formaldehyde (CH₂O) [Fried et al., 2003] as well as the buildup of HNO₃ through the photo-oxidation of anthropogenic and lightning NOₓ. SO₂ is the dominant secondary aerosol precursor and measurements are available for 1122 of the 1544 data points labeled. The SO₂ concentrations do not significantly (α=0.05) change with time. Mean, median and standard deviations of SO₂ in the convective outflow are 35, 25 and 44 pptv with a maximum observed concentrations of 660 pptv at an airmass age of only 2.2 hours since convection.

The second panel of Figure 4.11 shows the reduction of ultrafine (UCN > 3 nm) particle number concentration as well as the reduction in CN > 10 nm (Cold CN) with time. Refractory CN number is dominated by soot, a combustion tracer. Since there is no significant (α=0.05) change in refractory CN number with time there is no evidence of a chemical mechanism in the upper troposphere that can create new refractory particle number. Thus upper troposphere primary aerosol number appears to be governed by convective transport of boundary layer refractory aerosol, in-situ formation in aircraft exhaust [Anderson et al., 1998; Anderson et al., 1999] and entrainment of extraterrestrial refractory material from the stratosphere [d’Almeida et al., 1991].
The third panel of Figure 4.11 summarizes in-situ aerosol mass as determined from the UNH filter-based chemistry measurements and those derived from HiGEAR size distribution measurements. Relative acidity ($[\text{NH}_4^+] / (2[\text{SO}_4^{2-}] + [\text{NO}_3^-])$) of the aerosol have mean median values of 0.49, 0.39 with a standard deviation of 0.36. This indicates a composition between ammonium bisulfate and ammonium sulfate with little ammonium available for neutralization of aerosol nitrate. The sum of volatile ionic mass is sufficient to account for total aerosol mass as derived from size distribution measurements within instrument uncertainties at these low ($< 1.0 \mu g \text{ std m}^{-3}$) concentrations.

Due to the slower temporal resolution of the size distribution measurements compared to number concentrations, the data were re-grouped into three geometrically increasing time bins instead of six (0-12 hrs, 12-48 hrs, and 48-108 hrs). The duty cycle of the DMA instrument is only 20 seconds every 1-2 minutes while the cold CN counter operates continuously at 1-Hz. Additionally the particles sampled by the DMA LAG chamber and the DMA instrument is subject to poorly defined diffusion losses that are greatest for high concentrations of the smallest particles. Hence, the cold CN counter is a better measurement of the particle number in convective outflow.

Integral aerosol number determined from size distribution measurements (DMA + OPC + APS) is compared to aerosol number recorded by the cold CN counter in Figure 4.12. When integral particle number from the size distribution measurement is within a factor of 2 of the cold CN data the distribution integrals are considered accurate. Data points highlighted in red are outside the factor of 2 and their number integrals have been uniformly scaled to the cold CN values. As expected, the largest disagreements occur for
the data in the class for 0-12 hours since convection, the class for which concentrations of the smallest particles is highest.

The second row of Figure 4.12 plots the average aerosol number distribution corresponding to each of the three convective age classes. The average raw distributions are shown in blue, the fit to the distribution are shown in green. Two modes were used to fit each distribution. The first \( m_{\text{new}} \) represents the population of the newly formed particles whereas the second \( m_{\text{bk}} \) probably represents pre-existing aerosol detrained directly from the evaporating cloud and/or the background aerosol population into which the convected air was injected. No size-resolved information is available below 10 nm. However, the difference between the model 3025 (UCN) and model 3010 CN (cold CN) counter’s 50% counting efficiency thresholds (3 nm and 10 nm respectively) establishes the 3-10 nm particle concentration. During the fitting process an evenly spaced array of \( \frac{dN}{d\log D_p} \) values at the same \( d\log D_p \) spacing as the DMA \( (d\log D_p = 0.022) \) is inserted into the data array between 3 and 10 nm. The geometric mean diameter of this array is 5.5 nm and when integrated over the 27 bins it yields the 3-10 nm concentration. The hollow blue circle in figure 4.12 represents this data. As indicated in the figure the nucleation mode population experiences a doubling in geometric mean diameter after 12-48 hours of aging. In reality an individual airmass’s population of newly formed particles will exhibit a discrete, much narrower, distribution of particles. However, here I am interested in examining the average characteristics of the aerosol at spatial and temporal scales that are suitable for comparison to coarsely gridded GCM’s. The rapid evolution of the nucleation mode and a less significant increase in the background aerosol population is clear.
Finally, I examine the total aerosol mass at each of the three convective ages. The integral volume of the two modes appears to fluctuate widely with age. These differences dominantly reflect inaccuracies in the fitting routine when attempting to fit an average of numerous discrete samples. Since these airmasses could not be sampled in a Lagrangian fashion over the course of several days we instead focus on the total aerosol mass of the system as opposed to its partitioning between the nucleation mode and the background aerosol mode. As indicated in the bottom panel of Figure 4.11 and at the bottom of Figure 4.12 total aerosol mass does not show a significant change ($\alpha=0.05$) with time. Two alternative mechanisms can account for these observations:

1. The flux of condensing volatile species onto the aerosol size distribution is approximately equal to the dilution rate of the aerosol over time. In other words while coagulation is reducing total particle number; advection, dispersion and diffusion of the airmass is approximately offsetting the addition of particle mass to the system resulting in no observable net change in total aerosol volume with time.

2. At the time of their formation, $\lim_{t \to 0^+}$, the gas-to-particle conversion process exhausts the available supply of condensable vapours such that the particles are essentially in equilibrium with the gas phase. The result is that as the particles age there is negligible additional condensation and the system mass is simply redistributed (as a function of size) through coagulation.

Neither alternative can be confirmed with the available data. The conversion of NO$_x$ to HNO$_3$ indicates a potential flux of nitrate from the gas to the aerosol phase. This
processes is reversible but the system appears ammonium limited assuming ammonium preferentially reacts with aerosol sulfate. Regardless, the aerosol nitrate measurement is not sufficiently precise in order to determine whether or not there is a net increase in aerosol nitrate with time.
Figure 4.11 – Evolution of gas phase tracers CH$_2$O, HNO$_3$ and SO$_2$ as a function of hours since convection (top). Evolution of aerosol number as a function of hours since convection (middle). Total aerosol mass derived from filter-based chemistry measurements as well as independently using size distribution measurements (bottom).
Figure 4.12 – Comparison of size distribution integrals of total aerosol number (>10 nm) compared to the 1 Hz measurements of the Cold CN counter for three different airmass “ages since convection” (top row). Prior to fitting, distributions whose integral are +/- a factor of 2 were scaled to the concentration measured by the Cold CN (red) to account for under sampling and diffusion losses. Evolution of convective aerosol number (middle) and volume (bottom) distributions in the upper (>6 km) troposphere. Reduction in particle number and growth to larger geometric mean diameters are robust (α=0.05) and consistent with processes dominated by particle coagulation. Differences in total log-normal fit integrals are an artifact to fitting discrete samples of a time-varying phenomenon that has not been sampled in a Lagrangian fashion. There is no significant difference in total aerosol volume (mass) with time indicating further accumulation of condensable vapours is at a rate that is below our detection limit.
4.3 Discussion

In the preceding chapter we summarized vertical profiles of trace gases, aerosol number, mass and light extinction. We focused on light extinction by natural biomass burning aerosol and those of anthropogenic origin because of their direct effect on the Earth’s radiation balance. In this chapter we summarized some characteristics of background marine and FT aerosol as well as the influence of convection on the production of new particle number. Of primary importance to our understanding of the indirect effect of aerosols is their influence on CCN number and thus cloud properties. The global cloud field is dominated by cloud over the World Ocean. I therefore compare observations, a parameterization, and a simulation of background marine aerosol to our observations in the remote MBL. The goal is to evaluate the differences between each distribution’s predictions of aerosol number. I then conclude with a preliminary assessment of how the FT aerosol types might affect the clean background population of aerosol number if they were entrained from the FT into the clean background MBL of the Eastern North Pacific.

4.3.1 Comparison of airborne observations to surface measurements

In their 2000 review, Heintzenberg et al. (hereafter HNZ) developed a database of marine aerosol size and composition based on 30 years of marine aerosol data. They note that there is inadequate sampling of the supermicrometer marine aerosols and that large gaps exist in the database (see Figure 1 of HNZ). In their analysis they are careful to consider the completeness, methodology, representativeness and redundancy of the measurements. They exclude airborne data due to “large and unresolved inlet and
calibration issues”. They eliminate most optical particle counter data because they are not “calibrated with respect to geometric size”. Instead they use mobility (DMA) and aerodynamically (APS) based measurement techniques. They consider only measurements made at relative humidities of 40% or less and data that include at least 48 hours of data coverage in their 15° x 15° geographic grid.

With regard to airborne sampling of supermicrometer aerosols, McNaughton et al. [2007] demonstrate that aerosol size distributions and chemistry measured behind the University of Hawai‘i and University of New Hampshire solid diffuser type inlets effectively sample supermicrometer aerosols with aerodynamic diameters up to 5.0 μm. Although hydrated sea salt exist at sizes larger than this aerodynamic diameter their number concentration and contribution to global aerosol optical depth is small.

The aircraft data presented here meet HNZ completeness and redundancy criteria as they:

1. cover 3 orders of magnitude with respect to aerosol size,
2. and, there is overlapping distributions between instruments.

For INTEX-B there are 14 and 21, five-minute level leg averages of marine aerosol measurements north and south of 40°N (i.e. Hawai‘i and Alaska). At an aircraft true airspeed to wind speed ratio of 30:1 this represents the equivalent of approximately 35 hours of data in the trade wind regime and 50 hours of data in the Alaskan Low. Thus strictly speaking we do not meet the representativeness criteria of HNZ.

Nevertheless, figure 4.13 compares clean and polluted distributions from the Hawai‘i trade wind regime and the Alaskan Low to the HNZ distributions for these latitudes ranges. The HNZ data are global zonal average whereas our data are specific to
the Eastern North Pacific. Figure 1 of HNZ indicate that there are few data in this region with just 20 cases for the 15-45°N latitude range and only 4 cases for the 45-60°N latitude range. The data collected during INTEX-B could be considered another case for each of these regions.

The agreement, especially near Hawai‘i, is remarkable and the HNZ and HiGEAR distributions are effectively identical. It is interesting to note that the HNZ integrals of both number and volume are bracketed by the INTEX-B measurements stratified into “clean” background and anthropogenically influenced. While system variability is high and the number of samples are low, the comparison suggests that some of the data compiled by HNZ may have been contaminated by anthropogenic emissions and that the “clean” background concentrations summarized in this dissertation may be the more appropriate when simulating pre-industrial conditions.

For Alaska the 1-Hz CN counter measurements of total number are about equal for the polluted and clean cases (1300 and 1200 cm⁻³). Fast measurements of submicrometer sulfate are also similar (150 and 140 pptv). The largest difference between the measurements in the Alaskan low is the refractory aerosol number which is 300 cm⁻³ for the clean case and 500-900 cm⁻³ in the polluted airmasses. As discussed in section 4.1.2 this implies either higher wind speeds or a higher concentration of refractory soot. Since wind speeds were comparable I favour the latter interpretation of the Alaskan data even though differences between the clean and polluted unheated number and volume distributions are not significant. Also note that cyclone activity in the Alaskan Low was relatively intense during the INTEX-B study period compared to the climatological average. This likely contributes to some of the observed variability.
The disagreement between HNZ and INTEX-B volume median diameters in the Alaskan Low is problematic as these differences will significantly affect intensive aerosol optical properties. The HNZ VMD of 0.40 μm however, is larger than all other data presented in this dissertation save biomass burning aerosol. Since the HNZ global zonal average in the 45-60°N latitude range is based on just 4 samples, it is possible that the distributions presented here represent a more accurate representation of MBL aerosol in the Alaskan Low. More observations are needed to verify this hypothesis.

Figure 4.13 – Comparison of MBL Aitken and accumulation mode size distributions for marine aerosol measured in the Hawaiian trade wind regime (15-45°N) and in the Alaskan Low (45-60°N). In-situ airborne measurements are in excellent agreement with Heintzenberg et al. [2000] near Hawai‘i. Near Alaska the VMD’s published by Heintzenberg et al. are based on just four observations and are large compared to all other aerosol types studied in this dissertation.
4.3.2 Comparison to OPAC's "Maritime Clean" Aerosol Type

The OPAC parameterization for clean marine conditions considers three aerosol types; water soluble, accumulation mode sea salt and coarse mode sea salt. In figure 4.14 I compare the water soluble component and the accumulation mode sea salt distribution to the distributions measured near Hawai‘i and Alaska during INTEX-B.

Aerosol volumes are set equal in this comparison to approximate a model that accurately simulates dry aerosol mass. Aerosol scattering is computed at 40% and 80% relative humidity using the appropriate density and refractive indices [Tang et al., 1997]. Table 4.1 summarizes the ratio of OPAC integrals of number, volume and scattering to the values measured near Hawai‘i and Alaska. As tabulated the discrepancies between scattering are generally small but differences in aerosol number are large. The OPAC parameterization over predicts sulfate number because the distribution is broad and mono-modal. The OPAC parameterization under predicts seasalt number, modeled here as an external mixture, because it does not include ultrafine seasalt number [Clarke et al., 2006; Martensson et al., 2003].
Figure 4.14 – Comparison of OPAC “Water Soluble” and “Seasalt Acc.” parameterizations to the observations from INTEX-B in the Hawaiian tradewind regime and the Alaskan Low. When aerosol volumes there are relatively small discrepancies in aerosol light scattering. However, the mono-modal Water Soluble component does not accurately model the bi-modal Aitken and Accumulation mode aerosol and therefore over predicts CCN.

Table 4.1 – Ratios of OPAC integrals of number, volume and scattering compared to the HiGEAR values measured near Hawai’i and Alaska during INTEX-B.

<table>
<thead>
<tr>
<th>Observations</th>
<th>OPAC - Water Soluble &amp; Acc. Seasalt</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Number Ratio</td>
</tr>
<tr>
<td>IB - HI</td>
<td>Sulfate</td>
</tr>
<tr>
<td></td>
<td>Seasalt</td>
</tr>
<tr>
<td>IB - AK</td>
<td>Sulfate</td>
</tr>
<tr>
<td></td>
<td>Seasalt</td>
</tr>
</tbody>
</table>
Comparing INTEX-B observations to Caffrey et al. [2006]

In their 2006 publication Caffrey et al. (hereafter NRL) model MBL aerosol size distributions in the Hawaiian trade wind regime using a high resolution, one-dimensional (Lagrangian) sectional aerosol model (MARBLES). MARBLES is driven by the Navy’s 3-D Coupled Ocean/Atmosphere Mesoscale Prediction System (COAMPS). MARBLES includes 37 size sections for 4 chemical components; sea salt, sulfate dust and water, with vertical grid cell spacing of 2 m near the surface and 50 m at higher altitudes.

The sea salt aerosol source function (SSASF) is a modification of Monahan et al. [1986] and straddles laboratory measurements of Martensson et al. [2003] and shoreline studies of breaking waves [Clarke et al., 2006]. Entrainment of the clean FT aerosol is based on in-situ measurement of the FT aerosol at the Mauna Loa Observatory [Clarke et al., 1996; Weber and McMurry, 1996]. The model considers particle nucleation, condensation of gas-phase oxidation products, coagulation, cloud processing and heterogeneous oxidation of S(IV) on sea salt aerosol. The results from a 145-hour simulation with back trajectories that remain below the trade wind inversion are compared to airborne measurements near Hawai‘i in Figure 4.15.

In this comparison no normalization of aerosol volume or number has been performed so that the actual simulation can be compared to in-situ observations. Since the NRL simulation is for a single air parcel it would be more representative to compare several model simulations under varying initial conditions to the distribution measured in-situ. Nevertheless the results of the comparison are impressive (Table 4.2) and indicate the fidelity with which state-of-the-art models can represent aerosol in the ambient atmospheric environment. The Caffrey et al., results show that closure between
simulations and observations to within better than a factor of 2 is possible. When aerosol dynamics such as those included in the MARBLES model are included in GCM’s we can expect to simulate the indirect effects of aerosol with much greater accuracy.

**Figure 4.15** – Comparison between a MARBLES simulation of background MBL sulfate and seasalt size distributions to the average values measured near Hawai‘i. No corrections or normalizations of any kind have been applied. MARBLES does a remarkable job of simulating the background aerosol, particularly the *Hoppel* minimum at ~ 0.070 μm.

**Table 4.2** – Ratios of Caffrey et al. [2006] simulation of integral number, volume and scattering for the background MBL aerosol size distributions in the trade wind regime compared to the INTEX-B observations near Hawai‘i.

<table>
<thead>
<tr>
<th>Observations</th>
<th>NRL - Sulfate and Seasalt</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Number Ratio</td>
</tr>
<tr>
<td>IB - HI</td>
<td>Sulfate</td>
</tr>
<tr>
<td></td>
<td>Seasalt</td>
</tr>
</tbody>
</table>
Comparing INTEX-B measurements of sea salt aerosol to wind-speed dependent parameterizations

The key meteorological factor governing the production and life cycle of sea salt aerosol in the MBL is wind, the key oceanographic factor is breaking waves. In chapter 4.1.4, of their text, Lewis and Schwartz [2004] discuss three separate parameterizations for estimating the sea salt aerosol number distribution based on wind speed. Given the order-of-magnitude variability between observations of sea salt distributions for a given range of wind speeds, they note that such parameterizations should be used with caution. However, they also note that these parameterizations are often useful for scoping purposes or when attempting to “estimate light-scattering coefficients”. Here we compare INTEX-B distributions and their number, volume (mass) and scattering integrals to those generated by three separate wind-speed dependent parameterizations. The size distribution parameterizations are the:

1. Navy Ocean Vertical Aerosol Model (NOVAM) [Gathman and Davidson, 1993],
2. O’Dowd et al., [1997],
3. and the “canonical distribution” of Lewis and Schwartz (LS04), [2004].

Critical to our discussion here is the measurement of mean wind speed at 10 meters above the ocean surface, denoted $U_{10}$. The NOVAM model also employs the term $U_{10,avg}$ in order to calculate the 2nd mode of the sea salt number distribution. $U_{10,avg}$ refers to the wind speed at 10 meters averaged over the previous 24-hours. The reason for employing these differing measures of wind speed is an attempt to account for the average conditions experienced by the airmass over some time period prior to the conditions at the time of measurement. Lewis and Schwartz argue that when used for
parameterizations, $U_{10,\text{avg}}$ might be a better integrator of production, transport and removal processes. However, *Reid et al.* [2001], criticize $U_{10,\text{avg}}$ as unrealistic as it, in essence, "forecasts on persistence". Since our data provides no information about the wind speed prior to the time of measurement nor any information about the gustiness versus steadiness of the wind we equate $U_{10,\text{avg}}$ and $U_{10}$ in order to perform the necessary calculations. This is a common approximation whose validity will degrade if/when the airmass has experienced a recent change in $U_{10}$ compared to the wind speed at the time of observation.

Also relevant to our discussion is the size dependent vertical transport of sea salt. Wind speed dependent parameterizations are valid at 10 meters above the ocean's surface whereas the DC-8 aircraft's minimum altitude is 100 meters. Assuming a steady state vertical concentration profile and a mean net vertical particle flux of zero, we can estimate the size dependent sea salt aerosol concentration at a given altitude according to:

\[ n(z) = n(z_0) \cdot \exp \left\{ - \frac{z \cdot v_{\text{term}}}{z_0 \cdot D_{\text{eddy}}} \right\} \]  

(4.2)

where, $n(z_0)$ is the concentration at $U_{10}$ and the integral in the exponential term represents the size dependent balance between gravitational settling and turbulent eddy diffusion of the aerosol population. Under neutrally stable conditions and assuming that there is little difference between the relative humidity at the aircraft flight altitude compared to RH at 10 meters we can solve Eqn 4.2 to produce:
The exponential still represents the size dependent balance between aerosol settling and turbulent diffusion. By defining a characteristic particle radius, \( r_{\text{ma}} \), for which \( \nu_{\text{term}} = \nu_{\text{mix}} \) we can use Stoke's Law to redefine the ratio of the particle concentration at any height, \( z \), compared to \( z_o \), strictly as a function of a particle's radius, \( r \), compared to \( r_{\text{ma}} \). Performing the substitution,

\[
n(z) = n(z_o) \cdot \left( \frac{z}{z_o} \right)^{-\frac{\nu_{\text{term}}}{\nu_{\text{mix}}}}
\]

where the quantity \( r_{\text{ma}} \), is in micrometers, and is approximated using 10-meter wind speed, \( U_{10} \), in m s\(^{-1}\), according to:

\[
r_{\text{mix}} = 10 \cdot \left( U_{10} \right)^{\frac{1}{2}}
\]

Figure 4.16 shows vertical transport efficiency curves as a function of particle dry diameter for the maximum and minimum wind speeds recorded while sampling aboard the DC-8 in the Hawaiian and Alaskan regions. Efficiency curves are generated at the DC-8 flight altitude and have been corrected to dry particle diameters from ambient diameter using ambient RH and the sea salt growth curves of Tang et al. [1997].
In summary, this calculation allows us to correct the wind-speed dependent parameterizations of the ambient aerosol size distributions at 10 meters to those we would expect to observe at the DC-8 flight altitude based on the prevailing wind speed and ambient relative humidity. Again, the key assumptions are:

- no vertical gradient in wind speed
- neutrally stable atmospheric conditions
- no vertical gradient in relative humidity

**Figure 4.16** – Vertical transport efficiency curves between 10 m and the DC-8 flight altitude near Hawai‘i and Alaska during INTEX-B. Transport efficiency is a function of dry diameter, wind speed, relative humidity and DC-8 flight altitude.
Once each distribution is corrected by its individually determined vertical transport efficiency curve the degree to which the parameterizations can replicate INTEX-B observations is evaluated. By comparing the distributions to the parameterizations I determine:

1. Whether or not the parameterizations and the observations of the aerosol size distribution fall within a factor of 3 (3x or 1/3x) of the LS04 "canonical" distribution (i.e. within the range of the bulk of observations to date).
2. Whether or not large supermicrometer sea salt aerosols might be undersampled behind the UH and UNH inlets.
3. Whether or not under sampling large sea salt aerosol compromises our ability to determine the optical properties and thus the radiative effects of sea salt.

Figure 4.17 shows both the mean number and volume distributions generated using each of the three parameterizations. Number distributions are shown in the top panels while volume distributions are in the lower panels. Distributions generated from the Hawai‘i wind speed data are on the left while distributions from Alaska are on the right. The mean lognormal fit to the INTEX-B observations are shown as the black curve. The *O’Dowd* distributions are in green while the NOVAM distributions are in red. The LS04 canonical distribution is in blue while the 3x and 1/3x values are represented by dashed blue lines. The static (does not vary with wind speed and has not been scaled to observed total aerosol mass in this example) OPAC distribution is included for comparison and is shown in magenta.

The OPAC and NOVAM distributions are essentially identical except for small differences in the shoulder of the coarse mode particles. The average *O’Dowd* number distributions are similar than the NOVAM and INTEX-B observations but the volume
distribution consistently over predicts aerosol volume. This characteristic of the O'Dowd parameterization was previously criticized by Lewis and Schwartz and our data tend to support their conclusion that the O'Dowd formulation produces much larger aerosol volume than is commonly observed. The single, broad, “canonical” distribution of LS04 under predicts aerosol number compared to all the other distributions. When converted to aerosol volume, the INTEX-B observations are the only distributions wholly within a factor of 3 of Lewis and Schwartz. Note that in general the INTEX-B distributions show the least aerosol volume beyond ~5 μm, the diameter above which inlet losses become significant.

In figure 4.17 the parameterizations of accumulation and coarse mode sea salt aerosol were only compared to the log-normal fit of the INTEX-B accumulation mode aerosol. However, the INTEX-B data also include an Aitken mode refractory aerosol which dominates the number distribution. This component of the sea salt aerosol distribution is referred to as the “ultrafine” sea salt [Clarke et al., 2006]. Plotting the individual measurements of aerosol number and volume against the standardized (U_{100}, RH=80%) parameterizations (Figure 4.18) illustrates the behavior of the parameterizations compared to the INTEX-B data for a range of wind speeds.

Included separately in Figure 4.18 is the integral number of ultrafine sea salt from the lognormal fits to the observed size distributions. Their relative abundance compared to accumulation and coarse mode aerosol number demonstrates their importance as potential CCN. Furthermore, Martensson et al. [2003] proposed that the ultrafine sea salt flux displayed a temperature dependence; cooler sea surface temperatures being more effective at producing aerosols < 0.07 μm. Performing a two-tailed Student's t-test on
the 5-minute averaged INTEX-B data indicates that the concentrations of ultrafine sea salt near Hawaiʻi is lower ($\alpha=0.05$) than the concentrations observed near Alaska. While this appears to support Martensson et al.'s laboratory-based hypothesis, the same statistical test using the higher resolution 60-second data indicates the means are not distinct. More study is warranted as these ultrafine seasalt contribute to remote MBL CCN concentrations.

**Figure 4.17** – Dry aerosol number (top) and volume (bottom) distributions generated from three separate wind-speed dependent parameterizations compared to observations near Hawaiʻi (left) and Alaska (right) during INTEX-B. Parameterizations have been individually corrected from 10 meters to 100 meters using wind speed dependent corrections for the vertical transport efficiency of aerosols as a function of their ambient diameter (see Figure 4.16).
Figure 4.18 – INTEX-B aerosol number and volume compared to standardized (\(U_{10}=U_{100},\) RH=80%) integrals from O'Dowd, NOVAM and the LS04 parameterizations. The three parameterizations do not include ultrafine aerosol number (circles) which dominate CCN but which have insignificant mass compared to accumulation and coarse mode seasalt.

From figure 4.18 we see that the NOVAM model and the O'Dowd model are better predictors of the INTEX-B accumulation mode aerosol number than LS04. For sea salt volume the INTEX-B values are just below the NOVAM parameterization and within a factor of three of LS04. Note the tighter relation as a function of wind speed in the Hawai‘i data (i.e. trade winds of the East Pacific High) compared to the more scattered data in the Alaskan Low. A potential explanation for this behaviour is that the steady trade winds near Hawai‘i mean that \(U_{10} \approx U_{10,\text{avg}}\) whereas this assumption appears to break down near Alaska. During INTEX-B the weather patterns for the Hawai‘i phase of the deployment were climatologically “average” whereas the weather during the Alaskan
phase were climatologically “wet” due to the persistence of mid-latitude storms [H.
Fuelberg, personal comm.]. Also note that for wind speeds > 10 m s⁻¹, three of the five
INTEX-B data points indicate a substantially lower sea salt volume than predicted. For
the highest recorded wind speed, 15 m s⁻¹, the INTEX-B volume integral lies outside the
LS04 factor of 3. At wind speeds in excess of ~10 m s⁻¹ the production of spume droplets
becomes active and there is potential under sampling aboard the DC-8 due to inlet and
plumbing losses [McNaughton et al., 2007].

The UH solid diffuser inlet 50% passing efficiency for spherical particles with a
dry sea salt density of 2.2 g cm⁻³ is at least 3.3 µm. Doubling the concentration of
particles at this size indicates that the new volume would still be within the LS04 factor
of three. Computing the fraction of sea salt aerosol mass at sizes larger than 3.3 µm
shows that, on average, the LS04 and NOVAM parameterizations predict 58% or 26% of
the total aerosol volume resides at sizes larger than 3.3 µm. For the INTEX-B data, 37%
of the aerosol volume is above 3.3 µm in the Hawaiian regime and only 30% for the
Alaska region. Thus most of the data INTEX-B data is bracketed by the
parameterizations.

In order to evaluate the effects of possible under sampling of large sea salt on
calculations of optical properties I evaluate the discrepancies between light scattering for
these distributions. Figure 4.19 is a plot of scattering calculated for the HiGEAR size
distributions versus scattering calculated for each of the three parameterizations. In the
plot scattering is integrated only for particles > 3.3 µm (dry diameter) at both 40% RH
(top) and 80% RH (bottom) for both the Hawai‘i and Alaska MBL data. At 80% RH near
Hawai‘i the ratio of HiGEAR scattering values to the NOVAM values average 0.94, the
ratio to the 80% RH LS04 scattering values is 1.17. Near Alaska the ratios of HiGEAR to NOVAM and LS04 80% RH scattering values are 0.67 and 0.84.

Figure 4.19 - Comparison of scattering for dry particle diameters > 2.5 mm. The HiGEAR observations near Hawai’i (left) and Alaska (right) are compared to the Odowd (green), NOVAM (red) and LS04 (blue) parameterizations at both 40% RH (top) and 80% RH (bottom). Solid blue line denotes 1:1 while dashed lines are 3:1 and 1:3.

The wind speeds near Hawai’i averaged 7.6 +/- 2.8 m s⁻¹ and there is one scattering outlier for a wind speed of 1.4 m s⁻¹. Here a sea salt distribution was measured but the wind speed is too low to produce a distribution from the parameterization. This illustrates the “persistence” of sea salt aerosol after changes to U₁₀. For the Alaska phase of INTEX-B wind speeds averaged 8.4 +/- 2.5 m s⁻¹ and there are two scattering outliers. In these cases the parameterizations predict much higher scattering than the observed
value. The wind speeds during these periods were 12 and 15 m s\(^{-1}\) so the aerosol has potentially been undersampled. However, a recent increase in \(U_{10}\) would also account for the difference. In general the HiGEAR observations indicate that losses due to potential undersampling of seasalt aerosol is < 30% except for wind speeds in excess of \(\sim 12\) m s\(^{-1}\) or at RH >\(\sim\) 95%.

We can examine the data further by looking at the variability of scattering for particles smaller than 3.3 \(\mu\)m for which sampling efficiency is high. HiGEAR scattering values for particles less than 3.3 mm averaged 45-55% of the NOVAM scattering values and are 2.6-3.3 times the LS04 values. Based on the LS04 parameterization, scattering by particles above 3.3 \(\mu\)m accounts for only 20-35% of the total scattering regardless of wind speed (recall that they account for \(\sim 58\)% of aerosol volume). For NOVAM they account for only 4-10% of total scattering (\(\sim 26\)% of the volume) for the observed wind speeds.

From this analysis we see that airborne sampling using the UH solid diffuser inlet is comparable to wind speed dependent parameterizations of the sea salt aerosol size distribution so long as ambient relative humidity is less than \(\sim 95\)% and wind speeds remain below \(\sim 12\) m s\(^{-1}\). More detailed flyby comparisons with coastal stations during the DICE experiment are consistent with this finding [McNaughton et al., 2007]. In fact, the uncertainties associated with predicting aerosol optical properties are driven not by poorly sampled large sea salt aerosols but instead are driven by uncertainties associated with parameterizing the wind speed dependence production of the PM\(_{2.5}\) sea salt aerosol, its variability due to \(U_{10}\) and its removal by wet deposition.
4.3.5 Estimating the effect of airmass entrainment on background MBL aerosol number

The trade wind-regime of the Eastern North Pacific is a region of synoptic scale subsidence due to the persistence of the East Pacific High. As a result, the entrainment of FT aerosol influences both the number concentration and composition of aerosol in the remote MBL. Here I explore how the entrainment of polluted FT into the clean MBL can influence the concentration of potential CCN.

Mixing two air parcels of differing thermodynamic and chemical characteristics can induce particle nucleation [Nilsson and Kulmala, 1998]. This complicates calculations of entrainment as mixing alone can create new aerosol number. Refractory number cannot be created during air parcel mixing and is therefore a more conservative tracer for estimating entrainment. If we assume that air entraining from the FT during pre-industrial times has the same number concentration as that derived in section 4.2.1 then the concentration of refractory CN in the MBL is governed by the balance between its wind-speed dependent production [Clarke et al., 2006; Martensson et al., 2003], its wet and dry removal rate, and dilution by entrainment of FT air. Near Hawai‘i the HiGEAR measurements of refractory CN in the “clean” background remote MBL are $180\pm100$ cm$^{-3}$. Here I assume that the average concentration of $180$ cm$^{-3}$ represents a steady state concentration of refractory seasalt, with the $+/-100$ cm$^{-3}$ representing natural variability between the production rate, removal rate and entrainment dilution.

Under polluted conditions the remote MBL near Hawai‘i had an average refractory CN concentration $320\pm200$ cm$^{-3}$. This implies that $140\pm170$ cm$^{-3}$ of the MBL refractory CN are soot of anthropogenic origin which has entrained from the FT.
Near Hawai‘i the concentration of refractory CN in the lower free troposphere (C_{FT}) averaged 360 cm$^3$, 125 cm$^3$ of which can be assumed to be natural. Using these data we can estimate the timescale required to change the MBL RCN concentration from their steady state background value (C_0 = 180 cm$^3$), to the average (C_{ave} = 320 cm$^3$) observed under polluted conditions, according to the relation:

$$C_{ave} \frac{dh}{dt} + h \frac{dC_{ave}}{dt} = C_{FT} v_{ent} + C_{surf} v_{dep}$$

(4.6)

where $h$ is the boundary layer thickness ($h=1500$ m), $v_{ent}$ is the entrainment rate in cm s$^{-1}$, and $v_{dep}$ is the depositional velocity in cm s$^{-1}$. The entrainment of free tropospheric air results in boundary layer growth and dilution of the average particle concentration. If however we assume that over time scales of a few days airmass divergence approximately equals the addition of FT air then the boundary layer height growth term, $dh/dt$, can be set equal to zero. Additionally, I assume that over times scales of a few days wet deposition does not occur. Finally, assuming that the particle depositional velocity$^2$ is much less than the entrainment velocity, $v_{dep} \ll v_{ent}$, for the 0.11 μm particles internally mixed with the 0.050 μm refractory aerosol, then $v_{dep}$ can also be set to zero. Solving the integral:

$$C_{ave} (t) = \frac{C_{FT} v_{ent}}{h} t + C_o$$

(4.7)

While this is a somewhat simplistic treatment, Table 4.4 summarizes the time, in days, required to alter the clean MBL concentration to match the average concentrations

$^2$ Gravitational settling of a 0.1 μm particle is 9.0x10$^{-5}$ cm s$^{-1}$. 274
observed under polluted conditions using an entrainment rate of 0.6 +/- 0.2 [Clarke et al., 1996].

Table 4.3 – Estimates of the time scale (days) required to change remote MBL refractory aerosol number concentrations from average background values to average values observed under polluted conditions near Hawai‘i.

<table>
<thead>
<tr>
<th>$v_{exit}$ (cm s$^{-1}$)</th>
<th>$C_0$ (cm$^{-3}$)</th>
<th>$C_{exit}$ (cm$^{-3}$)</th>
<th>$C_{FT}$ (cm$^{-3}$)</th>
<th>t (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8 cm s$^{-1}$</td>
<td></td>
<td></td>
<td></td>
<td>1.3</td>
</tr>
<tr>
<td>0.6 cm s$^{-1}$</td>
<td>180</td>
<td>320</td>
<td>240</td>
<td>1.7</td>
</tr>
<tr>
<td>0.4 cm s$^{-1}$</td>
<td></td>
<td></td>
<td></td>
<td>2.6</td>
</tr>
</tbody>
</table>

For the particle flux to be sustained during entrainment the FT pollution layer depth must be at least 1.3 km at the onset of entrainment. This is thinner than Asian pollution plume thicknesses measured during INTEX-B. Reducing the MBL depth from 1.5 km to 1 km reduces the time scales by 1/3rd (0.9-1.7 days) and decreases the entraining layer depth requirement to 875 meters. Performing the same calculation but using the Alaskan refractory CN statistics results in a time scale of 1.5-3.1 days.

I check the validity of the assumption that dilution by entrainment is matched by air mass divergence by performing the same entrainment time scale calculation but for water vapour. In the polluted FT the average concentration is 1300 ppmv while for the clean and polluted MBL the average values were 16,300 ppmv and 14,600 ppmv. Using the same entrainment rates, the time scale to alter the Hawai‘i MBL concentration is 2.8-5.7 days, for Alaska the time scale is 2.3-4.7 days. Both time scales are longer than the time scale based on RCN number. However, I assumed no refractory CN deposition to the ocean surface, $v_{dep} = 0$, an unrealistic assumption. Increasing the $v_{dep}$ value will
lengthen the timescale required to reproduce the polluted MBL RCN number concentrations.

The same calculation cannot be performed for the Gulf of Mexico region, as the concentration of natural refractory aerosol of continental origin over the Gulf is probably non-negligible even under pre-industrial scenarios. Occasionally though Norte events [Madronich et al., 2004] can transport pollution from the Mexican Highlands out over the subtropical Eastern North Pacific. Therefore we can assess how Mexico’s pollution might affect the remote MBL of the ENP. To reflect aging I entrain the average RCN concentration from the anthropogenically influenced lower troposphere over the Gulf of Mexico (1600 cm\(^{-3}\) less a clean background of 125 cm\(^{-3}\)) rather than the near-source values from the Valley of Mexico (6100 cm\(^{-3}\)). The entrainment rate is fixed at 0.6 cm s\(^{-1}\) but the time over which entrainment is allowed to occur is 1 to 3 days. This allows an estimate of the final refractory aerosol concentration as a result of the entrainment of Mexico’s pollution and includes 180 cm\(^{-3}\) of natural, primary sea salt. The results are tabulated in Table 4.4.

Table 4.4 – Estimates of MBL refractory aerosol number concentration after entraining 1600 cm\(^{-3}\) of anthropogenic pollution aerosol at a rate of 0.6 cm\(^{-3}\) for 1-3 days.

<table>
<thead>
<tr>
<th>Entrainment Rate</th>
<th>(C_0) (cm(^{-3}))</th>
<th>(C_{ent}) (cm(^{-3}))</th>
<th>(C_{ent} (cm^3))</th>
<th>(t) (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6 cm s(^{-1})</td>
<td>180</td>
<td>1200</td>
<td>1600-125</td>
<td>2.0</td>
</tr>
<tr>
<td>0.6 cm s(^{-1})</td>
<td>1700</td>
<td></td>
<td></td>
<td>3.0</td>
</tr>
</tbody>
</table>

Each of these estimates, polluted MBL concentrations are lower than the mean refractory aerosol concentration in the Gulf of Mexico MBL, 2600 cm\(^{-3}\). So while this is
a simple approach, the calculation indicates that additional sources of BL refractory aerosol is needed to account for the refractory aerosol concentrations in the MBL over the Gulf of Mexico. This is consistent with the vertical integrals of dry aerosol optical depth.

Finally we can perform the same calculation but for the entrainment of natural, boreal forest biomass burning aerosol into the remote marine boundary layer, a scenario which occurs both in pre-industrial times and the present. In this calculation refractory CN from BB aerosol are entrained at 0.6 cm s\(^{-1}\) for 1-3 days using the average lower free troposphere value from INTEX-NA, 800 cm\(^{-3}\) (Table 4.5).

Table 4.5 – Estimates of MBL refractory aerosol number concentration after entraining 800 cm\(^{-3}\) of biomass burning aerosols at a rate of 0.6 cm\(^{-3}\) for 2-4 days.

<table>
<thead>
<tr>
<th>Entrainment Rate</th>
<th>(C_0) (cm(^{-3}))</th>
<th>(C_{entr}) (cm(^{-3}))</th>
<th>(t) (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6 cm s(^{-1})</td>
<td>410</td>
<td>800-125</td>
<td>1.0</td>
</tr>
<tr>
<td>0.6 cm s(^{-1})</td>
<td>650</td>
<td></td>
<td>2.0</td>
</tr>
<tr>
<td>0.6 cm s(^{-1})</td>
<td>880</td>
<td></td>
<td>3.0</td>
</tr>
</tbody>
</table>

This exercise demonstrates that in just 1-3 days the entrainment of FT aerosol into the remote MBL can increase CN number that may activate as CCN by a factor of 2-10. Total aerosol number also includes volatile secondary aerosol which, neglecting new particle production due to airmass mixing, results in \(\sim 35\%\) more CN.

The background and perturbed FT CN concentrations tabulated in Appendix B, along with the data for the vertical profiles presented in Chapter 3, should be used by modelers to evaluate their simulations. This will help to constrain these simulations and can potentially improve the difficult to model aerosol indirect effect [Penner et al., 2006].
4.4 References


SCOR/IAPSO, Improved seawater thermodynamics:-How should the proposed change in salinity be implemented?, in *SCOR/IAPSO Working Group 127 on the "Equation of State and Thermodynamics of Seawater"*, 2008.


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5.0 Aerosol size distributions, heterogeneous chemistry and the link to ocean biogeochemistry

Chapter 3 discusses aerosol over North America that dominate light extinction. Chapter 5 discusses long-range transport of Asian pollution and dust to the North Pacific and its effects on aerosol light extinction. During long-range transport acid gases of anthropogenic origin can react with mineral dust primarily of "natural" origin [Bauer et al., 2004; Phadnis and Carmichael, 2000; Song and Carmichael, 2001]. This chapter also evaluates these heterogeneous reactions using the in-situ size distribution measurements in conjunction with concurrent measurements of aerosol chemistry. These measurements are put into context by a brief analysis of the long-term, 1996-2006, record of aerosol chemistry from the Mauna Loa Observatory (MLO). The deposition of anthropogenic aerosol to the surface waters of the North Pacific can also potentially alter surface water chemistry [Doney et al., 2007]. This chapter investigates the potential increases in surface water concentrations of nitrogen and iron in an effort to evaluate its importance on ocean primary productivity, i.e. the Iron Hypothesis [Martin, 1990].

5.1. Anthropogenic pollution and Asian Dust over the North Pacific

Data from the Pacific Phase of INTEX-B is stratified into data collected near Hawai‘i (Latitude < 40°N) and Alaska (Latitude > 40°N) and roughly correspond to the climatological features known as the East Pacific High and the Alaskan Low. Sampling was conducted from between April 15 and May 1st, 2006 near Hawai‘i and between May 1 and 15, near Alaska. The free troposphere (GPS altitudes > 1.5 km) during this time
was widely influenced by anthropogenic pollution from Asia as well as Asian dust aerosol. 

After excluding airmasses with characteristics indicative of stratospheric influence (see section 5.1.2), the data were further stratified using the fine mode fraction of aerosol light scattering [Anderson et al., 2003].

\[
FMF_{\text{scat}} = \frac{\sigma_{ap,550,\text{Dust}<1.0}}{\sigma_{ap,550}}
\]

(5.1)

Values of \(FMF_{\text{scat}} < 0.6\) are labelled as “Mixed” pollution and mineral dust. When \(FMF_{\text{scat}} > 0.6\) the airmasses are considered fine mode dominated “Anthropogenic” pollution. No data met the “Dusty” \(FMF_{\text{scat}} < 0.3\) criteria of Anderson et al.

Lognormal fits of the anthropogenic and mixed aerosol size distributions measured near Hawai‘i are in figure 5.1. The top two panels are the number and volume distributions for the fine mode dominated case whereas the bottom panels are for the mixed airmass type. Differences between the unheated and refractory fits to the supermicrometer dust mode are not significantly different and thus the summary statistics in the data table of Appendix-C are pooled into a single supermicrometer aerosol fit.

Figure 5.2 assess the degree of aerosol number closure by comparing the integrals of the lognormal fits to the average concentrations measured using the hot and cold CN counters \((N > 10 \text{ nm})\). Size distribution integrals for the unheated and refractory fits are close to the hot and cold CN measurements and lead to RCN ratios that reasonably replicate the CN counter averages. This internal consistency supports using these fits to constrain the entrainment of Asian Pollution and dust from the FT into the remote MBL (Section 4.3.5). Figures 5.3 and 5.4 are the fits and the number closure assessment for
the data collected in the FT of the Alaskan Low. For these cases refractory number is somewhat higher in the fit data resulting in fair agreement between the RCN ratios.

After long range transport, the NMD of accumulation mode FT Asian aerosol over the North Pacific varies between 0.080 and 0.11 μm with an average value of 0.10 μm and σg of 1.75 +/- 0.15. This results in a range of VMD’s of between 0.19 and 0.34 μm. In the presence of dust the NMD of FT Asian aerosol varies over a wider range of values, 0.50-0.11 μm with a smaller average NMD of 0.075 μm. In the presence of dust the accumulation mode aerosol also showed a broader distribution, 1.98 +/- 0.15 which results in a range of VMD’s between 0.20 and 0.45 μm. These median diameters are slightly larger than the diameters predicted under dust free conditions. Also, for a fixed number of particles the fits to the “mixed” aerosol types result in 18% more aerosol volume than under dust free conditions. This appears to contradict the idea that the smaller NMD’s is the result of the uptake of volatile material by dust [Clarke et al., 2004]. Recomputing the VMD’s in the presence of dust but using the same σg as that determined in the absence of dust (1.75 +/- 0.15), results in VMD’s between 0.13 and 0.28 μm. For a fixed number of particles this results in 40% less mass for “mixed” cases compared to “fine” dominated cases. Recall that mixed aerosol was defined for FMFscat < 0.6 and that scattering is proportional to aerosol surface area. Thus using a σg of 1.75 +/- 0.15 seems more appropriate for the accumulation mode distribution with the larger, more variable fit for the mixed aerosol accumulation mode being the result of the tail of the dust distribution contributing to error during the least squares fitting procedure.
The total and refractory number distributions highlight the internally mixed nature of the refractory soot particulate coated with the more volatile compounds, $\text{NH}_4^+$, $\text{SO}_4^{2-}$, $\text{NO}_3^-$ and volatile organic carbon (volOC). The ratio of refractory number to total number in these airmasses averages 0.75 indicating only 25% of the pollution aerosol are composed entirely of volatile species. The NMD’s for the fits to the refractory aerosol for both the Hawai‘i and the Alaska data vary between 0.032 and 0.058 μm with a mean value of 0.043 μm. The geometric standard deviation is variable but averages 1.93 +/- 0.19. This results in a range of VMD’s between 0.11 and 0.23 μm for refractory soot. Models which simulate these aerosol should account for this internal mixing as surface coatings of volatile non-absorbing aerosol can enhance light absorption by internally mixed carbonaceous aerosol [Fuller et al., 1999; Schnaiter et al., 2005].

Even when FMF_{scat} > 0.6 Asian dust dominates the aerosol volume (mass) distribution. Aerosol single scatter albedo (SSA) is ~0.95 +/- 0.01 for the pollution dominated cases whereas when mixed with Asian dust the SSA increases to ~0.98 +/- 0.02 (Appendix – B, Table B.7). This indicates the dust SSA must be higher than 0.98 and that mixing dust with pollution increases co-albedo by a factor of at least 2. Direct measurements of both total and submicrometer aerosol absorption allow us to investigate the wavelength dependence of absorption for Asian aerosol after long range transport to the remote North Pacific. Table 5.1 summarizes the total scattering angstrom exponent as well as the total and submicrometer absorption angstrom exponents measured for fine mode dominated and mixed aerosols. The averages are computed from 5-minute level leg averages where the measured absorption is above 0.1 Mm\(^{-1}\). Values from the Mexican Highlands and the FT over the Gulf of Mexico are also included for
comparison. The Hawai‘i data show the lowest scattering angstrom exponents (i.e. the most dust) and the highest absorption angstrom exponents. Data from Mexico and Alaska are more comparable for both the fine mode dominated and the mixed aerosol.

Table 5.1 – Summary of total scattering Angstrom exponent as well as total and submicrometer absorption angstrom exponent for fine mode dominated aerosol (FMFscat > 0.6) and aerosol mixtures of pollution and dust.

<table>
<thead>
<tr>
<th>Region Class</th>
<th>Mexico &amp; Gulf</th>
<th>Hawaii</th>
<th>Alaska</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fine</td>
<td>Mixed</td>
<td>Fine</td>
</tr>
<tr>
<td>N</td>
<td>70</td>
<td>6</td>
<td>10</td>
</tr>
<tr>
<td>Total Scat. 450/700</td>
<td>1.6</td>
<td>0.57</td>
<td>1.0</td>
</tr>
<tr>
<td>Total Abs. 470/660</td>
<td>1.9</td>
<td>3.2</td>
<td>2.5</td>
</tr>
<tr>
<td>Sub. Abs. 470/660</td>
<td>1.7</td>
<td>2.1</td>
<td>2.0</td>
</tr>
</tbody>
</table>

Submicrometer absorption angstrom exponents are always higher when dust is present (Table 5.1). This is consistent with the f(RH) measurements which showed that submicrometer f(RH) is suppressed (0.39-0.44) compared to polluted values without dust (0.44-0.50). Thus at least a portion of the dust is passing the 1.0 μm aerodynamic cut-off of the RRNeph impactor plate. Ignoring shape factor the impactor’s 50% cut corresponds to a geometric diameter of 0.67 μm for a mineral dust aerosol with a density of 2.06 g cm⁻³. Based on the lognormal fit for the Hawai‘i mixed aerosol data (N=5.3 cm⁻³, NMD = 0.64 μm, σg = 2.06), this “submicrometer” dust is 0.3 μg m⁻³ of the total, 15.7 μg m⁻³. Using a refractive index of 1.53-0.0006i this “submicrometer” tail of the dust distribution, which accounts for just 2% of the dust mass, accounts for 11% of the extinction by mineral dust.

Near the East Asian, Saharan and Mexican Highland source regions, dust can dominate aerosol extinction. During transport gravitational settling will remove the
largest dust particles. The increasing $F_{scatt}$ will tend to increase scattering Angstrom exponent while reducing the absorption Angstrom exponent. Thus accurately simulating the evolution of the supermicrometer aerosol size distribution will increase the accuracy of the model’s simulation of the wavelength dependent aerosol optical properties. As shown, poorly modelling the lower tail of the mineral aerosol size distribution (2% of dust mass) can result in proportionately larger errors in aerosol extinction (11% of dust extinction at 550 nm) which directly affects the models ability to compute the radiative forcing of the mineral dust aerosol. And, as shown by the wavelength dependence measurements, this error will compound when calculating extinction at shorter visible wavelengths and in the UV [Sokolik and Toon, 1999].
**Figure 5.1** – Lognormal fits of the number (left) and volume (right) aerosol size distributions measured in the FT near Hawai‘i during INTEX-B. Total aerosol and the 2-mode fit are in green and blue while refractory aerosol is coloured red and black.

**Figure 5.2** – Assessment of number closure between the lognormal fits to the unheated and refractory aerosol distribution and to their ratio (RCN ratio) compared to the 1-Hz CN counter data.
Figure 5.3 – Same as figure 5.1 but for data collected in the FT near Alaska.

Figure 5.4 – Same as figure 5.2 but for data collected in the FT near Alaska.
5.2. Back trajectory analysis for airmasses sampled near Hawai‘i

Here back trajectories (Mike Porter, FSU) for the Hawai‘i phase of INTEX-B are presented as a series of figures. These give context to the airmass history and its transport pathway. Note that analysis of air parcel back trajectories is subjective as their accuracy degrades significantly beyond 3-5 days. The top panel of Figure 5.5 plots back trajectories from each of the “mixed” Asian pollution and dust airmasses. Most of the trajectories are sourced in the mid troposphere over arid basins in Asia and/or the mountains that fringe them. Unexpectedly two back trajectories are sourced over the Great Indian Desert, travel south of the Himalaya then over Shanghai in the mid-troposphere before being sampled near Hawai‘i 7 days later. Four trajectories are sourced directly over the Gobi desert to Loess plateau NW-SE transect, the classic Asian dust source region. A few trajectories are also sourced over the remote ENP and are then lofted into the FT prior to sampling. These trajectories may represent the often thin “ultraclean” layers with characteristically low O₃ (<25 ppbv) and RCN (< 100 cm⁻³) indicative of long residence times over the remote ocean followed by cloud processing and entrainment into the FT. The bottom panel of figure 5.5 plots Hawai‘i data for the “fine” dominated cases. These trajectories appear to be a combination of mid-troposphere and lower FT Asian airmass (> 850 mb). These airmasses are either carrying or mixing with Asian dust or dust of urban/industrial origin.

Figure 5.6 plots the back trajectories for “clean” background conditions in the ENP MBL near Hawai‘i. Each of the trajectories shows residence times → 4 days in the MBL. The trajectory from the Bering Sea is unexpected, having a residence time of more
than 7 days in the MBL. After subsiding from the mid troposphere some trajectories are entrain into the trade-wind regime and travel ~3000 km in the MBL. At an average wind speed of 8.0 m s\(^{-1}\) this indicates a MBL residence time of 4.3 days. The back trajectories indicate a transit time of 4-5 days thus for these data the \(U_{10} \approx U_{10,\text{avg}}\) assumption used in Chapter 4 appears to be valid. The bottom panel of 5.6 plots the anthropogenically influenced MBL back trajectories. Some back trajectories are no different than those for the “clean” cases. Others potentially indicate slow (> 4 days) long-range transport in the LT prior to entrainment near Hawai‘i.
Figure 5.5 – Back trajectories for the HI “mixed” airmasses (top). The trajectory from south of the Himalaya was unexpected. Asian pollution and dust airmasses are often interleaved with clean FT layers (RCN < 100 cm⁻³) which may account for the trajectory that lingered in the MBL. Back trajectories for the HI “fine” Asian pollution airmasses (bottom). These groups probably represent a combination of pre-existing airmasses and aged pollution lofted into the FT. These airmasses are either carrying and/or mixing with dust.
Figure 5.6 – Back trajectories for the “clean” background airmasses sampled near Hawai‘i (top). The trajectory from the Bering Sea was unexpected. The red line indicates a fetch of ~3000 km over a 4-5 day period. For the INTEX-B average wind speed, 8.0 m s⁻¹, 3000 km represents a BL residence time of ~4.3 days. The “polluted” MBL back trajectories (bottom) might represent aged pollution entraining into the MBL after being transported slowly across the ENP in the LT.
5.3. **Heterogeneous reactions between alkaline mineral dust and nitric acid**

5.3.1. Heterogeneous chemistry of Asian Dust over the North Pacific

The previous section demonstrated that dust and pollution aerosol is commonly mixed during long range transport. In this subsection I summarize the chemistry of accumulation mode and coarse mode aerosol found in the pollution/dust plumes over the Eastern North Pacific.

The upper left panels of Figs. 5.7 and 5.8 plot the volume distributions for unheated and refractory accumulation mode aerosol measured in the FT near Hawai‘i and Alaska. During lognormal fitting, seven of the Alaskan “Anthro” airmass types exhibited NMD’s and σg’s more typical of biomass burning aerosols. These data were separated from the AK-Anthro data and are included as an additional unheated and refractory distribution in figure 5.8. In the lower left panels of Figs. 5.7 and 5.8, accumulation mode chemistry is summarized. Note that the chemistry from the Hawai‘i distributions is effectively identical to that measured in Alaska. The average chemistry of the BB aerosol is also included and shows the larger mass fractions of volatile and refractory OC.

University of New Hampshire filter-based measurements of Ca$^{2+}$ can be converted into calcite (CaCO$_3$) mass assuming that the weak-acid eluent of the UNH ion chromatography analysis does not measure the aluminosilicate’s structural calcium. When these values are regressed against the HiGEAR data (upper right panels of figures 5.7 and 5.8) I calculate a calcite content of 11 wt% for the Hawai‘i region ($R^2=0.95$) and 10% ($R^2=0.55$) for the Alaska region. The low $R^2$ of the Alaskan fit is being driven by the two highest values of aerosol Ca$^{2+}$. A calcite weight percent of 11% is in close agreement with the range of calcite wt%‘s reported for the Chinese Loess parent material;
3.6-21% with a mean value of 12% [Liu, 1985]. The bottom right panel of Figures 5.7 and 5.8 plot molar equivalents of aerosol nitrate (neq std m$^{-3}$), versus molar equivalents of soluble calcium. As indicated there is a tight coupling between aerosol nitrate and aerosol calcium for both the Hawai‘i ($R^2=0.87$) and the Alaska ($R^2=0.55$) data. This is consistent with the findings from ACE-Asia indicating that Asian dust aerosol is a sink for reactive atmospheric nitrogen species [Kline et al., 2004; Tang et al., 2004].

Alkaline dust particulate is also a sink for $\text{SO}_2$ where it is irreversibly oxidized to form sulfate aerosol [Ullerstam et al., 2002; Usher et al., 2002]. The upper left panels of figures 5.9 and 5.10 plot total and supermicrometer sulfate aerosol versus calcium. The lower left panel is the same aerosol nitrate versus calcium plot as shown in figures 5.7 and 5.8. For both Hawai‘i and Alaska there is a weak correlation between sulfate and calcium compared to the correlation between nitrate and calcium. The two right hand panels of figures 5.9 and 5.10 plot the ratio of aerosol sulphur and nitrate to total sulphur and nitrate ($S_{\text{ratio}}$ and $N_{\text{ratio}}$). Here we can generalize that the presence of calcium, i.e. calcite, results in enhanced partitioning of sulfuric and nitric acid from the gas phase to the aerosol phase.
Figure 5.7 – Mean aerosol volume distribution for the FT near Hawai‘i (top-left). Regressions of CaCO₃ vs. size distribution integral volume multiplied by a Chinese Loess bulk density of 2.06 g cm⁻³ results in an 11 wt% estimate of the calcite content (top-right). Volatile and refractory accumulation-mode chemistry is summarized in the pie chart and is dominated by ammonium sulfate (bottom-left). Aerosol nitrate is highly correlated with calcium (bottom-right).

Figure 5.8 – Same as figure 5.7 but for FT Asian aerosol measured near Alaska.
Figure 5.9 - Regression of molar equivalents of total supermicrometer sulfate aerosol (top-left) and $S_{\text{mio}}$ (top-right) versus calcium in the FT near Hawai'i. Regression of molar equivalents of aerosol nitrate (bottom-left) and $N_{\text{mio}}$ (bottom-right) versus calcium.

Figure 5.10 - Same as figure 5.9 but for FT Asian aerosol measured near Alaska.
To further examine the relationship between acidic gases and alkaline dust I plot the equivalents ratio of the dominant cation and anion, $\text{NH}_4^+:2\text{SO}_4^{2-}$ versus $\text{Ca}^{2+}$ (upper left panels of figures 5.11 and 5.12). In the upper right panel I plot the same ratio but include the aerosol nitrate anion, $\text{NO}_3^-$. For both Hawai‘i and Alaska we observe lower anion:cation ratios with increasing concentrations of the dust tracer, $\text{Ca}^{2+}$. When the values drop below 1.0 this indicates that aerosol ammonium may be insufficient to neutralize any additional sulfuric or nitric acid condensed from the gas phase.

An alternative approach to plotting this relation is contained in the bottom halves of figures 5.11 and 5.12. Here I calculate excess aerosol acidity using the method of Jordan et al. [2003b]. Briefly, equivalents of ammonium is subtracted from equivalents of sulfate and plotted versus calcium. Positive values of the ordinate indicate an excess of aerosol sulfate which is available for heterogeneous reaction with supermicrometer dust, specifically calcite, to irreversibly form sulfate aerosol. Negative values of excess $\text{SO}_4^{2-}$ in figures 5.11 and 5.12 indicate an excess of ammonium. Any excess equivalents of ammonium are then subtracted from aerosol nitrate. The result, excess $\text{SO}_4^{2-} + \text{NO}_3^-$, is plotted versus calcium in the bottom right panels of the figures. Both computations of excess sulfate indicate only a weak correlation between $\text{Ca}^{2+}$ and any excess $\text{SO}_4^{2-}$. In fact most of the Hawai‘i data (Figure 5.11) indicate a deficit of $\text{SO}_4^{2-}$ with respect to ammonium. When excess nitrate is included there is a clear trend indicating higher concentrations of aerosol calcium result in higher concentrations of aerosol nitrate. This is the same conclusion drawn by Jordan et al. [Jordan et al., 2003a; 2003b] when measuring aerosol near the source regions of East Asia during TRACE-P but for $\text{Ca}^{2+}$ concentrations 5 times those measured over the remote North Pacific during INTEX-B.
Ammonium nitrate is thermally unstable in the dry free troposphere with equilibrium concentrations forming according to the reversible reaction:

\[ NH_3(g) + HNO_3(g) \rightleftharpoons NH_4NO_3(s) \] (5.2)

The right-hand panels in Figures 5.9 and 5.10 show that higher concentrations of \( \text{Ca}^{2+} \) is associated with more complete partitioning of nitrate into the aerosol phase. If the \( \text{Ca}^{2+} \) is present as \( \text{CaCO}_3 \) then nitric acid is being removed from the gas phase reservoir according to the irreversible reaction:

\[ \text{CaCO}_3(s) + HNO_3(s) \rightarrow \text{Ca(NO}_3)_2(s) + H_2O + CO_2(g) \] (5.3)

Since the availability of dust alkalinity far exceeds that of \( \text{H}_2\text{SO}_4 \) and \( \text{HNO}_3 \) acidity this reaction should continue to consume nitric acid as an airmass subsides from the upper troposphere to the lower troposphere and other thermally unstable nitrogen species (e.g. peroxyacyl nitrates, PAN's) begin to dissociate into \( \text{HNO}_3 \) (g) [Singh et al., 2007]. For this irreversible reaction to account for the increase in aerosol nitrate we need to determine whether or not the \( \text{Ca}^{2+} \) measured in the Asian plumes is actually calcite. We have already used the size distribution measurements to establish a wt% of \( \sim 11\% \) \( \text{CaCO}_3 \) for the dust aerosol. However the variability of the calcite wt% leaves a relatively large margin for error.

In figures 5.13 and 5.14 I plot Ca:Mg, Ca:Na and K:Na molar ratios and include the geochemical ratios previously reported for Chinese Loess [Arimoto et al., 2004] and sea salt. Note that the analytical techniques used aboard the DC-8 differs from that of Arimoto but that overall the measured ratios describe a crustal rather than oceanic source of \( \text{Ca}^{2+} \). In the bottom left panel of 5.13 and 5.14 I plot anions versus cations. Minor
cations such as Fe\(^{2+}\) are not measured by the UNH IC technique but their concentrations are expected to be a small fraction of the total. Similarly H\(^{+}\) is not reported thus the pH of the aerosol is unknown. The major missing anion in the analysis is CO\(_3\)^{2-}. Where a large anion/cation imbalance occurs we can assess the probability that the missing ion is CO\(_3\)^{2-} by plotting the imbalance vs. Ca\(^{2+}\) in the bottom center panels of figures 5.13 and 5.14. A slope of 1:1 would account for carbonate as calcite. Dolomite, CaMg(CO\(_3\))\(_2\) can also be a source of carbonate ions thus I also include a plot versus the sum of the molar equivalents of Ca\(^{2+}\) and Mg\(^{2+}\). For both the Hawai`i and Alaska data large ion imbalances occur up to ratios of 1:4. When plotted vs. calcium the imbalance is reduced to within +15%. When plotted vs. the sum of the calcium and magnesium the imbalance is reduced to within -15%. This 15% uncertainty can be considered the limit of the technique as a result of missing minor ions such as Fe\(^{2+}\) and H\(^{+}\).

In summary, back trajectories, geochemical ratios of major ions, Ca:Mg, Ca:Na, an analysis of cation/anion imbalances with respect to calcium and magnesium, and regressions to obtain the calcite wt% of the supermicrometer aerosol all point toward a dust composition consistent with Asian dust. Aerosol nitrate is highly correlated with Ca\(^{2+}\) but can be co-emitted. An analysis of excess nitrate (wrt. NH\(_4\)^{+}) shows increasing concentrations of aerosol nitrate with Ca\(^{2+}\). This can be explained by the irreversible conversion of nitric acid to calcium nitrate, a reaction that is not limited by aerosol alkalinity. These results confirm the results of previous observations [Jordan et al., 2003b] and predictions based on model simulations [Phadnis and Carmichael, 2000; Song and Carmichael, 2001].
Chinese Loess is not rich in gypsum, CaSO$_4$ [Liu, 1985]. Total aerosol sulfate shows a weak correlation with aerosol Ca$^{2+}$ but the two components are co-emitted at the source. For the Hawai‘i data only a weak correlation exists between supermicrometer SO$_4^{2-}$ and Ca$^{2+}$. However, sufficient ammonia exists to neutralize nearly all the SO$_4^{2-}$ to ammonium sulfate. Recent work has focused on simulating the heterogeneous reactions between alkaline dust and sulfuric acid [Bauer and Koch, 2005]. The data from East Asia indicate a tighter coupling between Asian Dust and nitric acid with implications for radiative forcing [Bauer et al., 2007], partitioning of reactive nitrogen species [Singh et al., 2007], and on ocean acidification [Doney et al., 2007].
Figure 5.11 – Sulfate (top-left) and sulfate plus nitrate (top-right) neutralization versus molar equivalents of calcium in the FT near Hawai‘i. Regressions of excess sulfate (bottom-left) and excess sulfate plus nitrate (bottom-right) versus molar equivalents of calcium.

Figure 5.12 - Same as figure 5.11 but for FT Asian aerosol measured near Alaska.
Figure 5.13 – Geochemistry ratios for major cations in Asian Dust (top row) measured near Hawai‘i. Anion-cation imbalances (bottom-left) can largely be attributed to the missing CO$_3^{2-}$ ion from calcite or dolomite (bottom-center and right).

Figure 5.14 - Same as figure 5.13 but for FT Asian aerosol measured near Alaska.
5.3.2. Heterogeneous chemistry of Asian Dust near the tropopause

Some tropospheric airmasses contained high concentrations of the stratospheric airmass tracer $^7\text{Be}$ [Dibb et al., 2003; Jordan et al., 2003c] indicative of mixing between tropospheric and stratospheric airmasses. In some of these airmasses supermicrometer aerosol is also detected. An example of this occurrence is shown in figures 5.15-17 for the May 4$^{th}$ INTEX-B flight. At ~0:00 UTC the DC-8 ascended into a high ozone cirrus cloud deck containing depolarizing aerosol. When sampling warm clouds the UH solid diffuser inlet is unable to sample aerosol due to droplet shatter on the inlet tip. Accuracy while sampling in cirrus clouds is also uncertain. During this leg however, both wing-probes and HiGEAR Relay-4 size distributions preheated to 420$^\circ$C indicate the presence supermicrometer aerosol. The measurements of $^7\text{Be}$ support the conclusion that stratospheric air is mixing into the FT as a result of this large frontal system, the motivation for the flight. Stratospheric concentrations of HNO$_3$(g) are higher than those observed in the FT. As a result, Asian dust lofted beyond the tropopause or into a FT airmass that mixes with stratospheric air could potentially be re-exposed to nitric acid. This would result in conversion of stratospheric HNO$_3$(g) to $\rightarrow$ Ca(NO$_3$)$_2$ in excess of the HNO$_3$ converted from the co-emission of anthropogenic precursors (NO$_x$ etc).

Replicating the analyses described in the previous section shows that once again, total nitrate is better correlated with Ca$^{2+}$ than supermicrometer sulfate. Nitrate is highly correlated ($R^2=0.78$) with Ca$^{2+}$ with more than 40% of the nitrate in the aerosol phase compared to the gas phase for Ca$^{2+}$ concentrations beyond ~$20$ µg std m$^{-3}$. Above $20$ µg std m$^{-3}$ of Ca$^{2+}$ there is excess ammonium compared to sulfate but not compared to the...
sum of sulfate and nitrate. When the excess nitrate is plotted vs. calcium (Figure 5.18) there is a clear trend of enhanced aerosol nitrate with Ca\(^{2+}\). The slope is also higher (0.24) compared to that of the pooled Hawai‘i and Alaska “Mixed” data, 0.17. Nitric acid concentrations are also higher ~350 pptv compared to 70-140 pptv for the pooled HI and AK “Mixed” airmasses. When excess nitrate is plotted against \(^{7}\)Be however (Figure 5.19), there is no clear trend between elevated excess NO\(_3^-\) (i.e. Ca(NO\(_3\))\(_2\) (s)) and \(^{7}\)Be. Thus the higher slope for the STE influence FT airmasses does not appear to be the result of secondary exposure to stratospheric nitric acid but more likely due to a higher initial concentration of anthropogenic NO\(_x\) and Asian dust at the source.
Figure 5.15 - DIAL LIDAR profile of aerosol depolarization during the May 4th INTEX-B flight.

Figure 5.16 – Dusty cirrus sampled along a frontal system in the Alaskan Low during INTEX-B.
**Figure 5.17** – DIAL LIDAR Ozone along the DC-8 flight path on May 4\textsuperscript{th}, 2006. Barely discernable through the central peak in O\textsubscript{3} (0:00 UTC) is the in-situ measurements of Avery et al., mapped to the local field in real time via the ICATS data system.

**Figure 5.18** – Excess sulfate and sulfate plus nitrate for FT aerosol measured in upper troposphere airmasses rich (> 800 fCi std m\textsuperscript{-3}) stratospheric airmass tracer \textsuperscript{7}Be.
Figure 5.19 – Excess (SO$_4^{2-}$ + NO$_3^-$) versus $^7$Be shows no clear trend indicating that higher excess nitrate values are a result of higher emissions of nitrate precursors at the source and not re-exposure to stratospheric sulfuric and/or nitric acid.

5.3.3. Heterogeneous chemistry in the nitrate rich boundary layer of the Central Highlands of Mexico.

Motivated by the success of the heterogeneous chemistry analysis over the remote Pacific I undertook a similar analysis for the nitrogen rich Mexican CBL and the FT over the Gulf of Mexico. These data are plotted sequentially in figure Figures 5.20-22. Data collected near Mexico City had the highest concentrations of mineral dust measured during INTEX-B. The calcite content and the Ca:Mg and Ca:Na ratios will not necessarily follow the trends observed for Asian dust but they should be uniquely crustal compared to the seawater ratios.

In figure 5.20 much of the sulfate and nitrate data lie in a low-calcium cluster. The $S_{ratio}$ and $N_{ratio}$ versus calcium in figure 5.20 are more variable than the North Pacific values as many of the plumes are fresh and have not had a long period of time to react with the mineral dust. For sulfate there is no clear trend between the highest
concentrations of Ca\(^{2+}\) and high concentrations of SO\(_4^{2-}\). The trend for nitrate versus calcium is better but the data show a lot of scatter.

In the nitrate versus calcium plot the highest nitrate value also has an SO\(_2\) concentration of 24 ppbv! The two high nitrate values with calcium concentrations of 150-200 neq m\(^{-3}\) (near the excess alkalinity line) are a fresh fire plume. Notably they, along with the 24 ppbv plume, have excess ammonium compared to sulfate of 100 to 200 neq m\(^{-3}\) (bottom left panel of figure 5.21). When excess nitrate is also considered the ammonium is exhausted resulting in excess nitrate values that lie along a regression identical to the regression obtained by Jordan et al., in the East Asian source regions during TRACE-P. The implication is that ammonium nitrate is clearly present in the ambient aerosol and that alkaline dust in the Mexico region also appears to be a sink for nitric acid derived from NO\(_x\).

Finally, it is well known that Mexico City is built on the dry lakebeds of the Valley of Mexico. In figure 5.22 the Ca:Mg ratios confirm the crustal composition of these mineral aerosols. However the Ca:Na and K:Na ratios exhibit two branches. The main cluster of Ca:Na values follow the crustal values observed for Asian Dust. The large outliers are for data collected in the heart of Mexico City and its suburbs. The two highest K\(^+\) values but with low Na\(^+\) are the fresh fire plume. The three high K\(^+\), high Na\(^+\) values are the measurements from the Mexico City environs. Dust sourced from the dry lakebeds may have a unique geochemical signature as the playa particulate may be relatively enriched in Na\(^+\) compared to urban/industrial dust from Mexico City or natural dust sourced from the mountain regions of the Central Highlands. When these large Na\(^+\) concentrations were measured I noted "dust appears to be sourced from the dry..."
"lakebeds" in the flight log. The photo in figure 5.23 was recorded at this time but does not show the observed aeolian erosion clearly. Chapter 3, figure 3.24, already highlighted the intensity of dust storm activity over the Central Highlands of Mexico. Outside the Mexico City area tall dust-devils were also observed such as the one photographed over the agriculture fields southwest of Mexico City on March 12th, 2006 (Figure 5.24). Simulating acid-base chemistry in light of these observations will likely be challenging and more study is warranted.

Figure 5.20 - Same as figure 5.9 but for CBL aerosol measured in Central Highlands of Mexico.
Figure 5.21 - Same as figure 5.11 but for CBL aerosol measured in Central Highlands of Mexico.

Figure 5.22 - Same as figure 5.13 but for CBL aerosol measured in Central Highlands of Mexico.
Figure 5.23 – Dust lifting off former lakebeds on the outskirts of Mexico City on March 19th, 2006. Note the burn scars in the lower left portion of the image and the intense light extinction in this unprocessed image of the Mexico City boundary layer.

Figure 5.24 – Dust devil with a vertical extent of ~1 km over agricultural land southwest of Mexico City during the March 12th, 2006 INTEX-B flight. This image has been colour and contrast enhanced.
5.4. 1996-2006 Record of aerosol chemistry at Mauna Loa Observatory

Airborne data collected from a single campaign is effectively a point measurement in both space and time. Here I put the INTEX-B measurements into context by comparing the data to the long-term record from the Mauna Loa Observatory.

For the past 12 years the University of Hawai‘i, led by Dr. Barry Huebert, has conducted long-term measurements of aerosol chemistry at the Mauna Loa Observatory (MLO) on the island of Hawai‘i [Huebert et al., 2001]. Using this data the molar concentrations of total nitrogen, aerosol sulfate, aerosol ammonium and weak-acid soluble aerosol calcium were subjected to a principle component analysis. The results for the first three principle components account for 53%, 21% and 17% of the total sample variance. The eigen vectors of the analysis are contained in Table 5.2.

Table 5.2 — Linear coefficients of the eigen vectors used to construct principle components 1 through 3 for the MLO data.

<table>
<thead>
<tr>
<th></th>
<th>PC-1</th>
<th>PC-2</th>
<th>PC-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Constant</td>
<td>1.77</td>
<td>-0.27</td>
<td>0.4</td>
</tr>
<tr>
<td>NH₃NO₃</td>
<td>-0.50</td>
<td>0.03</td>
<td>-0.78</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>-0.50</td>
<td>0.45</td>
<td>0.56</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>-0.60</td>
<td>0.16</td>
<td>0.01</td>
</tr>
<tr>
<td>Ca</td>
<td>-0.38</td>
<td>-0.88</td>
<td>0.27</td>
</tr>
</tbody>
</table>

The first component (PC-1) sorts the compounds by their molar concentrations, the heaviest weighting is for ammonium (-0.60) followed by sulfate (-0.50) and total nitrate (-0.50) equally. This is not a surprising result as the concentration of these three compounds vary over three orders of magnitude and have average values 4-5 times the average concentration of aerosol calcium. Mean, median and the standard deviations for
these data are summarized in Table 5.3. The mean sulfate value, 93 pptv, is slightly higher than Huebert et al. [2001] value of 80 pptv, but the data have not been screened to eliminate contamination by boundary layer air.

Table 5.3 – Mean, median and standard deviation of total nitrate, sulfate, ammonium and calcium (pptv) measured between 1996 and 2006 at MLO.

<table>
<thead>
<tr>
<th></th>
<th>Mean</th>
<th>Median</th>
<th>St. Dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>tHNO₃</td>
<td>84</td>
<td>71</td>
<td>70</td>
</tr>
<tr>
<td>SO₄</td>
<td>93</td>
<td>55</td>
<td>116</td>
</tr>
<tr>
<td>NH₄</td>
<td>86</td>
<td>67</td>
<td>80</td>
</tr>
<tr>
<td>Ca</td>
<td>18</td>
<td>3.0</td>
<td>53</td>
</tr>
</tbody>
</table>

The second principle component (PC-2) separates MLO airmasses based on their sulfate versus calcium content. Low calcium, high sulfate air is probably boundary layer air influenced by Kilauea's Pu' Billy O’o vent [Porter et al., 2002]. Anthropogenic Asian airmasses are probably those with intermediate values of calcium, while the highest calcium concentrations (most negative PC-2 values) are airmasses containing Asian dust.

The third principle component (PC-3) best separates total nitrate from aerosol sulfate. In figure 5.25 I plot PC-3 vs. PC-2 and colour the plots by the indicated molar fractions of sulfate, ammonium and aerosol nitrate; aerosol nitrate computed as the difference between total HNO₃ \([\text{HNO}_3(g) + \text{NO}_3(aer)]\) and HNO₃ (g). The upper portion of data are calcium-free (i.e. dust-free) airmasses. Near the center of the cluster the airmasses are dominated by sulfate aerosols partially neutralized by ammonium and labelled as “Low Acidity”. Airmasses located along the upper right hand branch of the data are dominated by high-acidity airmasses with very low ammonia (labelled as “High Acidity”).

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The airmasses containing the most calcium are in the bottom half of the data cluster in Figure 5.25. When coloured by molar ratio of aerosol nitrate, there is a secondary separation of the dusty airmasses (lower left panel). On the lower left branch are partially neutralized sulfate aerosols with the highest fractions of observed aerosol nitrate. On the lower right branch are airmasses with relatively low neutralization of the sulfates and lower molar fractions of aerosol nitrate. Interpretation of this result of the principle component analysis is difficult but may indicate the difference between "clean" and "polluted" Asian dust samples (i.e. dusty airmasses influenced/mixed with anthropogenic pollution and those with low concentrations of anthropogenic tracers). In the lower right panel of figure 5.25 I plot the same data but colour code the result by the scattering Angstrom exponent (450/700 nm) from concurrent measurements using a corrected TSI 3-λ nephelometer. This independent assessment of the aerosol measured at MLO confirms that the high calcium values occur during low values of the angstrom exponent, i.e. dust.

The 11-year record at Mauna Loa represents our best estimate on the composition of lower FT aerosol chemistry over the subtropical ENP. However, despite its temporal resolution, the Mauna Loa Observatory resides at a fixed point in space. If we assume that the estimate of the variance from the MLO measurement is robust then we can extrapolate the results of the PCA analysis to other data sets. In Figure 5.26 I again plot PC-2 versus PC-3, this time shaded by neutralization of sulfate and nitrate by ammonium. The INTEX-B data for fine mode dominated (FMF$_{\text{scat}} > 0.6$) and mixed (FMF$_{\text{scat}} < 0.6$) FT measured near Hawai‘i is mapped into the principle component space and are labeled along with other known dust events. The INTEX-B measurements from April 17th to
May 1\textsuperscript{st} 2006 is one of the most significant events ever measured at Mauna Loa; April 20\textsuperscript{th} being the 72\textsuperscript{nd} highest Ca\textsuperscript{2+} concentration measured (98.0 percentile for N=3546) and April 29\textsuperscript{th} being the 28\textsuperscript{th} highest Ca concentration measured (99.2 percentile).
Figure 5.25 - Principle component 2 versus PC-3 for the eleven-year MLO record. When shaded by major ion mass fractions airmasses of unique character can be identified as labelled. Independent confirmation of the aerosol character is assessed using TSI nephelometer angstrom exponent. Volcanic and pollution dominated aerosol are found in the central PC-2 values while supermicrometer dust and nitrate are found in the more negative PC-2 values.
Figure 5.26 - Principle component 2 versus PC-3 and shaded by ammonium neutralization of sulphate and nitrate. The INTEX-B data are mapped into the parameter space and labelled along with other significant events from the 11-year record.
Figure 5.27 plots the neutralization of sulphate (left) and sulphate plus nitrate (right) as a function of aerosol calcium for the 11-year MLO record. When colour coded by scattering Angstrom exponent there are two branches of dust data. The upper group corresponds to a neutralization ratio $\sim 0.5$ indicating a composition of ammonium bisulfate $\text{NH}_4\text{HSO}_4$. The lower branch of data indicates an ammonium to sulphate equivalents ratio of $\sim 0.2$ indicative of pure sulfate aerosol. When the long-term MLO data are instead plotted as excess sulphate versus aerosol calcium and excess sulfate plus nitrate versus aerosol calcium the coupling between alkaline dust and the acid gases $\text{SO}_2$ and $\text{HNO}_3$ becomes even more clear (Figure 5.28). Based on the regressions sulfate reacts with $\text{CaCO}_3$ in an equivalents ratio 1:0.16. The sum of excess sulphate plus nitrate ratio is 1:0.30 resulting in an excess nitrate ratio of 1:0.14, effectively identical to that of sulfate.

Recall that excess alkalinity exists below the dashed 1:1 line so that this reaction does not appear dust limited. Instead plotting the $N_{\text{ratio}}$ (nitric acid gas plus aerosol nitrate) in Figure 3.29 suggests the reaction is limited by transport time and the kinetics of the gas phase deposition flux to the mineral aerosol surface. More study is warranted.
Figure 5.27 – Degree of sulphate neutralization by ammonium as a function of aerosol calcium (left). Degree of sulphate plus nitrate neutralization by ammonium as a function of aerosol calcium (right). Both plots are shaded by scattering Angstrom exponent. High values indicate scattering dominated by accumulation mode aerosol, low values indicate scattering dominated by supermicrometer dust.

Figure 5.28 – Excess sulphate aerosol as a function of aerosol calcium (left). Excess sulphate plus nitrate as a function of aerosol calcium (right). Both plots are shaded by scattering Angstrom exponent. High values indicate scattering dominate by accumulation mode aerosol, low values indicate scattering dominated by supermicrometer dust.
Figure 5.29 – Ratio of aerosol nitrate to total nitrate as a function of aerosol calcium. Data are shaded by scattering Angstrom exponent. High values (red-shading) indicate scattering dominated by accumulation mode aerosol, low values (blue-shading) indicate scattering dominated by supermicrometer dust.
5.5. Influence of Asian emissions on the biogeochemistry of the Eastern North Pacific

The surface mixed layer of the Eastern North Pacific Subtropical Gyre (subtropical gyre) is an oligotrophic ecosystem whose biological productivity is limited by the availability of nitrogen, phosphorus and/or iron. The surface mixed layer of the Eastern North Pacific Subpolar Gyre (subpolar gyre) is a high-nutrient low-chlorophyll (HNLC) ecosystem whose biological productivity is limited by the availability of the trace element iron. Long range transport of Asian dust and pollution have the potential to deliver nutrients to these systems through wet and dry deposition of gas and aerosol species, thereby altering the biogeochemistry of the remote Pacific Ocean [Karl et al., 2004]. In this section I investigate the potential for atmospheric inputs of nitrogen and iron to enhance primary productivity of ocean phytoplankton, a process related to the Iron Hypothesis [Martin, 1990].

On April 23rd 2006 models predicted Asian pollution and dust was subsiding in the East Pacific High and may then entrain into the MBL. The NASA DC-8 flew northwest from Hawai‘i to intercept the layer (Figure 5.30). Model predictions proved accurate and Figure 5.31 shows visible and infrared scattering data from the DIAL LIDAR during the flight. The layer of pollution and dust can be seen as a 1-2 km thick layer which is separated from the trade wind inversion in the southeast but which dips to the northwest where it resides directly above the MBL. This can be seen more clearly in the DIAL aerosol depolarization ratio (Figure 3.32), depolarization being an indicator of mineral dust rather than spherical pollution or sea salt particulate. Not only does the
depolarization ratio show the dust layer resides just above the MBL but that at 30.75°N, 166°W the depolarizing dust has already begun to entrain into the MBL.

Figures 5.33 and 5.34 show *in-situ* measurements along the DC-8 flight path. Marker size is proportional to total aerosol light scattering while the markers are shaded according to scattering Angstrom exponent and f(RH) between 80%-40%. Data collected in the MBL in the vicinity of 37.5°N, 161°W met the “clean” MBL criteria and are characterized by a high f(RH) value. The data from the MBL near 30°N, 166°W have lower Angstrom exponents and slightly suppressed f(RH) values. This is the region where the FT pollution and dust have entrained into the MBL. Once entrained the fate of these aerosol is almost certainly removal by dry deposition and/or wet removal associated with fair-weather cumulus in the Hawai‘i trade-wind regime.
Figure 5.30 – STEM2K3 predictions of dust mass (µg std m⁻³) in the 5.4 km layer (top); 3 km layer (middle); and 1 km layer (bottom).
Figure 5.31 – Aerosol scattering ratio measured by the DIAL LIDAR during the April 23rd 2006 INTEX-B Flight. Anthropogenic pollution and Asian Dust are entraining into the MBL (~1-1.5 km) from the FT. Note the “ultraclean” layer above the dust. In the clean layer refractory CN \(-=0 \text{ cm}^{-3}\) and Ozone is \(~25 \text{ ppbv} \) indicative of the marine stratus cloud outflow “buffer layer”.

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Figure 5.32 – Aerosol depolarization ratio measured by the DIAL LIDAR during the April 23rd INTEX-B flight. High returns above the MBL are indicative of non-spherical dust while the spherical MBL sea salt and the FT pollution aerosol do not depolarize the LIDAR return.
Figure 5.33 – Scattering Angstrom exponent plotted along the April 23rd, 2006 DC-8 flight track. Markers are scaled by scattering intensity at 550 nm and indicate the presence of dust directly above the MBL inversion and its entrainment near 30°N, 165°W.

Figure 5.34 – Same as figure 5.33 but shaded by f(RH) at 80% RH. Note the suppression of f(RH) in the MBL at 30°N, 165°W, compared to 37°N, 161°W due to the entrainment of Asian Dust.
Although a single flight is only a snapshot of the processes associated with the entrainment of Asian pollution and dust into the remote MBL, it is of interest to examine the potential for these emissions to influence the biogeochemistry of the Eastern North Pacific surface waters. It is these events which future models will need to simulate in order to couple atmospheric processes with their biological response in the surface ocean. And, as discussed in Chapter 1.3, these events are not just of contemporary or future significance but relate to ocean biogeochemistry over glacial-interglacial timescales and/or the age of the Chinese Loess Plateau itself (~2.4 million years). Here I attempt to constrain the potential impacts of Asian pollution and dust deposition on surface water chemistry for the subtropical and subpolar gyres using our INTEX-B observations.

The surface mixed layer of the subtropical gyre is ~50 m in springtime with average concentrations of nitrogen, total iron and dissolved iron (< 0.2-0.4 μm filter) of 2.6 nM, 1.0 nM, 0.26 nM respectively [Boyle et al., 2005; Brown et al., 2005]. No direct measurements of mineral dust iron composition were made aboard the NASA DC-8 during INTEX-B. But based on previous studies (see Tables 1.4-1.6 in Chapter 1) molar ratios of Fe:Ca of 0.90 are a reasonable estimate for Asian dust. Using this ratio I calculate total aerosol iron (Fe_T) from the University of New Hampshire measurements of soluble aerosol calcium. Total nitrogen is computed as the sum of nitric acid (HNO_3), aerosol nitrate (NO_3^-) and aerosol ammonium (NH_4^+). In the Asian Dust/Pollution plumes the average concentrations for nitrogen and calcium are 830 pptv, and 440 pptv resulting in an estimate of Fe_T of 400 pptv. Assuming a soluble iron fraction of 6% [Buck et al., 2006] results in an estimated aerosol soluble iron concentration of 24 pptv.
In order to evaluate the maximum input potential, I assume complete removal of the soluble atmospheric nitrogen species, HNO₃ (g), NO₃⁻ (aer) and NH₄⁺ (aer), as well as all of the iron-bearing Asian dust from a 1 km deep layer similar to that sampled on April 23rd, 2006. For the oligotrophic waters of the North Pacific near Hawaiʻi, the airmasses sampled by the DC-8 during INTEX-B have the potential to increase the 50 m mixed layer concentrations of nitrogen, total and soluble iron by 0.68 nM, 0.32 nM and 0.02 nM respectively. These represent 26%, 32% and 9.5% increases to the standing stock of nitrogen, total and soluble iron in the surface waters of the Eastern North Pacific subtropical gyre. The same calculation is performed for data from the Alaskan phase of INTEX-B. Average pollution/dust plume concentrations of nitrogen and calcium are 750 pptv and 400 pptv resulting in estimates for total and soluble iron of 360 and 22 pptv. Seawater concentrations of nitrate, total and soluble iron are 10⁴ nM (10 μM), 0.13 nM and 0.10 nM [Nishioka et al., 2001; Wong et al., 2006] to which atmospheric inputs add 0.61 nM, 0.30 and 0.02 nM. This results in a <1%, 230% and 18% increase in surface water concentrations of the Eastern North Pacific subpolar gyre.

Based on Martin [1990] we hypothesize that deposition of nitrogen and iron will promote a biological response in these ecosystems. To examine this potential for the oligotrophic waters near Hawaiʻi I analyze 9km resolution merged SeaWiFS and AQUA-MODIS satellite retrievals of surface ocean chlorophyll-a. The upper two panels of Figure 5.35 show the average chlorophyll concentrations for April and May from 2003 until 2007. The bottom two panels show the chlorophyll concentration for the two weeks of the dust storm, April 15-30th, 2006 and the two weeks after the dust storm, May 1-15th, 2006. The steep chlorophyll gradient between 30°N and 35°N is associated with a steep
gradient in sea surface temperature (SST) and represents the boundary between the subtropical and subpolar gyres. Visually there is an apparent increase in the chlorophyll retrievals after the dust storm especially near 30°N, 165°W, the location where the DC-8 observed mineral dust aerosol entraining into the MBL (Figure 5.33 & 5.34). The TRMM satellite retrievals of precipitation show abundant rainfall between 35°N and 45°N as two consecutive fronts moved eastward through the region (Figure 5.36). The warm sector of the front contains the pollution and dust subsiding in the East Pacific High (see Fig. 5.30). As the pollution and dust laden air is drawn into the front these aerosols are likely removed through wet deposition.

In Figure 5.37 I perform a statistical analysis of the SeaWiFS/MODIS chlorophyll retrievals in a region bound between 20-30°N and 140-180°W. The data north of 30°N is excluded because of the heterogeneity induced by mesoscale eddies at the SST front. Based on the 2003-07 retrievals we expect chlorophyll concentrations to be lower in May than in April. For late April 2006 chlorophyll is below average, due mostly to a positively skewed mean for the April average, the result of some contamination by high chlorophyll values between 170-180°W at 30°N. When these data are excluded from the histogram the late April values are no different ($\alpha=0.05$) than the 2003-07 mean. The early May 2006 data however are significantly higher than both the late April 2006 values and the 2003-07 May mean. Using either the mean or median values, satellite retrievals of surface ocean chlorophyll show an 8-9% increase over the two week period. This increase can be evaluated further by plotting the times series of mean values for the 8-day, 9km resolution SeaWiFS/MODIS chlorophyll images along with monthly averages from SeaWiFS/MODIS between 2003 and 2007 (Figure 5.38). I also include
the monthly averages of in-situ measurements (0-25 m depth) recorded at the University of Hawai‘i’s Station ALOHA (22°45’N, 158°W) [Karl and Lukas, 1996] from 1989-2006.

Figure 5.35 – April (top-left) and May (top-right) 2003-07 monthly averaged surface ocean chlorophyll retrievals from the 9 km resolution merged SeaWiFS/MODIS satellite retrievals. The bottom panels plot the same data but for the two week period of the April 2006 dust storm (bottom-left) and the two week period after the dust storm (bottom-right). Chlorophyll concentrations north of Hawai‘i, especially near 30°N, 165°W are elevated in the two weeks after the dust storm. This is the region where the NASA DC-8 measured Asian dust in the MBL after it entrained from the FT.
Figure 5.36 – TRMM satellite retrievals of precipitation for the weeks of April 22-30 and May 1-8, 2006. Precipitation north of 30°N is associated with the passage of two frontal systems. In each case the warm sector of the front (south of 30°N) contained Asian pollution and dust which is likely being removed by wet deposition. A deeper (6-8 km) convective cell formed NE of Hawai’i on April 30th, when both the DC-8 and the Mauna Loa Observatory were recording Asian pollution and dust in the FT near Hawai’i.
Figure 5.37 – Chlorophyll histograms between 20-30°N and 140-180°W for the maps shown in figure 5.35. Chlorophyll concentrations the week of the dust storm are no different than the April mean when the outliers skewing the 2003-07 April mean are ignored. Data from two weeks after the dust storm are significantly higher than the 2003-07 May average and the two weeks prior to the dust event. Using either the median or the mean the histograms show an 8-9% increase in chlorophyll two weeks after the April 15th-30th dust storm period indicative of a biological response to the input of anthropogenic nitrogen and/or mineral dust, i.e. iron.
Figure 5.38 – Top panel is the time series of 8-day average 2006 SeaWiFS/MODIS chlorophyll retrievals between 20-30°N and 140-180°W (red) compared to the 2003-07 monthly averages (green line, +/-1σ dashed line). Monthly averages from 1989-2006 in-situ chlorophyll measurements at Station ALOHA are shown as blue lines, the 2006 data as blue squares. Bottom panel records the night time measurements of total nitrogen (green) and calcium (black) at Mauna Loa and show that calcium measured on April 30th is the 28th largest event in the 12-year record.

It is difficult to directly attribute the 8-9% increase in surface ocean chlorophyll to the ~25% increases in surface mixed layer nitrogen or the ~10-30% increase in iron predicted from the in-situ aerosol measurements. The SeaWiFS/MODIS retrievals tell us nothing about the increase in chlorophyll below the surface. Also, the presence of mineral dust in the atmosphere may affect the chlorophyll retrieval during the dust storm period (April 15-30th). As a result the apparent increase could potentially be a retrieval artefact not a true biological response to nutrient input. I attempt to corroborate the April
2006 event through an analysis of the March/April 1999 event previously reported inClarke et al. [2001].

SeaWiFS chlorophyll retrievals at 9 km resolution are available from 1998-2007 and are used exclusively to generate the averages in Figure 5.39. Again chlorophyll concentrations over large regions of the Eastern North Pacific appear to increase two week after a large dust/pollution transport event. The histograms for the 1998-2007 April and May averages as well as the 2-week averages are summarize in figure 5.40. For the 1999 event there is also an 8% increase in the surface ocean chlorophyll. The time series in Figure 5.41 shows the evolution of chlorophyll as well as the Mauna Loa measurements. Notably the March 1999 event had the highest calcium concentrations measured at MLO during the 12-year record yet there is no obvious increase in surface ocean chlorophyll. The April 1999 event is arguably the largest ever measured at MLO, is associated with high nitrogen concentrations, and appears to result in an 8% increase in chlorophyll. It is interesting to note that the April 1999 event contains substantially more total nitrogen than the March 1999 event. The extent to which photo-autotrophs in the Eastern North Pacific subtropical gyre are nitrogen versus iron limited is an active topic of research. The data summarized here for the 1999 and 2006 dust events suggest that the input of iron with nitrogen is more likely to induce a biological response than a large input of iron alone. This case study is an exciting glimpse into the role of Asian pollution and dust aerosol in biogeochemical cycling, i.e. Martin's [1990] Iron Hypothesis. As a potential negative feedback on the contemporary concentration of atmospheric CO₂, more study is warranted.
Figure 5.39 – April (top-left) and May (top-right) 1998-2007 monthly averaged surface ocean chlorophyll retrievals from the 9 km resolution SeaWiFS satellite retrieval. The bottom panels plot the same data but for the two week period of the April 1999 dust event (bottom-left) and the two week period after the dust storm (bottom-right). Chlorophyll concentrations north-east of Hawai‘i are elevated in the two weeks after the dust storm. This is the region where the NASA P3-B measured Asian dust and pollution above the trade-wind inversion during the PEM Tropics B mission [Clarke et al., 2001].
Figure 5.40 – Chlorophyll histograms between 20-30°N and 140-180°W for the maps shown in figure 5.39. Chlorophyll concentrations the week of the dust storm are less than the April mean. Data from two weeks after the dust storm are significantly higher than the 1998-2007 May average and the two weeks prior to the dust event. Using either the median or the mean the histograms show an 8% increase in chlorophyll two weeks after the April 7th-22nd dust storm period, indicative of a biological response to the input of anthropogenic nitrogen and/or mineral dust, i.e. iron.
Figure 5.41 – Top panel is the time series of 8-day average 1999 SeaWiFS chlorophyll retrievals between 20-30°N and 140-180°W (red) compared to the 1998-2007 monthly averages (green line, +/-1σ dashed line). Monthly averages from 1989-2006 in-situ chlorophyll measurements at Station ALOHA are shown as blue lines, the 1999 data as blue squares. The bottom panel records the night time measurements of total nitrogen (green) and calcium (black) at Mauna Loa and show that calcium measured on April 15-18th is the largest dust transport event measured during the 12-year MLO record.
5.6. References


Dibb, J.E., R.W. Talbot, E. Scheuer, G. Seid, L. DeBell, B. Lefer, and B. Ridley, Stratospheric influence on the northern North American free troposphere during


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AT THE TIME OF MICROFILMING
6.0 Conclusions

6.1. Aerosol size distributions and the direct effect

Chapters 3 and 5 summarize vertical profiles and lognormal fits to aerosol number and volume distributions that dominate tropospheric light extinction over North America and the North Pacific. Size distributions of natural boreal forest biomass burning aerosol exhibited a range of number mean diameters, \( (NMD = 0.062 - 0.20 \, \mu m) \) with a \( \sigma_N \) of 1.77 +/- 0.28. This variability results in a range of volumetric mean diameters (VMD) between 0.18 and 0.52 \( \mu m \). North American anthropogenic pollution exhibited smaller average NMD’s of 0.051-0.093 \( \mu m \) with an \( \sigma_N \) of 1.80 +/- 0.21 resulting in VMD’s between 0.13 – 0.30 \( \mu m \). After long range transport, the NMD of accumulation mode FT Asian aerosol over the North Pacific varies between 0.080 and 0.11 \( \mu m \) with an average value of 0.10 \( \mu m \) and \( \sigma_N \) of 1.75 +/- 0.15. This results in a range of VMD’s of between 0.19 and 0.34 \( \mu m \). In the presence of dust the NMD of FT Asian aerosol varies over a wider range of values, 0.050-0.11 \( \mu m \) with a smaller average NMD of 0.075 \( \mu m \), and a \( \sigma_N \) of 1.75 +/- 0.15 resulting in VMD’s that vary between 0.13 and 0.28 \( \mu m \). Smaller geometric mean diameters and total accumulation mode volume in the presence of dust is the result of competition between supermicrometer dust and the accumulation mode aerosol for condensing semi-volatile inorganic and organic compounds [Clarke et al., 2004].

In the continental boundary layer the size distribution’s geometric mean diameter increases while the standard deviation of the distribution decreases as a function of the aging indicator, \( S_{ratio} \). This behaviour is due to condensation of volatile inorganic ions...
and volatile organic species onto the pre-existing and primary aerosol. Recently formed volatile aerosol also coagulates with the pre-existing and primary aerosol. Comparing light extinction calculated from the aging size distributions against values generated using the static OPAC parameterization shows that the OPAC distribution overestimates fresh aerosol extinction by 30%. After aging the observed and OPAC aerosol optical properties derived from size distributions are approximately equal (<10% difference). Urban/industrial plumes were also associated with supermicrometer dust. Compared to the in-situ observations, light extinction by these aerosol is under-predicted by a factor of 0.25-0.60 depending on which OPAC mineral aerosol type is employed.

Intensive aerosol optical properties such as scattering Angstrom exponent, single scatter albedo and f(RH) also evolved with the aerosol size distribution. Static parameterizations of the aerosol size distribution cannot capture these dynamics and as a result do not accurately estimate aerosol radiative forcing. These errors can be compounded by poorly simulating the wavelength dependence of absorbing species such as dust. Near their sources, dust aerosol dominate total aerosol extinction and the optical properties, however even after long range transport the submicrometer tail of the dust distribution can enhance submicrometer aerosol light absorption while simultaneously suppressing f(RH). This has important implications for both modeling the aerosol direct effect and for satellite and other remote sensor retrievals (e.g. AERONET) of ambient aerosol.

The largest error related to the aerosol direct effect occurs for pristine aerosol in the FT. The in-situ observations of aerosol volume are in good agreement with long-term averages of aerosol chemistry from the Mauna Loa Observatory in Hawaii. Based on this
comparison the best lognormal fit parameters for clean FT aerosol in the Northern 
Hemisphere are, \( N=500 \) cm\(^3\), NMD=0.040 \( \mu m \), and \( \sigma_g=2.00 \). For the internally mixed 
refractory aerosol the fit parameters are; \( N=125 \) cm\(^3\), NMD=0.025 \( \mu m \) and \( \sigma_g=1.60 \). 
These values result in total and refractory masses of 0.26 \( \mu g \) m\(^3\) and 5.0x10-3 \( \mu g \) m\(^3\), an 
RCN ratio of 0.25, and a refractory volume fraction of just 2%. Compared to the 
measured clean FT distributions, the OPAC parameterization of water soluble aerosol 
overestimated light scattering by a factor of 1.6-1.4 between 40% and 80% RH. This has 
important implications for models which are attempting to compare pre-industrial climate 
simulations to contemporary values of aerosol optical depth as they will tend to over 
predict Earth's pre-industrial FT AOD by ~50%.

Comparing campaign average values of aerosol mass and optical properties to a 
simulation by the STEM-2K3 chemical transport model indicated that errors associated 
with simulating black carbon were, in general, comparable to errors associated with 
simulating CO. Where large discrepancies did occur the data indicate it was the result of 
insufficient removal of BC mass by wet deposition in the STEM model. Simulations of 
mineral aerosol were also poor but could be improved by assigning the simulated dust 
mass to the coarse rather than fine mode, by updating the mass extinction efficiency of 
the aerosol type, and by employing a steeper vertical profile which prevents dust mass 
from being transported above the boundary layer inversion.

The biggest challenge related to modeling the direct effect of aerosols on climate 
is errors associated with the state variable water vapour mixing ratio, \( w \), which, along 
with ambient \( T \) and \( P \), define model relative humidity. The magnitude of the error in the 
driver model's relative humidity field results in uncertainties which can overwhelm the
measurement uncertainty and composition-dependent variability for the increases in light scattering as a function of RH. Thus even where global climate models accurately predict the contributions of relatively hydrophobic organic species and hydrophilic organic and ionic aerosol species to dry aerosol light scattering, their optical properties at ambient RH cannot be predicted with sufficient precision to capture the effect of the aerosols’ composition on f(RH). Improving the effects of aerosol composition on f(RH) beyond simple parameterizations (e.g. [Quinn et al., 2005]) results in little improvement in simulating ambient aerosol optical depth compared to efforts that improve simulations of ambient relative humidity. Improving water vapour mixing ratio should be considered a priority for the modeling community as its effect and the effects of sub-grid-scale variability on RH [Petch, 2001] casts considerable doubt on the fidelity of global models’ predictions of global aerosol radiative forcing.

6.2. Aerosol size distributions and the indirect effect

Accurately predicting ambient atmosphere concentrations of cloud condensation nuclei remains a challenge [Penner et al., 2006]. In Chapter 3 I summarize vertical profiles of refractory and total aerosol number in the troposphere for three distinct geographic locations. These profiles were further stratified into airmasses commonly found there. These profiles will be of use to the modeling community because they represent a testable database of vertically resolved aerosol number. These data provide an important constraint as this quantity cannot be accurately derived from satellite or ground-based (AERONET) remote sensing technologies.
In-situ airborne measurements in the clean remote MBL are in excellent agreement with other observations [Heintzenberg et al., 2000]. Supermicrometer sea salt size distributions are within a factor of 3 compared to the canonical distributions in Lewis and Schwartz, [2004]. Sea salt distributions also resolve the ultrafine seasalt mode [Clarke et al., 2006; Martensson et al., 2003] which is currently neglected by wind speed dependent parameterization and most global climate models. Static parameterizations of the marine aerosol number distribution do not accurately predict number concentrations observed in the ambient marine atmosphere. This problem is particularly acute when modeling clean background conditions in the pristine MBL. The static OPAC parameterization over predicts Aitken and accumulation mode sulfate aerosol number by a factor of 2 while underpredicting “ultrafine” seasalt aerosol by a factor of 10.

Deep convection over North America in summer results in new particle production in the upper troposphere (alt > 6 km). During aging of convective airmasses aerosol mass is conserved while number is reduced. Due primarily to coagulation, new particle number double in median diameter after 12 hours of aging while aerosol number is reduced by $1/e$ after $\sim$48 hours. As a result, this process and its effect on aerosol number in the Earth’s troposphere can only be resolved by aerosol models which simultaneously resolve both aerosol mass and number. Static parameterizations of the aerosol number distribution will not be able to simulate this process. Additionally the current OPAC parameterization of water soluble aerosol under-predicts aerosol number in the pristine FT by a factor of 2.5. This will results in too little number being entrained into the BL during subsidence and will affect the predicted number of CCN activating in BL cloud. The analysis of convected airmasses also show no evidence of in-situ
formation of refractory aerosol number. Thus the FT population of refractory CN
number appears to be controlled by convection of anthropogenically influenced air, in-
situ emissions by aircraft, and the entrainment of extraterrestrial refractory material from
the stratosphere.

An analysis of aerosol number in clean MBL conditions indicates that polluted
aerosol entraining from the FT over 1-3 days can account for the observed number
concentrations in polluted MBL airmasses. A simple analysis of this entrainment shows
that polluted FT airmasses can potentially enhance CN concentrations in the clean ENP
MBL by a factor of 2-10. More detailed analysis is warranted and should include BL
aerosol removal in order to better constrain the replenishment time and residence times
for FT aerosol after it entrains into the MBL.

6.3. Aerosol size distributions and ocean biogeochemistry

Chapter 5 summarizes the characteristics of Asian pollution and supermicrometer
dust measured in the FT over the remote Eastern North Pacific. Back trajectory analyses,
derived calcite wt%, and ratios of conservative elemental tracers all confirm the source
provenance of the supermicrometer aerosol is the arid regions of central Asia including
the Gobi desert and Chinese Loess Plateau. During transport these alkaline dust
particulate interact with the acidic gases SO₂ and HNO₃ to irreversibly form aerosol
sulfate and nitrate in excess of that which would be present in the aerosol phase in the
absence of dust. These results confirm earlier observations in the East-Asian source
regions [Jordan et al., 2003a; Jordan et al., 2003b; Kline et al., 2004] as well as
predictions using climate models [Phadnis and Carmichael, 2000; Song and Carmichael, 2001].

The INTEX-B observations over the ENP were put further into context through an analysis of the long-term (1996-2006) record from the Mauna Loa Observatory. The MLO data confirm the INTEX-B results and show that when ammonium sulfate and ammonium nitrate are accounted for, excess sulfate and nitrate increase with increasing concentrations of calcium. Both acidic gases are present in molar equivalents ratios greater than 0.15:1 but always less than 1:1. This indicates the reaction is limited not by dust aerosol alkalinity but possibly by the kinetics of gas-phase transfer to the available aerosol surface area during transport.

Finally, dry/wet deposition of Asian pollution and dust can alter the surface ocean chemistry [Doney et al., 2007] and surface ocean primary productivity [Martin, 1990]. Assuming complete removal of soluble nitrogen and dust by wet deposition, I compute a 26% increases in nitrate and a 9.5 % and 32% increase in soluble and total iron for the surface mixed layer (50 m depth) of the Eastern North Pacific subtropical gyre. For the subpolar gyre the relative increases for nitrate, soluble and total iron are <1%, 18% and 230% respectively. SeaWiFS/MODIS retrievals of surface ocean chlorophyll show a statistically significant (\( \alpha=0.05 \)) 8-9% increase over a two week period for the region bound by 20-30°N and 140-180°W. The increase in chlorophyll is also significant compared to the 2003-07 monthly averages. Visually large increases also occurred near the sea surface temperature and chlorophyll front north of 30°N, the same region where the TRMM satellite retrievals indicate precipitation and probably wet removal of the dust/pollution aerosol measured in-situ. An analysis of the increase in chlorophyll in this
subregion is not possible due to the heterogeneity induced by mesoscale eddies. A similar analysis was undertaken for the 1999 dust event sampled by Clarke et al., [2001] during the NASA PEM Tropics-B experiment. Again an 8% increase in surface ocean chlorophyll was recorded by SeaWiFS satellite retrievals for the region bound by 20-30°N and 140-180°W. Both the 2006 and 1999 events were significant at the 98th percentile for all daily night-time measurements of aerosol calcium at the Manua Loa Observatory from 1988-2006. Notably these events contain an abundance of total nitrogen \([\text{HNO}_3 (g), \text{NO}_3^- (\text{aer}), \text{NH}_4^+ (\text{aer})]\) as well as calcium, i.e. iron, indicating that anthropogenic pollution as well as mineral dust may be enhancing primary productivity in the surface waters of the Eastern North Pacific Subtropical Gyre. In order to accurately simulate glacial-interglacial, as well as contemporary and future effects of aerosol on ocean biogeochemistry, climate models will need to simulate these transport events, their heterogeneous chemical reactions, as well as their effects on ocean primary productivity.
6.4. References


Appendix A – Refereed Publications


Biomass burning and pollution aerosol over North America: Organic components and their influence on spectral optical properties and humidification response

A. Clarke,1 C. McNaughton,4 V. Kapustin,1 Y. Shinozuka,1 S. Howell,1 J. Dibb,2 J. Zhou,1 B. Anderson,3 V. Brekhovskikh,1 H. Turner,4 and M. Pinkerton1

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1. Introduction

[1] Thermal analysis of aerosol size distributions provided size resolved volatility up to temperatures of 400°C during extensive flights over North America (NA) for the INTEX/ICARTI experiment in summer 2004. Biomass burning and pollution plumes identified from trace gas measurements were evaluated for their aerosol physiochemical and optical signatures. Measurements of soluble ionic mass and refractory black carbon (BC) mass, inferred from light absorption, were combined with volatility to identify organic carbon at 400°C (VolatileOC) and the residual or refractory organic carbon, RefractoryOC. This approach characterized distinct constituent mass fractions present in biomass burning and pollution plumes every 5–10 min. Biomass burning, pollution and dust aerosol could be stratified by their combined spectral scattering and absorption properties. The "nonplume" regional aerosol exhibited properties dominated by pollution characteristics near the surface and biomass burning aloft. VolatileOC included most water-soluble organic carbon. RefractoryOC dominated enhanced shortwave absorption in plumes from Alaskan and Canadian forest fires. The mass absorption efficiency of this RefractoryOC was about 0.63 m² g⁻¹ at 470 nm and 0.09 m² g⁻¹ at 530 nm. Concurrent measurements of the humidity dependence of scattering, γ, revealed the OC component to be only weakly hygroscopic resulting in a general decrease in γ with increasing OC mass fractions. Under ambient humidity conditions, the systematic relations between physiochemical properties and γ lead to a well-constrained dependency on the absorption per unit dry mass for these plume types that may be used to challenge remotely sensed and modeled optical properties.

aerosol can absorb appreciably, particularly at shorter wavelengths [Kirchstetter et al., 2004], has refocused attention on light absorbing properties of this so-called “brown carbon” and the need for multifrequency measurements [Andreae and Gelencser, 2006]. Measurements of MAE for OC aerosol from typical sources are rare but provide an important tool for models that carry OC mass and use it to estimate aerosol optical effects.

[a] Recently, so-called Humic Like Substances (HULIS) have been suggested as a major component of absorbing OC. Humic substances include fulvic acid (water soluble), humic acid (base soluble) and humin (insoluble) components [Grabr and Rudich, 2006]. HULIS also includes both water soluble and insoluble fractions. However, most studies have focused upon the water soluble fraction or fulvic acid component and not the humic acid or insoluble humin found to be more absorbing in the shorter wavelengths [Grabr and Rudich, 2006]. These authors also suggest transformation of OC components can occur in the atmosphere over time and large uncertainties exist regarding the various sources, transformations and properties of both soluble and insoluble components. However, other fuels like lignite coal can have much more light absorbing properties than OC. Other studies have also found that burning of lignite coal can yield enhanced shortwave absorption indicative of coal tar or incompletely aromatized carbon [Bond et al., 1999b].

[b] The water uptake by aerosol must be quantified to correctly calculate or model optical effects under actual atmospheric conditions. Recent evaluations of aerosol humidity-dependent growth demonstrate the influence of OC in suppressing aerosol growth compared to that of common ionic species alone [Quinn et al., 2005]. Although OC may suppress aerosol growth, the presence of WSOC may enhance the nucleating properties of some insoluble aerosols (such as dust) and making them more effective cloud condensation nuclei [Mayol-Bracero et al., 2002b]. Hence OC properties can influence both the direct and indirect radiative effects of aerosol.

2. Aircraft Measurements
2.1. Aircraft Inlet Sampling Performance
[c] Our data is part of the extensive airborne data set from the NASA INTEX-NA experiment taken aboard the DC-8 [Singh et al., 2006]. The University of Hawaii (UH) solid diffuser inlet was used to sample in situ aerosol size distributions and optical properties aboard the NASA DC-8 [McNaughton et al., 2007]. Aerosol filter samples were measured for bulk-chemistry behind the University of New Hampshire (UNH) solid diffuser inlet. Inlet performance during the 2003 DC-8 Inlet Comparison Experiment (DICE) demonstrated that the UH and UNH inlets perform similarly while sampling both supermicrometer sea salt at high (80–95%) relative humidity and supermicrometer mineral dust in desert environments [McNaughton et al., 2007]. Comparisons with ground based instrumentation show that the UH and UNH inlets and transport system pass particles with aerodynamic diameters of 5 μm with better than 50% efficiency. Significant dust was infrequent and aerosol optical properties were typically dominated by smaller particle sizes. Hence we conclude that the DC-8 inlets effectively sampled the aerosol dominating the surface area and optical effects during INTEX-NA.

2.2. Thermally Resolved Aerosol Size Distributions
[d] A modified Particle Measurement Systems (PMS, Boulder, Colorado) laser optical particle counter (OPC, 632 nm) was used to measure the dry (RH < 30%), optically effective aerosol size distribution between 0.1 μm and 5 μm every 3 s [Clarke et al., 2004]. The He-Ne OPC laser (632 nm) detects light scattered by individual particles over 35–145°. Dry size distributions were ensured by mixing sample air with an equal flow of desiccated filtered air. This minimizes size and particle refractive index variability due to water uptake and thereby reduces OPC measurement errors. The OPC was calibrated before and during deployment using a combination of National Institute of Standards and Technology (NIST) traceable polystyrene, silica, and borosilicate glass microspheres (Duke Scientific). Since the OPC measures optically effective sizes (D_eff), the data is well suited to modeling aerosol optical properties. Linear regression of total and submicrometer scattering calculations from the size distributions compared to measured scattering values gives a slope of 0.91 and a correlation coefficient, r^2, 0.95 [Shinozuka et al., 2007].

[e] The OPC operates in series with a redesigned thermo-optical aerosol discriminator (TOAD) [Clarke, 1991] with a 400°C temperature channel added to the original 40°, 150° and 300°C (later increased to 350°C). Peak temperatures were measured by a thermocouple in the center of the airflow. The TOAD cycles between temperature channels every 30 s during horizontal flight legs. This results in thermo-optical characterization of the optically effective size range every 2 min. During vertical profiles the OPC does not cycle between temperatures. At a typical DC-8 ascent/descent rate of 450 m min⁻¹ this usually gives a vertical resolution of 25 m for submicrometer size distributions. Larger particle sizes require longer averaging due to lower count statistics.

[f] Volatility data was interpreted in conjunction with inorganic ionic compositions measured on filter samples using ion chromatography as described elsewhere [Dibb et al., 2003]. These generally limited the time periods used here as they were exposed for 5–10 min below 6 km and somewhat longer aloft. These filters were usually analyzed within 24 hours.

2.3. Aerosol Optical Properties and Humidity Dependence
[g] Total and submicrometer aerosol light scattering (σ(sp, tot), σ(sp, sub)) was measured at 450, 550, and 700 nm wavelengths using two TSI model 3563 integrating nephelometers [Anderson et al., 1996; Heintzenberg and Charlson, 1996] corrected according to [Anderson and Ogren, 1998]. The submicrometer TSI nephelometer employed a 1 μm aerodynamic impactor maintained at 30 lpm using an Alicat Scientific volumetric flow controller. Sample air residence time inside the nephelometers was less than 10 s and the instrument relative humidity (RH) is typically less than 30%. Two single-wavelength (λ = 540 nm) Radiance Research
During INTEX-NA a new three-wavelength particle soot absorption photometer (PSAP, Radiance Research) was provided by David Covert (University of Washington) to measure aerosol light absorption at 470, 530, 660 nm wavelengths. There is not yet a consensus in the literature about the best methods for correcting this new instrument for multiple scattering and loading artifacts. We have chosen to use the corrections modified for the other channels using wavelength dependence of the scattering correction factor “s” from Virkkula et al. [2005]. There is some discrepancy between these corrections and those of a 1 wavelength PSAP [Bond et al., 1999a] resulting in about 25% lower absorption than measured with single wavelength PSAPs. The reason for the discrepancy is not clear, but there are a few possibilities: the light source and optical path in the PSAP was somewhat different; the tested particles were all either nonabsorbing or very strongly absorbing, making them poor models for the high single-scatter albedo experienced during INTEX-NA; or particle loadings were much higher than we experienced. Other soot studies and comparisons are underway to resolve these differences (D. Covert, personal correspondence, unpublished results, 2006). These differences will not affect the general behavior and properties discussed in this paper.

3. INTEX-NA Plumes

Plumes from North America biomass burning sources can evolve and mix with continental pollution plumes and diffuse sources to contribute to regional pollution outflow from North America [Li et al., 2005]. Repeated encounters with diverse plumes aloft during INTEX-NA [Singh et al., 2006] provide a statistical characterization of their chemistry, physics and optical properties. Background concentrations of various signature species such as CO, O₃, NO₂, SO₂, HCN, C₃H₈, and C₂H₂ were established by dividing the measurements into 1-km altitude bins and creating vertical profiles of each species. A plume encounter was identified when one of the tracer species exceeded the 95th percentile of the measured values within a given altitude region. 84 plumes were detected this way and characterized as biomass burning (BB) or pollution (P). These plumes represent about 24 hours of flight time or about 17% of the research hours flown. The remaining measurements are referred to here as nonplume cases. In order to facilitate the classification, 10-day back trajectories were analyzed for each plume. BB plumes were associated with high levels of HCN, CO, ethyne, absorption, and CH₃CN. P plumes were associated with high concentrations of O₃, CO, alkanes, SO₂, NMHC, and ultrafine condensation nuclei (3–3000 nm). Some plumes reflect a mix of plume and nonplume air encountered over a given leg. This classification is available on the NASA INTEX-NA archive (ftp://ftp-air.larc.nasa.gov/pub/INTEXA/MERGES/DC8/1_MINUTE/). The number of data points for P and BB plumes in the following plots vary depending upon the availability of concurrent data being compared.

The spatial distribution of these plumes is shown as circles for our 60 s data collected over eastern NA superimposed on the flight tracks (thin lines, Figure 1a). The size of the circles is proportional to the 60 s average light scattering values. These plumes are also evident in flight leg average values averaged over 250 m altitude bins in
4. Thermal Analysis and Aerosol Carbon

Our thermal treatment provides information on the size-resolved volatility of the aerosol components, state of mixing and the residual refractory component remaining at the highest temperature used. Refractory materials remaining at high temperature (400°C) include dust, fly ash, black carbon (BC, soot) and some OC components. Organic and elemental carbon measurements using thermal evolved gas analysis in air provide an opportunity to examine the effects of thermal treatment on particulate carbon. It is now clear that some OC evolves over a range of temperatures that overlap those at which BC evolves [Andreae and Gelencser, 2006; Bond and Bergstrom, 2006; Mayol-Bracero et al., 2002b]. BC may oxidize at temperatures below 450°C depending upon origin, state of mixing and aging, but these references indicate that at 400°C, very little BC is lost while much of the OC is gone. Henceforth we refer to the fraction of OC lost during heating to 400°C as VolatileOC, while that remaining we identify as RefractoryOC.

[15] A common assumption has been that soot is the only significant light absorbing form of carbon in atmospheric aerosol. However, the papers above (and references therein) discuss at length how some of the aerosol OC is also light absorbing, in addition to aerosol BC, and suggest the term light absorbing carbon (LAC) for the possible mixtures of these components. Laboratory samples of lignin and humic acid (two materials believed to be similar to those found in some aerosols) were shown to have multiple peaked structure in their thermal evolution up to temperatures of 700°C [Andreae and Gelencser, 2006]. Enhanced light absorption at shorter wavelengths is characteristic of these and other HULIS such as those observed in biomass-burning aerosols over the Amazon [Hoff et al., 2005].

[16] In order to clarify our thermal approach we reference the observations shown in the papers by Kirchstetter et al. [2004] and Mayol-Bracero et al. [2002a]. Kirchstetter et al. [2004] show the thermally evolved CO₂ before and after extraction of the samples using acetone to remove acetone soluble OC. Mayol-Bracero et al. [2002a] show the change in absorption concurrent with the evolution of CO₂. These measurements include biomass burning, pollution and diesel exhaust. Peaks in evolved CO₂ as a function of temperature correspond, in diesel exhaust cases, with light absorbing aerosol near 400–500°C. Diesel soot is a common LAC that is high in BC and it has been found to combust over a narrow temperature range between 470°C and 510°C [Wittmaack, 2005]. However, there is evidence that mixing with other inorganic species and aerosol aging can catalyze oxidation [Andreae and Gelencser, 2006] and shift thermal evolution to lower temperatures by as much as 100°C [Novakov and Corrigan, 1995] in response to the presence of metals such as Na⁺ or K⁺. These diverse measurements demonstrate that OC can evolve at many temperatures including those associated with BC (a) and that the temperature where absorbing BC can evolve can vary with sources, composition, state of mixing, trace metals etc.

5. Aerosol Composition and Thermal Volatility

[17] Our thermal analysis of volatility [Clarke et al., 2004] was originally developed for clean marine regions where sea salt, sulfates and low mass fractions (ca. 15%) of organic components typically characterize the aerosol [Clarke, 1991]. Recent development of fast measurements (ca. 1 min) of soluble ions [Weber et al., 2001] enabled us to extend our interpretation of volatility to the more chemically complex aerosols in polluted areas [Clarke et al., 2004; Howell et al., 2006b].

[18] Although BB and P plumes (Figure 1) are identified primarily by gas phase measurements, the plumes also differ in aerosol properties, including their volatility. Figure 2
shows examples of the effect of thermal heating to 40°C, 150°C, 360°C and 400°C on the volume distributions for a representative P and BB plumes. In this paper only unheated and 400°C heated volumes will be used. For the remainder of this paper, aerosol mass fractions derived from the thermally resolved size distributions are based on the following assumptions.

[19] 1. Accumulation mode pollution aerosol is internally mixed, as generally observed after several hours of aging using our thermal Tandem Differential Mobility Analyzer (unpublished INTEX-NA data) and in other polluted regions [Clarke et al., 2004].

[20] 2. Supermicron particles contain little of the soluble inorganic ions. The nephelometers showed that coarse particles contributed significantly to less than 10% of the time during INTEX-NA and absorption was dominated by small particles.

[21] 3. Particulate volumes calculated from OPC size distributions are representative. Optical sizing errors are primarily due to refractive index differences between the sampled particles and the calibration spheres (which have n = 1.588). As mentioned above, the desiccated dilution air serves to reduce water in the particles, increasing refractive index but reducing its variability, both of which suppress sizing errors. Remote sensing of biomass plumes over the east coast yielded a refractive index of 1.55 at 670 nm [Colarco et al., 2004] and 1.54 for Indian pollution [Müller et al., 2003] at 532 nm. Hence, since particle refractive index probably remained below 1.588 for normal pollution, OPC volumes may be systematically underestimated. Good agreement (within about 10%) between scattering calculated from size distributions and measured by nephelometers [Shinozuka et al., 2007] provides confidence that the size distributions are realistic and we expect calculated volumes to be no more than 20% low. This would make little difference in the arguments that follow.

[22] 4. Submicrometer aerosol components volatile below 400°C include all measured soluble ions [Dibb et al., 2003] along with any volatile organic carbon (VolatileOC). We estimate VolatileOC mass by subtracting the volume of measured ions from total volume and assigning a density of 1.3 g cm$^{-3}$ for the remaining VolatileOC volume. This is based on a suggested range of 1.2 to 1.4 g cm$^{-3}$ for organic aerosol [Stelson, 1999; Turpin and Lim, 2001] and a reported value of 1.4 g cm$^{-3}$ for biomass smoke [Reid et al., 2005]. We expect the VolatileOC density to be less than that of BC and RefractoryOC in smoke.

[23] 5. Aerosol volume (mass) remaining at 400°C includes refractory organic carbon (RefractoryOC) and absorbing black carbon (BC). The BC inferred from absorption (InferredBC) is based on a nominal mass absorption efficiency (MAE) of 10 m$^2$ g$^{-1}$ at 550 nm. We have argued previously for a value near 7.5 m$^2$ g$^{-1}$ at 550 nm [Clarke et al., 2004], consistent with a recent survey of likely values [Bond and Bergstrom, 2006]. However, we use the higher value here in order to allow for a possible optical enhancement due to other internally mixed components [Bond et al., 2006; Fuller et al., 1999]. As shown below, the relative mass of BC is small so the resulting uncertainty has little effect on inferred OC.

[24] 6. We use volume based mixing rules with component densities of 1.8 g cm$^{-3}$ for the refractory BC [Fuller et al., 1999]. We are not aware of density data for RefractoryOC and use a value of 1.5 g cm$^{-3}$ for bulk HULIS [Hoffer et al., 2004] as we expect RefractoryOC density to be greater than VolatileOC but less than BC.

[25] 7. We use a mean density of inorganic components of about 1.75 g cm$^{-3}$ [McMurry et al., 2002; Stelson, 1990] and assume any potential interaction between mixed components does not influence their effective density.

[26] 8. RefractoryOC volume is computed as the volume remaining at 400°C less the volume of inferred BC (i.e., area under the black curve in Figure 2 less the volume of inferred BC).

[27] In this manner we resolve the accumulation mode into inorganic, VolatileOC, RefractoryOC, and BC mass. If coarse dust or fly ash had been a common contributor then additional procedures could be implemented to extract these components based upon their size distributions [Clarke et al., 2004] but neither were identified as important during INTEX-NA. We do not include the possible changes in refractive index for heated OPC sizes arising because of volatilizing some components.

[28] The results of this procedure for examples of elevated P and BB size distributions reveal marked differences and are illustrated for two cases here as pie charts in Figure 2. The inferred P aerosol dry mass is dominated by soluble inorganic ions (79%) with about 16% VolatileOC and 4% RefractoryOC. The estimated BC is only 2% of the mass and confirms the choice of MAE for BC has little impact on determination of other constituents. The inferred BB mass fractions are quite different from those of P. The BB inorganic fraction of 22% is about a factor of 4 lower than P; VolatileOC at 58% (factor of 3 higher) and RefractoryOC at 18% (a factor of 4 higher). Inferred BC remains a small fraction of the total mass at 3%.

[29] We apply this approach to all thermally resolved size data for which corresponding inorganic and BC estimates are available. These are stratified into BB and P categories based upon the trace gas analysis described earlier. Statistically representative composition and properties are constructed for P and BB plumes and the nonplume data. Figure 3 shows histograms of the accumulation mode mass fractions of ions, VolatileOC, RefractoryOC, Inferred BC and γ for the BB, P and nonplume cases. The differences for P and BB illustrated in Figure 2 are consistent with these histograms although there is clearly variability within each plume class. This reflects both variability in plume composition and that of the preexisting aerosol into which the plumes are mixed.

[30] The largest differences in BB and P mass fractions are for ions that dominate the mass fraction of P plumes. VolatileOC and RefractoryOC together dominate BB plumes. The typical values for BB are similar to mass fractions reported for BB in Africa [Haywood et al., 2003] of 5%BC, 70%OC and 25% inorganic. Visual inspection of the nonplume histograms suggest a BB influence in approximately 20% of the data, indicating that pollution was the dominant contributor to regional aerosol properties during INTEX-NA. These differences in chemical composition are responsible for the large difference in the measured γ, or water uptake, evident in Figure 3 for the BB and P cases.
In-flight side-by-side comparisons of CO measurements on both aircraft differed by less than 2\% making it a convenient reference.

[32] We reproduce the Sullivan et al. [2006] data here in Figure 4a originally reported as WSOC $\mu$gC m$^{-3}$ for non-biomass-burning sources (grey stars, P and nonplume data) and their four BB cases (blue stars) below 2 km versus measured CO. In order to compare to their data in Figure 4a we have multiplied their carbon concentrations by 2.1 [Turpin and Lim, 2001] to account for the noncarbon organic mass. This allows direct comparison with our plotted VolatileOC in $\mu$g m$^{-3}$ (for estimated density of 1.3 g cm$^{-2}$) against fast CO measured on the DC-8 below 2 km [Sachse et al., 1987]. Our data for BB (blue), P (red)
and background (grey) clearly overlay the Sullivan et al. [2006] data and show the same trend of higher values for BB cases. For clarity, Figure 4b shows the regression lines and 95% predictability limits separately for the various data and the associated statistics are included in Table 1. We note that the scatter in our data, the overall data distribution, the slopes and the grouping of near zero VolatileOC for CO values over 100–150 ppbv are very similar to the WSOC data of Sullivan et al. [2006].

Table 1. Statistics for Line Fits in Figure 4a

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>R²</th>
<th>Std. Dev.</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volatile OC = A + B* CO (Figures 4a and 4b)</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>2.1 * Sullivan et al. [2006] &quot;P + Background&quot;</td>
<td>−4.05 ± 0.22</td>
<td>0.053 ± 0.001</td>
<td>0.53</td>
<td>1.77</td>
<td>1271</td>
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<tr>
<td>P plumes</td>
<td>−7.88 ± 1.31</td>
<td>0.072 ± 0.007</td>
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<td>89</td>
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<td>BB plumes</td>
<td>−10.04 ± 0.65</td>
<td>0.091 ± 0.003</td>
<td>0.96</td>
<td>1.31</td>
<td>27</td>
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<td>Background</td>
<td>−5.06 ± 0.36</td>
<td>0.053±0.003</td>
<td>0.58</td>
<td>1.10</td>
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<tr>
<td>Refractory OC = A + B* CO (Figure 4c)</td>
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</tr>
<tr>
<td>P plumes</td>
<td>−0.98 ± 0.07</td>
<td>0.010 ± 0.004</td>
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<tr>
<td>BB plumes</td>
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<td>0.034 ± 0.002</td>
<td>0.90</td>
<td>0.75</td>
<td>36</td>
</tr>
</tbody>
</table>

A, intercept and uncertainty; B, slope and uncertainty; R², correlation coefficient; Std. Dev., standard deviation; N, number of points.

As described earlier, this comparison required various assumptions including the density and refractive index for our OPC size data as well as density values for the indicated OC components. Moreover, these data were collected on separate aircraft sampling a large region with different objectives. This makes it difficult to establish a quantitative evaluation in spite of these similar relationships. However, we note that VolatileOC is the second most dominant component after ions for our P and nonplume cases (Figure 4) which together correspond to the Sullivan et al. [2006] non-BB cases. Hence a dominant fraction of what we report as VolatileOC must be their reported WSOC.

Figure 4c shows our RefractoryOC has a distinct relation to CO for P and BB plumes with about four times as much RefractoryOC per CO concentration evident in the latter. Flight legs with encounters of both P and BB plumes (so-called mixed plumes) also show RefractoryOC elevated relative to P plumes. VolatileOC for BB plumes is the dominant component (see Figure 4) and its concentration relative to CO is similar to WSOC in these plumes (Figure 4). This suggests most RefractoryOC in BB plumes (Figure 4b) includes insoluble OC, in contrast to a more soluble refractory component for BB plumes in the Amazon [Mayol-Bracero et al., 2002b]. Given the smaller amount of RefractoryOC in P plumes compared to VolatileOC (Figure 4) it is not clear to what extent the RefractoryOC is water soluble.

Because VolatileOC appears dominated by WSOC and makes up most of the OC we can explore its relationship to the total ion mass fraction. In Figures 5a and 5b, γ is plotted versus the total ion mass fraction for BB plumes. In Figures 5a and 5b, γ is clearly different for the P and BB cases but shows no clear relation to the VolatileOC fraction. Even though VolatileOC is a larger fraction of total mass in BB plumes (Figures 2 and 4) the values for γ are actually lower for these plumes, indicating it is only weakly hygroscopic.

We note that the PILS assessment of WSOC is under dilute conditions with significant time for dissolution and, though soluble, it is not indicative of rapid hygroscopic growth under concentrated conditions. Figure 5b shows γ is significantly related (R² = 0.34) to the ion mass fraction for the background data. The P data shares this dependency while BB data has generally lower γ for a given ion fraction. A plot of γ against the TotalOC fraction of accumulation mode mass (Figure 5c), clearly shows that RefractoryOC and VolatileOC both tend to reduce γ (R² = 0.35) as they become a larger fraction of the total aerosol mass. This confirms that the relationship found for surface
A plot of absorption measured at 470 nm against absorption at 660 nm (Figure 6) for all the data clearly reveals an enhanced absorption for BB plumes in the shorter wavelengths, consistent with other measurements on BB aerosol [Kirchstetter et al., 2004]. The tight relationship in this dependency for BB plumes confirms instrument stability for both wavelengths and implies that the greater scatter evident for P plumes is due to more variable spectral response, presumably related to a more variable physico-chemistry. Histograms of this wavelength dependence for these plumes are also shown for P, BB and nonplume data. We find that $\alpha_{660}$ for P is commonly near 1.1 and close to the 1.0 expected for absorbing particles that are small compared to the wavelength but consistent with values (0.7–1.1) observed elsewhere for pollution aerosol [Kirchstetter et al., 2004]. Values of $\alpha_{660}$ for BB peak near 2.1 and are consistent with the range of 1.2–2.2 reported by the same author for African biomass smoke. The regional nonplume cases (Figure 6c) clearly show a distribution of $\alpha_{660}$ values peaking near 1.3 and with a spread suggesting a dominant P aerosol with some BB influences, also evident in the mass fraction histograms (Figure 3).

The steeper wavelength dependence for BB is related to the enhanced organic fraction in the BB aerosol (Figure 3). It is of interest to determine whether the volatile
or refractory organic carbon species are most responsible for the steeper wavelength dependence (Figure 7a). To do this we define BC mass as that derived using the thermal volatility, estimated BC mass from light absorption and ionic mass provide estimates of VolatileOC and RefractoryOC. These OC components comprise about 30% ± 10% of pollution plumes and about 80% ± 10% of biomass burning aerosol in plumes measured over North America during INTEX-NA. Both OC components suppressed relative light scattering (aerosol growth) under increasing humidity as their mass fractions increased. VolatileOC was shown to be related to WSOC while RefractoryOC appears to account for most enhanced absorption at shorter wavelengths in BB over North America. Hence the absorption properties of the RefractoryOC component are important to determine. Because the mass of RefractoryOC is distributed over a well-defined size range (Figure 2), it is useful to establish the mass absorption efficiency (MAE) of this component as this allows calculation of absorption from the relevant OC mass measured or present in the models.

We estimate the MAE of RefractoryOC by recognizing absorption at 660 nm is dominated by BC and OC generally contributes a negligible amount at this wavelength [Hoffer et al., 2005; Kirchstetter et al., 2004]. We account for the BC absorption at shorter wavelengths by applying a $\lambda^{-1}$ dependence for the P plumes dominated by absorbing BC (Figure 6b). If we assume the BC component in BB plumes absorbs with this wavelength dependence then the BC contribution to absorption can be estimated for all wavelengths. When subtracted from total BB absorption measured at 530 nm and 470 nm this leaves an absorption enhancement ($\Delta \sigma_{ap}$) due to OC. On the basis of Figure 7a we argue that this is primarily due to the RefractoryOC.

The resulting $\Delta \sigma_{ap}$ data for BB plumes are shown versus RefractoryOC mass in Figure 7b. The linear slope for $\Delta \sigma_{ap}$ versus RefractoryOC mass defines the MAE at 470 nm with a value of 0.63 m$^2$ g$^{-1}$ while at 530 nm it drops to 0.09 m$^2$ g$^{-1}$. These values are small compared to the MAE for BC but the RefractoryOC present in BB aerosol can be ten times the mass of BC (Figure 3). In such cases the RefractoryOC will have about 10–15% of BC absorption at 530 nm but may equal that of BC at 450 nm. The effect of adding increasing RefOC to BC is shown as a heavy black dashed line for BB in Figure 7a where the absorption values in equation (2a) have been replaced with the product of the relative mass of BC and RefOC and their respective MAE. Clearly, the line fit using the BB value for MAE does not represent the Pollution data. If a lower MAE of 0.25 is arbitrarily taken for the absorption by RefOC for Pollution we get the dotted curve that better matches the Pollution data. Hence this suggests lower values in general for the MAE of this component in pollution plumes. There is no reason MAE for the refractory OC of P aerosol should be the same as the BB value.

[3] These MAE values are based upon the 3-3 PSAP absorption, OPC volumes and the assumed density of 1.8 g cm$^{-3}$. While the latter are reasonable their possible
uncertainty could possibly bias these estimates by as much as 20%. We also note that our RefractoryOC is operationally defined based upon the 400°C temperature separation discussed earlier. Hence the absorbing OC component may have a mass somewhat larger or smaller than we estimate here depending upon its thermal behavior near 400°C as well as possible volatility of nonabsorbing components near this temperature. This thermal behavior is also likely to depend in a complex way upon fuel type and combustion conditions, as in the case of coal [e.g., Bond et al., 1999b; Bond et al., 2002]. Furthermore, we have treated RefractoryOC here as a separable component from BC but it is likely to be a primary emission that is absorbing and mixed with the BC at the source. As such, it may act to enhance BC absorption and/or “shield” some of the encapsulated BC from the full intensity of incident radiation [Fuller et al., 1999]. Understanding such effects will require careful modeling of the effective absorption of the combined mixture.

The wavelength dependence of scattering, $\alpha_{ap}$, is closely coupled to the size distribution. The examples of BB and P plumes shown in Figure 2 reveal BB plume aerosol sizes to be larger. If this is typical of aged BB sources, then BB plumes should be distinguishable not only by their absorption Angstrom coefficient but also their $\alpha_{ap}$. This is evident in Figure 8a where these coefficients are plotted against each other and show a clustering of the BB and P cases. The few cases of $\alpha_{ap}$ below 1.0 are due in part to low absorption values (obtained from a differential measurement) and the influence of pressure and RH fluctuations on PSAP measurements. These data include $\sigma_{ap}$ values as low as 0.2 Mm$^{-1}$ that can have large uncertainties. However, after raising the threshold to 3 Mm$^{-1}$ (not shown) the cluster behavior evident here remained unchanged although many outliers were appreciably reduced. This clustering follows form the larger size (smaller scattering Angstrom) and enhanced shortwave absorption (larger $\alpha_{ap}$) of BB plumes relative to P. However, some apparent P data appear to be exceptions and are circled.

In Figure 8b, the same data is color coded by the measured ion Ca/so$_{4}$ ratio whenever this ion data was available. Circled data are clearly most enhanced in Ca/so$_{4}$ and all occurred during Flight 18 over the Gulf of Mexico in an air mass coming from the south. Enhanced coarse particle volume (OPC) and coarse scattering (not shown) also confirmed the presence of a mixture of coarse dust and pollution for these cases. Increasing dust concentration lowers the $\alpha_{ap}$ [Clarke et al., 2004] and dust has enhanced absorption at short wavelengths that exceeds those of RefractoryOC [Patterson, 1981]. Hence the observed behavior of these circled points makes sense and demonstrates the value of these spectral signatures for identifying aerosol types and their mixtures.

The color gradient in $\alpha_{ap}$ within the dense P cluster in Figure 8b also reveals an elevated Ca/so$_{4}$ ratio but the high $\alpha_{ap}$ above 2 indicates small particles and not dust. However, this is consistent with the high Ca/so$_{4}$ ratio present in coal fired power plants in the eastern USA [Anderson et al., 2002] and the measured fugitive emissions from such plants that often peak at sizes near 0.3 $\mu$m [Mohr et al., 1996]. The displacement of this cluster from the nearby $\alpha_{ap}$ values having a $\lambda^{-1}$ dependency characteristic of BC (cluster of blue points), probably represents the influence of brown LAC on the wavelength dependence of absorption in coal combustion plumes [Bond et al., 1999b].

These intensive aerosol optical properties and their link to physiochemistry and $\gamma$ also influence ambient values of the aerosol single scattering albedo. Although SSA is often reported for measured dry aerosol, the ambient SSA of “wet” aerosol is essential for modeling atmospheric radiative effects and interpreting remotely sensed products. Here we show how systematic differences in size, composition and $\gamma$ for the BB and P plumes lead to variability in ambient SSA. In this evaluation we assume absorbing properties are not affected by water uptake [Nessler et al., 2005].

The mean accumulation mode aerosol size can be expressed as an effective volume mean diameter defined by the ratio of measured OPC accumulation mode volume (Vacc) to accumulation mode number (Nace) [Seinfeld, 1986]. Figure 9a shows the dry SSA versus the aerosol absorption (530 nm) and color coded with this effective diameter. A “rainbow” effect for a given absorption value reveals that dry SSA depends on size and not just absorption. The horizontal spread of data points for BB plumes with larger size (blue) shows that SSA is constant for this aerosol over a large range in absorption. This implies scattering and absorption scale together in these BB plumes while effective particle size remains the similar.

Figure 8. (a) Plot of the wavelength dependence of scattering against the wavelength dependence of absorption for P and BB plumes with anomalous P plumes circled. (b) Same as Figure 8a only color coded with Ca/so$_{4}$ (relative units) revealing probable influence of coal fired emissions (colored cluster) and elevated dust contributions (circled) (see text). Grey points mean no Ca or so$_{4}$ available.
Figure 9. (a) Dry SSA versus absorption color coded with accumulation mode effective mean diameter (Dmean) revealing generally steeper slopes for smaller sizes (red) with a larger absorption to scattering. (b) Dry SSA versus MAEacc revealing "rainbow" showing a clear effect of size on dry SSA (see text). (c) Same as Figure 9b only color coded with Scattering Angstrom as a size index and (d) same as Figure 9c only SSA recalculated for ambient humidity and color coded by plume type.

The accumulation mode SSA can be written as $(1 + \text{MAEacc}/\text{MSEacc})^{-1}$ [Clarke et al., 2004] where MAEacc and MSEacc are for the accumulation mode only. For a monodisperse aerosol with an increasing absorbing component this would lead to a simple inverse dependency of SSA on MAE because the MSE will vary weakly with changes in MAE. However, MSE is quite sensitive to size such that the slope of this dependency will be influenced by the MSE through changes in effective size. In Figure 9b we plot dry SSA against the absorption per unit mass of the accumulation mode, MAEacc. This "collapses" the BB data points and "tightens" the spread of the data while preserving and enhancing the "rainbow" effect. For a given color (i.e., indicated effective diameter) an increase in MAEacc results in the expected reduction in SSA. The strongest dependency (steepest slope) is evident for the smallest sizes (red). This dependency is clear if one considers the range of SSA for particles with a particular absorption per mass (say 0.5 m² g⁻¹). These exhibit a dry SSA from about 0.87 to 0.97 as their effective size increases from about 0.15 to 0.4 μm. Because the scattering Angström exponent is more conventionally measured and can be sensed remotely as a size indicator (lower values indicating larger sizes, ref.) we show that it has a similar rainbow effect in Figure 9c.

All of the plots in Figures 9a–9c are for the dry aerosol. However, we are most interested in the behavior of SSA under ambient conditions, SSA_{ambient}. This is shown in Figure 9d where we have recalculated the scattering at ambient RH based upon our measured γ. The greatest increase in SSA_{ambient} is for the smaller sizes with lower dry SSA. This is in part because for a given composition or humidity-dependent diameter change, g(RH), the smaller accumulation mode sizes have significantly higher γ [Howell et al., 2006b]. Also, the largest accumulation mode aerosol in INTEX-NA were measured in the BB plumes (Figure 2) having the largest OC fraction and the lowest γ (Figure 2). Both considerations imply that, for a given absorption per unit mass, SSA_{ambient} increases more relative to SSA_{dry} for the smallest sizes with the largest ion fractions and changes least for the largest sizes with the lowest ion fraction. Although these dependencies are expected, the most common values are difficult to predict because of the range of
aerosol sizes, hygroscopic components, refractory constituents as well as their distributions relative to altitude (and relative humidity). Hence Figure 8d provides a representative empirical assessment of SSA_{ambient} and its relation to the absorption per unit aerosol mass over North America.

[51] These data reflect the intersection of large-scale aerosol fields and hygroscopic fields over NA during summer of 2004. Both fields may change over time or may be quite different in other regions. However, to the extent that these INTEX-NA measurements are representative of aerosol over North America, this observation is promising for models that use MSExcc, MAExcc, aerosol mass and RH to calculate ambient aerosol extinction and SSA. Figure 9d suggests the range of SSA_{ambient} simulated by a model can be constrained by the regressions indicated for P and BB plumes. Models that include the absorbing aerosol component and the accumulation mode mass should obtain typical ambient SSA values indicated in Figure 9d. The results also indicate that, for the same absorption per unit mass, P plumes will have a somewhat lower SSA_{ambient} values than BB plumes. The lower correlation coefficient indicated for the BB plumes is a result of the fewer data points and the greater scatter at large MAExcc for these cases.

8. Conclusion

[52] Thermal volatility of dry size distributions was used in conjunction with concurrent measured ion concentrations, BC mass estimated from measured light absorption and realistic density values to provide estimates of the OC mass concentration by difference. Heating to 400°C is effective at separating out a more volatile and refractory organic component. The relation between VolatileOC and OC was shown to be similar to that for water soluble OC (WSOC) measured on the NOAA P-3 B during the same campaign, indicating that these are likely dominated by the same OC species. On the other hand, the RefractoryOC remaining at 400°C was the OC component that exhibited the short wavelength enhancement in absorption characteristic of biomass burning aerosol. It is likely that many of these condensed out near the source at temperatures above 400°C and constitute a primary emission component. The same is probably true for some of the aromatics in pollution aerosol that yield enhanced shortwave absorption [Bond et al., 1999b; Schnatter et al., 2006]. Enhanced shortwave absorption was not evident for the VolatileOC fraction presumably dominated by secondary aerosol formation at ambient temperatures.

[53] This rapid in situ thermal technique characterized the OC aerosol mass related fundamental physiochemical properties. This provided a surrogate OC measurement for INTEX-NA as no measurements of aerosol OC were available on the DC-8. Statistically significant differences in mass fractions of ions, VolatileOC, RefractoryOC, and BC were obtained for biomass (BB) and pollution plumes (P) independently identified by trace gases. These differences resulted in less growth under increasing RH for BB plumes due to their larger OC mass fractions. Comparison of P and BB plume properties with nonplume data (regional background) showed the latter was more strongly influenced by P and BB emissions below about 2 km but BB plumes had a greater contribution above that altitude.

[54] Multiwavelength measurements of absorption and scattering coefficients distinguished BB, P and dust influenced plumes. The absorption Angström coefficient (470–660 nm) for BB plumes had a value centered about 2.1 while that of P plumes was often near 1. Most data driving this value above 1.0 for P aerosol had an enhanced Ca/SO₄ ratio suggestive of coal fired boiler emissions. This implies absorbing RefractoryOC is also emitted from this source. Shortwave absorption in BB plumes was enhanced over that expected for BC and increased with RefractoryOC. The slope of this dependency for BB yielded a mass absorption efficiency, MAE, for this OC component of about 0.63 m² g⁻¹ at 470 nm and dropping to 0.09 m² g⁻¹ at 530 nm. The latter is about three times the value reported for HULIS in bulk samples at 532 nm [Hoffer et al., 2004] and described by these authors as being a lower limit compared to the aerosol phase. For these BB aerosols the fraction of total absorption due to RefractoryOC was comparable in magnitude to BC at 470 nm but on the order of 10% of BC at 530 nm. Refractory OC associated with P cases was a smaller fraction of mass and more variable but appeared to have a lower MAE than BB by a factor of two or so.

[55] The RH dependence of light scattering expressed as γ was shown to depend upon composition and size in ways that were linked to spectral optical properties and chemistry, including the OC component. Smaller but more absorbing aerosol in pollution exhibited the largest values for γ while the BB aerosol exhibited the lowest γ. Under ambient RH the SSA_{ambient} depended upon absorption per unit mass and the identified regressions for P and BB plumes provide useful constraints for model values of ambient SSA.

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References


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Results from the DC-8 Inlet Characterization Experiment (DICE): Airborne Versus Surface Sampling of Mineral Dust and Sea Salt Aerosols

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INTRODUCTION

Sea-salt and mineral dusts are primary aerosols generated mechanically during air-sea interactions and land surface processes (i.e., aeolian erosion). Though low in particle number, these aerosols can dominate the aerosol surface area and volume distributions and on a mass basis have the highest global emission rate (Tg yr−1) of all aerosol species (Raes et al. 2000). Despite the vast surface area of the world oceans, the effective removal of sea salt aerosols by wet deposition typically confines these aerosols to the marine boundary layer (MBL). Mineral dust from the Sahara (Haywood et al. 2001; Reid et al. 2003; Reid et al. 2003b), from Asia (Clarke et al. 2001; Husar et al. 2001), and from continental North America (Yalbot et al. 1998) has been sampled by aircraft at altitudes as high as 12 km.

Recent collaborative multi-national, inter-agency experiments such as ACE-1, PEM-Tropics A & B, INDIOEX, ACE-Asia, and TRACE-P have included airborne in-situ measurements of aerosol optical, chemical, and microphysical properties (Bates et al. 1998; Hoell et al. 1999; Huiebert et al. 2003; Jacob et al. 2002; Ramanathan 2001; Raper et al. 2001). These data sets are used to characterize aerosol sources/sinks, to initialize and evaluate chemical transport models (CTMs), to quantify aerosol direct and indirect radiative effects, and to validate satellite retrievals of aerosol optical properties. Use of the airborne observations in these types of investigations requires accurate determination of aerosol properties over a broad range of particle diameters. Aspiration of supermicrometer (Dp >
1.0 μm) particles into high velocity sampling platforms is a significant challenge because of inertial and turbulent losses of the particles within the sampling inlets and carrier tubing (Sheridan and Norton 1998; Wendisch et al. 2004). This difficulty has been known for some time (Huebert et al. 1990) and has stimulated a number of experiments designed to evaluate the magnitude of large particle losses and the efficiency of both active and passive airborne sampling systems (Blomquist et al. 2001; Huebert et al. 2004; Murphy and Schein 1998; Porter et al. 1992). Results from these experiments have shown that discrepancies can exist not only between ground based and airborne sampling systems (Dibb et al. 2002) but also between aircraft flying wingtip-to-wingtip and employing nearly identical instrumentation behind similar inlets (Moore et al. 2004).

NASA sponsored the DC-8 Inlet Characterization Experiment (DICE) in order to characterize the transmission efficiency of aerosol inlets that would potentially be deployed aboard aircraft during the Intertropical Transport and Chemistry Experiment (INTTEX-NA) as well as to investigate measurement discrepancies identified between the NASA DC-8 and NASA P-3B during the TRACE-P mission (Moore et al. 2004). Flights were based out of NASA’s Dryden Flight Research Center at Edwards Air Force Base, CA, during May/June 2003. DICE was undertaken to address the following specific questions:

- Does inlet-specific performance compromise our ability to establish submicrometer and supermicrometer aerosol optical properties?
- How do our sampling limitations impact our ability to quantify submicrometer and supermicrometer aerosol surface area and mass?
- What are the size dependent differences of the DC-8 inlet systems?
- How do these differences vary as a function of altitude, air speed, aircraft attitude (pitch, roll, yaw), ambient relative humidity, and aerodynamic type?
- Whether an actively controlled low turbulence inlet (LTI, Wilson et al. 2004)) would significantly improve assessment of aerosol surface area or optical properties aboard the NASA DC-8?

DICE instrumentation and flight plans were designed to acquire data over a broad range of aerosol types and sizes within both dry and humid air masses. In this report we focus on quantifying:

- Differences in submicrometer and supermicrometer optical properties measured behind the UH inlet compared to those measured at a ground based station at Edwards Air Force Base (EDW), California and the NOAA/ESRL Coastal Observatory at Trinidad Head (THD), California.
- Differences between supermicrometer aerodynamic size distributions measured behind each of the inlets compared to those measured on the ground at EDW (an environment dominated by mineral dust).
- Inter-inlet differences for supermicrometer scattering and the aerosol size distribution when coarse mode scattering is dominated by mineral dust or sea salt.

Inlets

Ground based measurements of aerosol optical properties and size distributions were conducted on top of the air traffic control tower at Edwards Air Force Base. The EDW ground-station’s omni-directional aluminum inlet, modeled after Liu et al. (1983) without a 10 μm impactor, quantitatively sampled aerosols up to 10 μm diameter and has approximately a 50% sampling efficiency for 15 μm diameter particles in wind speeds at least up to 7 m s⁻¹ (Maring et al. 2000). Ground based measurements of marine aerosol optical properties were conducted at the NOAA/ESRL Observatory at Trinidad Head, California. The 50% sampling efficiency is calculated at 8 μm aerodynamic diameter for light to moderate winds (J. Ogren, personal communication).

University of Hawai‘i Shrouded Solid Diffuser Inlet

The University of Hawai‘i shrouded solid diffuser inlet was designed by Dr. Antony Clarke and used aboard the NASA P3-B during PEM-Tropics A & B and TRACE-P (Clarke et al. 2004; Moore et al. 2005). It was designed for a nominal volumetric flow rate of 100 lpm and features a shrouded constant-area flow region around the inlet; a 4.5-degree diffuser half-angle and, a 3.8 cm (inner diameter) tube with the largest possible radius of curvature to complete a 45 degree bend to bring the air into the fuselage (Table 1 and Figure 1a). Spacer rings (not shown) at the base of the shroud can be inserted to adjust the shroud position and the cross sectional area between the shroud and the tip face. The inlet tip has a minimum diameter of 5.13 mm with a curved leading edge (0.25 mm radius) to reduce flow separation at the tip. During the DICE experiment the inlet was tilted down six degrees from horizontal to facilitate iso-axial sampling. This offset is based on the modeled flow field for the DC-8 fuselage during normal flight speeds and pitch. During DICE the bracing window plate was also fitted with a wind vane in order to qualitatively evaluate the degree of iso-axial sampling. The system has since been upgraded to electronically evaluate iso-axial sampling with 0.25° precision.

Previously, Huebert et al. (2004) have shown that the University of Hawai‘i shrouded solid diffuser inlet (UH-SDI in Huebert et al.) performs far better than the community aerosol inlet (CAD) deployed aboard the NCA R C-130 during INDOEX and the ACE-1 experiments (Blomquist et al., 2001). Figure 12 of Huebert et al. (2004) indicates that the ratios of silicate mass passed by the UH inlet (UH-SDI) compared to the uncorrected low turbulence inlet (LTI) was within the values expected for LTI.
enhancement effects for up to 10 \( \mu \)m. Calculating LTI enhancements for marine aerosol is more difficult by the hygroscopic nature of sea salt under ambient conditions (i.e., RH > 40%). Thus the ratio of marine aerosol mass measured by the UH solid diffuser compared to the LTI is more difficult to assess. Nevertheless the Huebert et al. result indicates a 50% passing efficiency (w.r.t. uncorrected LTI) of dry diameters in the 3–4 \( \mu \)m range. During PELTI no direct intercomparison with ground or ship-based measurements of aerosol optical properties or size distributions was possible. As a result, it was impossible to independently measure the optical properties and size distribution of the ambient aerosol from a surface platform in order to ascertain the absolute passing efficiencies of the airborne active and passive inlet systems.

**NASA Langley Research Center Small Shrouded Diffuser Inlet**

The LaRC inlet (Figure 1b) is a scaled-down version of the University of New Hampshire shrouded diffuser inlet (Figure 1c) described below. It has an inlet tip diameter of 3.35 mm, a diffuser half-angle of 7\(^\circ\) and expands to a transport tube diameter of 25.4 mm (Table 1). The inlet mates to a standard, window-mounted gas-sampling probe with an inner diameter of 22 mm and a 20 cm radius of curvature to complete a 70\(^\circ\) bend into the aircraft cabin. The inner surface of the gas probe was expanded at a 20\(^\circ\) angle to a 25.4 mm diameter to seamlessly mate with the aerosol inlet diffuser. Inlet flows were monitored with a 0–100 lpm mass flow meter located just upstream of the system’s venturi exhaust port. Excess flow was adjusted manually to maintain the tip flow velocity within 10% of the aircraft true air speed. At a typical DC-8 air speed of 180 m s\(^{-1}\) under isokinetic sampling, the inlet system reduces the flow velocity by a factor of 57 and provides 95 liters per minute of volumetric flow. Constructed for use measuring aerosol scattering and absorption properties aboard the DC-8 aircraft during the TRACE-P field deployment (Jordan et al. 2003a), the inlet was subsequently used aboard the NASA aircraft to support aerosol optical property and soot mass measurements during SOLVE-D. During DICE it was mounted in the same window position, but on the opposite side of the aircraft as the UH inlet.

**University of New Hampshire Shrouded Diffuser Inlets**

The University of New Hampshire (UNH) shrouded diffusers were based on preliminary design of Dr. Robert Talbot used aboard the NASA Electra during the ABLE campaign. Dr. Talbot and engineers at NASA Ames redesigned the inlets prior to their deployment aboard the faster NASA DC-8 during PEM West A & B, PEM Tropics A & B, SUCCESS, SONEX, and TRACE-P (Dibb et al. 1996, 1997, 1998, 1999a, 2000, 1999b, 2003; Jordan et al. 2003b; Talbot et al. 1998). The probe includes two identical inlets, each employing curved leading edge diffusers centered in a shroud that extends 20 cm forward of the nozzle (Figure 1c). The diffusers expand from the initial diameter of 7.77 mm at 8\(^\circ\) to meet the 5 cm outer diameter seamless stainless steel inlet which bends 30\(^\circ\) with a radius of curvature of 43 cm to penetrate the aircraft window plate (Table 1). Sampling isokinetically at an air speed of 180 m s\(^{-1}\), the inlets supply 526 lpm of volumetric flow that is manually adjusted to be isokinetic within 10\% along each level flight leg. On each deployment one inlet was used to quantify soluble ions in the aerosol phase while the second was used to quantify the radionuclides tracers \(^{7}\)Be and \(^{210}\)Pb.

### Table 1

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<td>4.1</td>
</tr>
<tr>
<td>( D_{50,50} ) (\mu m) @ 220 m/s</td>
<td>3.2</td>
<td>3.2</td>
<td>2.2</td>
<td>2.6</td>
</tr>
<tr>
<td>( D_{5,50} ) (\mu m) ( \rho = 2.6 , \text{g/cm}^3 ) @ 120 m/s</td>
<td>3.1</td>
<td>2.2</td>
<td>2.2</td>
<td>2.5</td>
</tr>
<tr>
<td>( D_{5,50} ) (\mu m) ( \rho = 2.6 , \text{g/cm}^3 ) @ 220 m/s</td>
<td>2.0</td>
<td>1.4</td>
<td>1.4</td>
<td>1.6</td>
</tr>
</tbody>
</table>
Particle sizing (APS) instruments. These instruments classify aerosol in the 0.523–20.0 μm aerodynamic size range and include the upgraded firmware components reducing the so-called “ghost particles” problem identified in the TSI model 3320 APS units. Periodically the APS units were removed from the aircraft in order to conduct flow calibration and instrument comparisons. APS sample flows were calibrated to 1.000 ± 0.025 lpm while sheath flows were calibrated to 4.000 ± 0.010 lpm (i.e. ± 2.5% nominal) using a NIST traceable Gillian Gilibrator-2 bubble flow meter calibration system. Sample flow was delivered from each inlet through identically machined flow-splitting manifolds mounted on each instrument rack and then through identical lengths of 1.27 cm (inner diameter) carbon-impregnated conductive silicone tubing. APS sample temperature and relative humidity were measured using Vaisala 50Y RH & T sensors. The sensor’s protective sheaths were removed to increase time response and were nested in Swagelock tees upstream of the APS inlets such that they did not impede flow into the APS units.

Each instrument rack measured aerosol scattering at a single wavelength (λ = 540 nm) using Radiance Research Model M903 nephelometers (RRNeph) plumbed with identical lengths of 0.95 cm ID carbon-impregnated conductive silicone tubing. Flow rates were controlled at 4.000 vlpm using Alicat Scientific volumetric flow controllers. RRNeph temperature and relative humidity were also measured using Vaisala RH & T sensors. The sensors were embedded directly in the RRNeph sample outlet without their protective sheath.

Total and submicrometer aerosol scattering (σsp,tot, σsp,sub) was measured behind the University of Hawai'i solid diffuser inlet using two TSI model 3563 3-λ integrating nephelometers (Anderson et al. 1996; Heintzenberg and Charlson 1996). The submicrometer TSI nephelometer employed a 1-μm aerodynamic impactor dynamically controlled at 30 vlpm using an Alicat Scientific volumetric flow controller. Surface sites at

FIG. 1. The University of Hawai'i (A), NASA Langley Research Center (B) and University of New Hampshire (C) solid diffuser inlets mounted on the NASA DC-8. A schematic of the UH (top schematic) and UNH (bottom schematic) inlet tips and shrouds (dimensions in mm) are also included. Below the University of Hawaii's round observation port is a small wind-vane used qualitatively during DICE to evaluate the degree of iso-axial sampling due to airspeed, pitch, roll and yaw. The wind-vane system has since been upgraded and now records deviations from iso-axial sampling conditions electronically with ~0.25° precision.

\[\text{National Institute of Standards and Technology (USA).}\]

\[\text{Manufacturer stated accuracy ±2% RH and ±0.1°C.}\]
Edwards Air Force Base and the observatory at Trinidad Head also measured aerosol scattering using TSI three-wavelength integrating nephelometers. Similar nephelometer measurements at Trinidad head included five minutes of operation in “total” mode followed by five minutes with a 1-μm aerodynamic impactor in “submicrometer” mode. Except where noted, the nephelometer data have not been corrected for truncation effects according to (Anderson and Ogren 1998) since we are interested in comparing inlet performance and not in determining precise estimates of the radiative properties of the coarse mode aerosols.

Instrument Calibration
Initially and prior to flights 4 and 7 and after flight 8 (last DICE flight) the RRNephps were calibrated using filtered air and room temperature CO2 as the zero and span gases. Slight deviations from the target zero and span were noted during the calibration prior to flight 7. As a result the RRNeph data from flights 5 and 6 have been adjusted according to:

UH.$\sigma_p = 0.0 \cdot 10^{-6} + \frac{1}{0.96} \cdot \text{UH}.\sigma_p$  \[1\]

LaRC.$\sigma_p = 1.1 \cdot 10^{-6} + \frac{1}{0.95} \cdot \text{LaRC}.\sigma_p$  \[2\]

UNH.$\sigma_p = -0.5 \cdot 10^{-6} + \frac{1}{1.0} \cdot \text{UNH}.\sigma_p$  \[3\]

The DC-8 TSI nephelometers were calibrated prior to flights 4 and 6 and following flight 8 using filtered air and CO2. In-flight Raleigh zeros and checks of system zero using a low pressure-drop HEPA filter were periodically performed. The TSI nephelometer on the air traffic control tower was calibrated prior to its installation and after the field campaign. The TSI nephelometer at Trinidad Head (NOAA/ESRL) is periodically calibrated using the same methods (J. Ogren, personal communication).

The sum of nephelometer uncertainties due to noise and calibration for the 550 nm wavelength (δσp) is estimated at 0.4 Mm−1 for a 25-second measurement based on a 300-second calibration and 300-second zeroing period (Anderson et al. 1996). This error is propagated in quadrature with the standard deviation of the mean during the 25-second time periods included in the statistical analysis in the Appendix. For longer integration times at the ground stations (all longer than 3 minutes) nephelometer uncertainties are assumed to be negligible.

Prior to flight operations, extensive calibrations and intercomparisons were made on the APS units installed aboard the DC-8 and the EDW tower using polystyrene latex spheres (PSL) and borosilicate glass beads (glass) of geometric diameters 0.672, 0.852, 1.01, 1.31, 1.60, and 2.5, 5.1, and 7.8 μm (Figure 2, left). The instruments were also operated for several hours at a location adjacent to the flight line where they sampled ambient air including local pollution and mineral dust. This comparison (Figure 2, right) revealed concentration differences and differing values of the volumetric median diameters (VMD) that were largest for submicrometer sizes. Consequently, except where noted, APS size distributions and integral properties are reported for $D_{90} \geq 0.84 \mu m$ ($D_f = 0.49 \mu m$ for, $\rho = 2.6 \ g \ cm^{-3}$).

During flights 5 and 6 the APS installed on the University of New Hampshire instrument rack (UNH APS) appeared to be under-sizing the aerosol size distribution. Post-processing of APS integral volumes indicated that when performance tests included switching between inlets (i.e., the UH inlet was sampled by the UNH instrumentation and vice versa) obvious differences occurred that were not matched by corresponding differences...
in the RRNeph scattering data. Prior to flight 7, laboratory tests conducted using calibration spheres indicated that the UNH APS was under-sizing by about 2 channels (channel offset ranged from 1–4 with no size dependence) and the UH APS was under-sizing by about 1 channel (channel offset ranged from 0–3 with no size dependence) whereas the LaRC APS size registration was accurate. Inlet tips were cleaned and sample and sheath flows for each of the APS units were checked and recalibrated to eliminate these sizing offsets. Because of these considerations the APS data from flights 5 and 6 were corrected for this sizing offset (i.e., UH and UNH dN/dlogDp data have been reallocated to larger size classes by 1 and 2 bins, respectively). This effectively eliminated these instrument differences, which were not a result of differing inlet performance.

Experimental Design

Comparison of airborne to ground or ship-based in-situ measurements of aerosols and trace gases is notoriously difficult due to instrument and calibration differences, flight altitude and aircraft performance issues as well as the shallow and sometimes layered structure of the planetary boundary layer. Less obvious and seldom discussed is the necessary consideration of integration times. Aircraft flying at 50–220 m s–1 sample a larger airmass volume in a shorter time period than either ground or ship-based instrumentation. As an example, a one-minute sample obtained aboard an aircraft traveling at 100 m s–1 corresponds to a 20-minute sample obtained on the ground assuming a wind speed of 5 m s–1. Not only wind speed but wind direction must also be considered for representative comparisons and in order to avoid contamination of either platform. In order to compare the airborne and surface-based measurements during DICE we assume there is no temporal evolution of the aerosols during the required sampling intervals. As we will see, in some cases this assumption is not valid.

Our approach is to first compare aerosol light scattering from the TSI 3-λ nephelometer measured behind the University of Hawaii’s solid diffuser inlet to similar ground-based measurements during horizontal flybys and vertical profiles. Flybys were conducted in both a dry dust-influenced environment (Mojave Desert, CA) and the wet sea-salt influenced environment (Pacific Ocean near Trinidad Head, CA).

We then compare the relative performance of the three different inlets. These comparisons include measurements of aerosol light scattering from the Radiance Research nephelometers and APS aerodynamic size distributions. The airborne vs. ground-based APS size distribution allow us to determine the 50% passing efficiencies of the inlets for mineral dust particles. No concurrent ground-based measurements of the aerosol size distribution were made in the marine airmasses near THD. This precludes a determination of the 50% passing efficiency of supermicrometer sea salt particles.

During the DICE field campaign an APS and a 3-λ nephelometer were installed on top of the air traffic control tower (~50 m) at Edwards Air Force Base. The aircraft would typically approach the runway complex from the NE then descend to less than 100 m over the flat, dry surface of the Rogers Lake playa. The aircraft then passed ~100 m south of the EDW tower before climbing to 300 meters approximately five kilometers down range to avoid low hills. Digital videos of three DC-8 flybys can be found at: http://www-gte.larc.nasa.gov/dice/DICE_Video.htm.

The EDW flybys were designed to compare airborne and ground based measurements in a region where the coarse mode aerosol is dominated by mineral dust. The extremely dry conditions at the NASA Dryden Flight Research Center (DFRC) site within the Mojave Desert also eliminated concerns associated with changing aerosol size in response to relative humidity. Thermal convection coupled with persistent winds over the dry lakebeds typically mix dust over a relatively deep (~1 km) planetary boundary layer. Although the airborne and tower observations were usually well correlated, high winds and/or mobile emission sources (aircraft) at times produced spatially patchy aerosol loadings (dust devil, exhaust plumes) that lead to significant differences between samples collected from the two platforms, even when flight paths were performed at the same altitude and within 100 m of the EDW tower.

On the Pacific coast near Bureka California, the National Oceanic and Atmospheric Administration (NOAA) Earth System Research Laboratory (ESRL) operates the Trinidad Head Observatory (THD) (http://www.cmdl.noaa.gov/obepf/). This site was selected for sampling marine aerosol due to our ability to descend near the site over the AnzaQ airport on approach. The proximity of the small airport allowed the DC-8 to complete multiple passes of THD at altitudes as low as 100 meters. The goal of flybys at THD was to compare optical properties in a region with coarse mode aerosol dominated by sea salt.

THD is often overcast due to orographic lifting of maritime air. Sea-surface temperatures can be colder than the air temperature. This leads to high boundary layer humidity resulting in significant growth of soluble aerosol (e.g., sea-salt) and coastal fog. Wind speed and direction can change by tens of degrees between the coast and further offshore. Measurement differences due to boundary layer gradients between aircraft flight altitude and the ground station were assumed small as the observatory resides on a seaside cliff (elev. 107 ft) and the DC-8 aircraft was able to fly at ~100 m for most passes. More uncertain is the prevailing wind speed and directions near the coast compared to those found offshore when the DC-8 attempted to sample "upwind" of the surface site. Where relevant these issues are discussed in more detail in the case studies that follow.

Finally, despite careful calibrations and intercomparisons of instruments on the aircraft and at the ground stations, absolute differences in instrument performance are to be expected. Since this potential problem was identified early in the field campaign we devised alternate flow paths whereby either the LaRC or the UNH instrument rack could periodically draw sample air from the UH inlet and vice versa. The required crossover sample lines...
are longer, increasing large particle losses due to gravitational settling. However, losses in each line should be nearly identical as the crossover tubing was identical in length. This “inlet swapping” was often employed during alternating passes of EDW and THD allowing us to check for instrument zero and span offsets as well as to troubleshoot flow and/or pressure differences. When inlets were “swapped” figures and tables have been annotated to guide the reader.

Preliminary Flight Data and Re-Design of the LaRC Shrouded Diffuser Inlet

Early flight results (Figure 3) from a series of low passes over THD indicated that the LaRC shrouded diffuser inlet was much less efficient at transmitting large particles than either the UNH or the UH inlets. Exchanging sample inlets produced a significant decrease in the UH RNeph scattering coefficient and a corresponding increase in the LaRC RNeph scattering coefficient. This indicated that the large discrepancy between measurement systems is primarily related to inlet and not instrument performance. Comparison of APS size distributions recorded behind the inlets confirmed that the LaRC inlet suffered much higher relative losses in the supermicrometer size range (not shown).

Ideally, downstream of the diffuser we expect to see a slight increase in inlet pressure with respect to ambient conditions associated with the decrease in flow velocity (i.e., ram pressure). Tests of the pressure drop inside the inlets relative to ambient pressure and as a function of isokinetic flow rate were conducted on DICE flight 4. These tests revealed that the LaRC inlet pressure began to decrease significantly at about 60% of isokinetic flow and dropped dramatically as isokinetic flow was approached. The inlet was experiencing “choked flow,” i.e., for tip velocities lower than isokinetic conditions flow rates could not be increased without significantly decreasing the pressure within the inlet.

To better understand and potentially correct the poor performance of the LaRC inlet, its shroud was removed prior to flight 5; this had little obvious effect on the sampling efficiency. After flight 5 the inlet tip diameter was increased from 3.18 mm to 5.13 mm to simulate the UH inlet tip. For flights 6, 7, and 8 the LaRC inlet pressure was similar to the other inlets and the relative performance (with shroud) improved. Even so, this analysis confirmed that the discrepancies noted in Moore et al. (2004) were real and that the inlet itself requires redesign. For the purpose of this manuscript we will show data only from flights 6, 7, and 8, as these are most representative of the inter-inlet performance.

Comparisons of Airborne and Ground-Based Measurements of Aerosol Scattering

Aerosol Scattering Over the Mojave Desert of California

During flight 5 (RF05) the DC-8 completed two passes by the EDW tower while all of the inlets ran isokinetically. Although the TSI nephelometer on the EDW tower was operating at a very low flow rate (~2 lpm) that resulted in losses of large particles, its measurements allowed us to compare the tower and DC-8 values of \( \sigma_g \text{,\ nm} \). Using a 12.5-minute integration time corresponding to 25 seconds of flight data, the mean for the tower and aircraft measurements of \( \sigma_g \text{,\ nm} \) are within 2% for the two passes. We refer to this as the “instantaneous” comparison between the aircraft and the tower. Appendix Table A contains a detailed statistical analysis of the mean and standard deviations of each pass.

Mean values and one standard deviation for \( \sigma_g \text{,\ nm} \) and \( \sigma_g \text{,\ nm} \) measured during flight 5 vertical profiles at EDW are binned into

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**Figure 3.** Total scattering measured by the RNeph behind each inlet during flight 3 (left). Swapping sample air between UH and LaRC inlets at 22:06 indicated that the LaRC inlet was not sampling coarse mode aerosols effectively. Tests of the pressure drop through the inlet as a function of the isokinetic flow ratio showed the problem was partly due to choked flow in the LaRC inlet (right).
100-meter increments for comparison with $\sigma_{eq,sub}$ measured at the tower. The aircraft measurement of $\sigma_{eq,sub}$ in the lowest 100 meters (40.5 ± 3.6 Mm$^{-1}$) is in excellent agreement with the tower measurements of $\sigma_{eq,sub}$ (42.8 ± 2.4 Mm$^{-1}$). Note that the aircraft data are all points collected in the lowest 100 meters (50 to 150 meters) including the inbound descent profile, two race-track passes of the tower, and the outbound ascent. We refer to these near tower operations as the aircraft “dwell time.” The tower data is the average during the aircraft dwell time. Since the profile data cannot be compared to an equivalent volume of sample air at the tower, this comparison is not suitable for statistical analysis in Appendix Table C.

During DICE research flight 6 (RF06), the DC-8 completed two passes by EDW tower with all inlets sampling isokinetically. The tower nephelometer now operated at 30 lpm flow rate allowing us to compare $\sigma_{eq,loc}$ between the tower and the DC-8 (Figure 4, top). Tower integration time is 3.75 minutes for an equivalent aircraft sample period of 25 seconds (DC-8 TAS = 125 m s$^{-1}$, EDW WS = 14 m s$^{-1}$).

Results from the first pass indicate only three of the five 5-second data points are comparable to the ground measurements (Figure 4, top). For the second pass, four of five points show excellent agreement. However, the time-series of scattering from the DC-8 over the EDW runway (Figure 4, bottom) shows that there were two large deviations of $\sigma_{eq,loc}$ with smaller deviations in $\sigma_{eq,sub}$ compared to the remainder of the data collected at low altitude. Winds were from 214° at 14 m s$^{-1}$ and would have a tendency to blow along the main runway, oriented along 250°, and located south of both the aircraft taxi ramp and the tower. The approach was made from the NE and the time series shows that it is the downwind (w.r.t. EDW tower) portions of the approach that are most influenced by what appears to be aircraft activity over the airfield. By eliminating the influence of this localized aerosol plume (the first two data points of pass #1 and the first data point of pass #2) variances converged and percent differences between the tower and the DC-8 are reduced to at most 4% (compare “RF06 pass #1 & #2” to “RF06 pass #1 & #2—corrected” in Appendix Table A). This exercise illustrates the care needed to identify small-scale atmospheric structures that can influence inter-platform comparisons of aerosol optical properties.

Comparisons of $\sigma_{eq,loc}$ show excellent agreement during vertical profiles on RF06 despite the fact that the standard deviation in the aircraft measurements was three times that measured at the tower. The larger standard deviation is due to the small scale but relatively high aerosol scattering downwind from the runway. If we eliminate sixteen consecutive data points from each pass (1.3 minutes of data from 6.5 minutes of data during each pass) which corresponds to the large deviations from the background observed in the time series data, the difference in aircraft mean of $\sigma_{eq,loc}$ is reduced from 7.5% to only 1.5%. Again, the comparison of tower samples and the aircraft samples during
the vertical profile are only indicative as they do not sample identical airmass volumes.

During DICE research flight 8 (RF08) six isokinetic passes of the EDW tower were made, two in the morning and four in the afternoon (Figure 5). Mean and standard deviations for the ground station measurement (25-minute integration time) and the 5-point aircraft values for the two flybys agreed to within 5% (Appendix Table A). For the afternoon flybys the winds remained light and variable at the tower and the integration time is the same as the morning. Panel C of Figure 5 shows that over the 130-minute comparison period the $\sigma_{\text{a},\text{tot}}$ decreased approximately 20% from 30 Mm$^{-1}$ to 24 Mm$^{-1}$ at the EDW tower. Results from the instantaneous comparisons are excellent (less than 3% difference) and they capture not only the magnitude but also the decreasing trend in aerosol scattering. Note that the trend is not the same for total and submicrometer scattering. The airborne measurements indicate an increase in coarse mode fraction of scattering from 24% to 29% (±2%) between the first and the last afternoon passes.

FIG. 5. Instantaneous values (left) and vertical profiles (right) of aerosol scattering measured aboard the DC-8 compared to the values measured at the EDW tower during the morning (Panels A & B) and afternoon flybys (Panels C & D) for DICE flight 8 on June 17, 2003.

Vertical profiles of $\sigma_{\text{a},\text{tot}}$ and $\sigma_{\text{a},\text{sub}}$ over EDW for the morning and the afternoon flybys are plotted in panels B & D of Figure 5. The tower and aircraft mean $\sigma_{\text{a},\text{tot}}$ are identical for the morning profile (<1% difference). In the afternoon this difference is 15%. The standard deviation of $\sigma_{\text{a},\text{tot}}$ for the afternoon profile is comparable to morning, however the magnitude of $\sigma_{\text{a},\text{tot}}$ is approximately half the values measured earlier in the day. Thus the coefficients of variation in the lowest 100 m of the airmass are also higher than measured locally by the DC-8 earlier in the day (5% vs. 22%). The apparent increase in heterogeneity is probably linked to the light and variable winds as well as localized convection above the desert/dry lakebeds up and down-range from the air traffic control tower in the late afternoon. Recall that the mean of the aircraft data are for all points below 150 meters whereas the tower's mean is that of the aircraft dwell time (1 hour 10 minutes for the afternoon) so the means being compared are not samples of equivalent airmass volume. Agreement between the aircraft and the tower for the morning profile data is excellent and probably linked to relatively homogeneous conditions. However, as
patchiness increases, inter-platform comparisons must consider spatial and temporal collocation of the measurement and include appropriate integration times based on platform velocities, wind speed, and direction.

Aerosol Scattering in the MBL at Trinidad Head (THD), California

On DICE research flight 7 (RF07) the DC-8 completed a vertical descent over the Arcata airport, two passes by THD, followed by an upwind leg over the ocean. Figure 6 shows the vertical structure of $\sigma_{\text{sp, tot}}$ and $\sigma_{\text{sp, sub}}$ during the DC-8’s descent into Arcata as well as the average $\sigma_{\text{sp, tot}}$ and $\sigma_{\text{sp, sub}}$ measured at THD during the aircraft dwell time.

The difference between ground and aircraft $\sigma_{\text{sp, tot}}$ are $-3.2\%$ and $+7.7\%$ for passes #1 and #2 while the differences in $\sigma_{\text{sp, sub}}$ are $-16\%$ and $<1\%$ (Appendix Table B). The large difference between the DC-8 and the THD measurements of submicrometer scattering during the first flyby is in part due to changing airmass character as measured by the THD station just prior to the aircraft comparison at 23:30 UTC (Figure 6, right).

After the THD flyby the DC-8 continued NW of the surface site at an altitude of 300 meters in order to characterize aerosols within the maritime air blowing onshore at THD. At an aircraft speed of 120 m s$^{-1}$ traveling NW for 6.5 minutes the corresponding integration time for the THD tower at an average wind speed of 6 m s$^{-1}$ is 130 minutes. Variability of aerosol scattering over the open ocean was low and Figure 6 (right) shows the mean and standard deviation for the scattering measured during the upwind aircraft leg ("regional ocean"). $\sigma_{\text{sp, sub}}$ at THD prior to 24:42 UTC was, in general, elevated with respect to the values measured upwind by the DC-8 instrumentation. When the THD scattering values are averaged until the shift in wind speed and direction at 26:06 UTC the difference between the DC-8 and THD is reduced to $\sim10\%$.

Total scattering, $\sigma_{\text{sp, tot}}$, measured aboard the DC-8 is within 6% of the THD values for the first hour of the integration time (23:30–24:36 UTC). After 24:36 total scattering begins to diverge from the values measured aboard the aircraft. Since submicrometer scattering remains the same this indicates temporal evolution of the supermicrometer aerosol over the 130-minute integration time. This divergence is likely the result of shifting wind direction (315° to 330°). Due to the orientation of the coastline, coastal aerosols including those generated by nearshore breaking waves possibly influenced the aerosol sampled at THD. While flying over the open ocean the DC-8 samples would not include coarse mode aerosols generated in the nearshore environment. Despite the possibility of these influences the aircraft and ground-station data agree within 30%.

On June 17, 2003 (DICE flight 8) the DC-8 completed another vertical descent over Arcata airport followed by four racetrack passes by THD. Winds were light and variable from the South at the surface. Under these conditions, the aircraft’s 25-second sampling time integrates an equivalent of 25 minutes surface data.

The profile values of $\sigma_{\text{sp, tot}}$ and $\sigma_{\text{sp, sub}}$ were $4.8\%$ and $28\%$ higher than THD but were conducted over the Arcata airport and therefore poorly collocated spatially. For the lowest 100 m of the DC-8 profile $\sigma_{\text{sp, tot}}$ accounts $\sim40\%$ ((24.8–15.2)/24.8 Mm$^{-1}$) of $\sigma_{\text{sp, tot}}$ indicating that the airmass contains significant supermicrometer sea salt aerosols. Using the average over the 1-hour integration of $\sigma_{\text{sp}}$ at THD the coarse mode fraction of scattering estimate is $\sim30\%$ ((23.7–11.9)/23.7 Mm$^{-1}$).
Differences between the DC-8 and THD range from -16% to +30% for the total and submicron aerosol scattering. However, the systematically lower UH total scattering and systematically higher UH submicrometer scattering results in a UH supermicrometer estimate only 55% of the THD value (Appendix Table B and C). Relative humidity was comparable between the instrument systems and variability of $\sigma_{sp,scat}$ measured aboard both the DC-8 and at the ground station are both low. This suggests the regional airmass was homogeneous in the horizontal. The cause of the large supermicrometer discrepancy is not readily apparent but is probably related to difficulties associated with airborne sampling of marine aerosols at high (95%) ambient relative humidity.

### Inter-Inlet Comparisons of Aerosol Scattering Using Radiance Research Nephelometers

A detailed examination of the scattering coefficients measured behind each inlet allows us to evaluate their relative performance. For this analysis, our standard is the previously discussed $\sigma_{sp,scat}$ and $\sigma_{sp,sub}$ measurements provided by the two TSI model 3563 nephelometers that drew sample from the UH inlet. Also, by subtracting the TSI $\sigma_{sp,sub}$ (free of inlet losses as indicated by pass #1 & #2 from RFU5) from $\sigma_{sp,scat}$ measured by the Radiance Research (RRNeph) and the TSI nephelometer ($\sigma_{sp,scat}$), we can evaluate the inter-inlet performance with regard to coarse mode scattering ($\sigma_{sp,coarse}$) in these environments.

Two corrections were made to the RRNeph data to facilitate these comparisons. First, the total RRNeph $\sigma_{sp,540}$ were increased by the empirical relationship:

$$ \sigma_{sp,540}^{RR} = \frac{\sigma_{sp,540}^{RR}}{0.94 - 0.25 \cdot (1 - FF_{scat})} $$  

where

$$ FF_{scat} = \frac{\sigma_{sp,540}^{TSI}(Da < 1 \mu m)}{\sigma_{sp,540}^{TSI}(total)} $$

This relation was derived by Anderson et al. (2003) and normalizes Radiance Research nephelometer performance to TSI nephelometer performance based upon the relative coarse mode fraction of scattering (1 minus fine-mode fraction of scattering, $FF_{scat}$). Second, time lags due to sample line lengths, sample-volume flushing times, and instrument averaging were computed and a 7-point smoothing Gaussian filter was applied to the TSI nephelometer data. Co-registration of peaks in supermicrometer scattering as well as the shape of the signal decay is well represented by this averaging scheme.

Figure 7a shows RRNeph $\sigma_{sp,coarse}$ versus TSI $\sigma_{sp,coarse}$ for each 5-second data point collected during research flights 5, 6, and 8 where the aerosol volume was dominated by mineral dust. Intercepts were forced through zero because when left unconstrained the intercepts were ±1 Mm$^{-1}$, which is at the level of RRNeph instrument precision. Linear regression for the RRNeph $\sigma_{sp,coarse}$ versus TSI $\sigma_{sp,coarse}$ are not shown, but produced slopes of 1.01 ($R^2 = 0.977$), 0.87 (0.950), and 1.00 (0.977) for the UH, LaRC, and UNH inlets, respectively.

![Figure 7a](image_url)
The correlation coefficients for RRNeph $\sigma_{r,n=0.002}$ are somewhat lower compared to the regressions based on RRNeph $\sigma_{r,n=0.005}$. For both the UH and UNH inlets, slopes remain within 10% of each other and within 5% of unity (recall that TSI $\sigma_{r,n=0.005}$ and $\sigma_{r,n=0.002}$ are measured behind the UH inlet exclusively). Based on this level of agreement, we conclude that the UH and UNH inlets are performing comparably in the desert environment whereas the LaRC inlet only samples ~55% of the supermicrometer aerosols responsible for coarse mode scattering. We also surmise that the Anderson et al. (2003) correction to the RRNeph scattering values is an effective means of normalizing Radiance Research nephelometer scattering to that derived from TSI nephelometers.

In order to determine the relative performance of the inlets while sampling sea salt aerosols in the marine environment, an analysis similar to that described above was performed for scattering coefficients measured within the marine boundary layer during flights 7 and 8. Results are shown in Figure 7b. Again, intercepts were forced through zero ($\pm 1$ Mm$^{-1}$ when left unconstrained). The slope near unity (1.06) for the UH inlet confirms relative performance is consistent with the mean Anderson et al. correction. The higher slope (1.46) for $\sigma_{r,n=0.002}$ measured behind the University New Hampshire inlet suggests the inlet sample marine aerosol with a greater efficiency than the University of Hawaii's inlet. However, the slightly lower relative humidity and higher average RH within the UNH RRNeph, 37% (+2% for Vaisala RH sensors) compared to 23% within both the UH and LaRC RRNeph (29% and 26% within the TSI "total" and "submicrometer" nephelometers) coupled with the hygroscopic nature of sea salt aerosols may account for part of this difference even though these RH values are "low." For example, although Carrico et al. (2003) measured crystallization relative humidities (CRH) of 41% ± 1% for marine aerosols in the Pacific between Hawaii and Japan during ACE-Asia, they also observed f(RH) values of 1.05--1.10 for relative humidity changes between 38% and 40%, when marine/pollution aerosols crystallized and transformed from the upper to the lower branch of their hysteresis loop. This is consistent with the observations of Tang et al. (1997) that, unlike pure NaCl particles, sea salt particles do not return to their initial weight immediately after drying. The author's state, "There is always some residual water remaining in sea salt particles." It is also possible that the aerosol matrix sampled in the MBL during the DICE flights may include sulfates and organic aerosols, which do not dissolve in the same manner as sea salt.

To illustrate the potential for scattering enhancements due to residual bound water, we divide the total UNH RRNeph scattering values (at 37% RH) by f(RH) = 1.10 before subtracting $\sigma_{r,n=0.002}$ measured by the TSI nephelometer (25% RH). The dashed line in Figure 7b represents the best fit for the UNH f(RH) "corrected" data. The UNH inlet appears to transmit more particles responsible for ~14% more light scattering compared to the UH inlet. For comparison the slope of RRNeph:TSINeph $\sigma_{r,n=0.005}$ is 1.03 ($R^2 = 0.888$), 0.70 (0.831), and 1.20 (0.911) for the UH, LaRC and UNH inlet without corrections and 1.09 (0.911) for the UNH inlet with the humidity correction. Consequently, the difference between UH and UNH performance could be largely a result of differing instrument relative humidity.

Comparisons of Aerodynamic Aerosol Size Distributions

A number of factors make comparison of supermicrometer aerosol mass or volume-based size distributions difficult. Volume median diameters (VMD) measured by some optical particle counting methods (like the FSSP-300) have been reported as 2-3 times greater than aerodynamic counting methods (such as the APS) or inversion methods (e.g., size distributions derived from AERONET data) (Reid et al. 2006; Reid et al. 2003a). Since the mission was conducted in regimes where large particles are present in low concentrations, poor sampling statistics in the supermicrometer size range could potentially impact our inter-platform comparisons of aerosol volume. This is particularly problematic when comparing data from sampling platforms (or instruments), such as aircraft and towers that employ different techniques, sample flows, and integration times.

During the DICE experiment coefficients of variation of supermicrometer aerodynamic aerosol volume for the ground-based APS measurements were on the order of 25-50% over 25-minute time intervals. After pooling the same data into five, 5-minute intervals coefficients of variations were on the order of 10-20%. In our analysis we have been careful to appropriately scale (through ratios of tower wind speed to aircraft speed) and then pool the tower size distributions before comparing them to the five-second APS size distributions measured aboard the DC-8. This is an important consideration as it ensures that the volume of the boundary layer air sampled by the instrument platform is comparable and that variability of the aerosol properties is adequately accounted for.

The omni-directional aluminum inlet on top of the EDW air traffic control tower has a 50% sampling efficiency for 15 µm diameter particles in wind speeds at least up to 7 m s$^{-1}$ (Maring et al. 2000). In our analysis we implicitly assume that there were no aerosol particle losses in this inlet. Appendix Table D compares airborne and ground based supermicrometer aerodynamic aerosol volume using two-tailed Student’s $t$-tests for each pass of the EDW tower during flights 6 and 8. Appendix E compares aerosol bulk chemistry measurements between the DC-8 and the tower as well as between mass derived from the APS instruments. Appendix Table P compares supermicrometer light scattering calculated from the size distributions for the two high-dust cases and four low-dust cases during DICE flight 8.

Theoretical Versus Observed Passing Efficiency of Mineral Dust

Flow regime, either laminar or turbulent, is governed by the ratio of the inertial force of the fluid (in this case air) to the forces of friction of the air moving over the aerosol particles' surface (Baron and Willeke, 2001). This dimensionless quantity, the Reynolds Number ($Re$), as a function of altitude for each inlet at the tip of the diffuser as well as in the carrier tubing
and UNH inlets have tip areas of 20.7 and 50.3 cm², but do not experience choked flow while sampling isokinetically (Figure 3, right).

Turbulent inertial losses for each inlet system were modeled using equations 8–61 and 8–68 of Baron and Willeke (2001). Tubing losses ($\eta_{tube,turbine}$) are modeled over a 2 m length for each inlet. Losses in the tubing bend ($\eta_{bend,turbine}$) are modeled as 45° bend for the UH inlet, 70° bend for the LaRC inlet and a 30° bend for the UNH inlet. Losses in the inlet diffuser and at the flow splitting manifolds aft of the aircraft inlets are not considered here.

Figure 8b shows the theoretical turbulent inertial losses for each component of the UH inlet at both the surface and 12 km. Figure 9a compares the airborne vs. EDW aerodynamic size distributions during RF08 Pass #1 a case where aircraft aerosol volumes are all statistically ($\alpha = 0.05$) lower than the ground based measurements (Appendix Table D). This case, along with RF08 pass #2, are the only cases during DICE where particles with aerodynamic diameters larger than ~5 µm were measured by the EDW tower APS.

FIG. 8. Reynolds numbers for the inlet tips and carrier tubing (A). Theoretical turbulent inertial losses for the UH inlet inside the carrier tubing and for a 45° bend (computed at the surface and at 12 km) compared to the observed losses at the surface (B). Observed compared to theoretical losses for all three inlets at the surface (C). Theoretical losses for all three inlets at 12 km compared to an estimate based on the observations at the surface (D). Truncation of the observed transmission efficiency curves is due to poor counting statistics at a threshold uncertainty of 50%.
The observed UH inlet efficiency curve (steep truncated curve in Figure 8b) is calculated by pooling the data from all the EDW passes where inlet swapping had not occurred and where significant (α = 0.05) differences were identified between the ground-based and the airborne aerodynamic size distributions. Truncation occurs at a threshold instrument count of four particles over the integration time corresponding to an estimate with 50% uncertainty. The relatively sharp cut is probably due to the observation that aerosol measured at the EDW tower rarely contained supermicrometer particles larger than ~5 μm.

All three-inlet efficiency curves are shown in Figure 8c along with the combined, theoretically derived, losses in the inlet tubing and through the tubing bend. For the University of Hawai‘i and University of New Hampshire inlets $D_{50}$ is 5.0 μm and 4.1 μm and the inlets show a relatively steep cut. The modified LaRC inlet $D_{50}$ value is 3.6 μm but the shape of the curve indicates that a ~10% loss of aerosol volume is occurring at an aerodynamic diameter of 2.0 μm. The aerodynamic efficiency curves measured at the surface were converted to the corresponding efficiency curves at 12 km (T = 217K, $P = 19.4$ hpa, $\mu = 1.56 \times 10^{-3}$ Pa s) by matching the Stokes' number of the particles and ignoring the effects of fluid compression at high Mach number. These are compared to the combined theoretical losses for 12 km in Figure 8d. The $D_{50}$ at 12 km correspond to diameters of 3.2, 2.2, and 2.6 μm for the UH, LaRC, and UNH inlets.

![Graphs showing efficiency curves for different inlets](image-url)
Converting the aerodynamic equivalent diameter (i.e., \( \beta = 1.0 \)) to geometric equivalent diameter using a particle density of 2.6 g cm\(^{-3}\), the 50% passing efficiency for the UH inlet is 3.1 \( \mu \)m at the surface and 2.0 \( \mu \)m at 12 km. For the LaRC inlet the values of \( D_{10,6} \) are 2.2 \( \mu \)m at the surface and 1.4 \( \mu \)m at 12 km. For UNH, \( D_{10,6} \) is 2.5 \( \mu \)m at the surface and 1.6 \( \mu \)m at 12 km. Incorporating a dynamic shape factor, \( \chi \), would tend to increase the geometric diameter that can be effectively sampled but has not been applied.

**Inter-Inlet Comparisons in the Marine Environment Near Trinidad Head, California**

No measurements of the aerosol size distributions were made at the THD ground station thus inter-inlet performance when sampling sea salt is a relative comparison only. Dry aerodynamic size distributions of marine aerosols measured near Trinidad Head California were first corrected for near-particle non-Stokesian flow in the APS 3321 using a dry sea salt density of 2.2 g cm\(^{-3}\). The UH and UNH inlets recorded dry (RH < 40%) aerosol aerodynamic volumes of 8.7 \( \mu \)m\(^3\) cm\(^{-3}\) for flight 7 and volumes of 23 and 20 \( \mu \)m\(^3\) cm\(^{-3}\) respectively, during flight 8. Ambient atmospheric relative humidity for RF07 and RF08 were 85% and 95% with \( \pm 2\% \) uncertainty. APS aerodynamic particle sizes were converted to equivalent geometric sizes using a dry sea salt density of 2.2 g cm\(^{-3}\). To scale geometric particle sizes at instrument relative humidity (dry) to ambient humidity, we use humidity growth factors, GF, of 2.15 (\( \Delta \)GF = 2.08-2.22) and 2.89 (\( \Delta \)GF = 2.62-3.42) for sea salt at a relative humidity of 85% (\( \pm 2\% \)) and 95% (\( \pm 2\% \)) (Howell et al. 2006). Ambient geometric diameters were then scaled to ambient aerodynamic diameters using hydrated particle densities of 1.15 g cm\(^{-3}\) (\( \Delta \)DPS = 1.16-1.14) and 1.05 g cm\(^{-3}\) (\( \Delta \)DPS = 1.08-1.04). Thus supermicrometer aerosol aerodynamic volume at ambient RH was 30 \( \mu \)m\(^3\) cm\(^{-3}\) behind both the UH and the UNH inlets during RF07 and 175 and 155 \( \mu \)m\(^3\) cm\(^{-3}\) behind the UH and UNH inlets during RF08 (Figure 9c, 9d).

Figure 9c and 9d illustrate that the UH and the UNH inlets have nearly identical performance characteristics (within instrument precision) and outperform the modified LaRC inlet. The truncation of the aerodynamic distributions measured in the marine environment at 85% RH (Figure 9c) appear to support the steepest Dm,30 cut established at 5.0 and 4.1 \( \mu \)m for the UH and UNH inlets. The LaRC inlet only records 76% the volume recorded behind the other two inlets consistent with its much broader efficiency curve. However, the UH and UNH distributions adjusted to 95% relative humidity are truncated at diameters in excess of 7.0 \( \mu \)m. Although the efficiency of their transmission is not known, and humidification growth factors are uncertain at high RH, UH, and UNH cut sizes of 5.0 and 4.1 \( \mu \)m appear to be conservative estimates.

**Comparison of Ground-Based and Airborne Bulk Aerosol Chemistry Measurements**

Filter-based bulk aerosol chemistry measurements were collected at the EDW tower as well as aboard the DC-8 behind the second UNH inlet. Filters are then extracted with methanol and deionized water and analyzed by ion chromatography (Dibb et al. 2002).

A comparison of filter-based chemistry measurements at the EDW tower and the DC-8 was not possible for RF06 due to small-scale differences in the aerosol field (see Figure 4). On RF07 and RF08 chemistry measurements were obtained over the ocean during operations near the Trinidad Coastal Site. Although no chemistry measurements were made at THD the DC-8 bulk chemistry results can be compared to APS derived mass behind the UH and UNH inlets.

APS aerodynamic diameters were corrected to volume equivalent diameters using a dry sea salt density of 2.2 g cm\(^{-3}\) without a shape-factor correction. The filter measurements during RF07 were consistent with nearly pure sea salt in the coarse mode, with Ca:Mg = 0.18 and Ca:Na = 0.024 (seawater ratios are 0.19 and 0.021). Nearly identical masses from the chemical measurements and calculated from the APS using a sea salt density of 2.2 g cm\(^{-3}\) suggest that there was no significant mass other than sea salt and that the sample inlet and plumbing to the filters and APS had essentially the same particle transmission efficiency (Appendix E). In contrast, the filter data from RF08 showed elevated calcium ratios (Ca:Mg = 0.51 and Ca:Na = 0.037) and the calculated mass from the APS exceeded the sum of the ionoe constituents by about 50%, suggesting that dust was present. Assuming that 5% of dust mass is soluble Ca, the excess calcium implies that approximately 20% of the supermicrometer mass was dust. The added mass reduces the filter:APS discrepancy to roughly 35%, within one standard deviation of the APS data. This implies that the sea salt growth factor used in Section 9.2 is an overestimate for ~20% of the particulate mass. The size distributions of the dust and sea salt are presumably different, but we lack size-resolved chemistry, so cannot determine what fraction of the particles should be assigned a lower growth factor. Aerosol bulk chemistry measurements were also made during both the morning and the afternoon passes of the EDW tower during flight 8. APS aerodynamic diameters were corrected to geometric diameters using a dust density of 2.6 g cm\(^{-3}\). Total dust mass was calculated from the Ca\(^{2+}\) concentration assuming calcium is 5% by weight of the total dust mass. The table in Appendix E shows that both the DC-8 bulk chemistry measurements (UNH inlet) and the pooled APS measurements behind the UH and UNH inlets are indistinguishable from the EDW tower chemistry measurements for both the morning and the afternoon RF08 flybys. We do note that our assumption of calcium as 5% by weight of the total dust mass is the best fit to the data and is uncertain.

**Inter-Inlet Comparisons of Aerosol Scattering using APS Derived Scattering**

Here we use direct measurements of aerosol optical properties (\( \varepsilon_{\text{optical}} \)) to evaluate the optical properties calculated from the aerodynamically measured size distributions. These calculations are based on realistic assumptions about particle densities, refractive indices, particle morphology, and so on.
Below we document the parameter values selected for our analysis in an effort to standardize our methods with those of previous publications.

The APS is calibrated with spherical polystyrene (PSL) or borosilicate glass (glass) spheres of known density ($\rho_{\text{PSL}} = 1.05$ g cm$^{-3}$, $\rho_{\text{glass}} = 2.52$ g cm$^{-3}$). Aerodynamic diameters measured by the APS are slightly larger than the true aerodynamic diameters ($D_a$) due to small-scale turbulence in the flow field induced by the APS on the aerosol particles (near-particle non-Stokesian flow). For 1.0 $\mu$m particles this difference is 3.5% for $\rho = 2.6$ g cm$^{-3}$ or 3.0% for $\rho = 2.2$ g cm$^{-3}$ at $T = 298.15$K. At 10 $\mu$m the difference is 15% and 12%, respectively. Corrected aerodynamic diameters ($\bar{D}_a$) were transformed to geometric diameters ($D_g$) assuming that the particles are spherical and that the densities are the same as used in the Stokes correction (Peters et al. 1993). Light scattering coefficients (550 nm) were calculated using a refractive index of $m_{\text{dust}} = 1.53 - 0.0006i$ for mineral dust (Clarke et al. 2004) and a refractive index for dry sea-salt of $m_{\text{sea-salt}} = 1.5688 - 0.0i$ (Tang et al. 1997). Although the real part of the dust refractive index is uncertain and could vary between 1.5 and 1.7, we are most interested in relative agreement between instruments so can ignore this contribution to uncertainty.

Inter-instrument performance of the various APSs generally agreed within about 15% for $D_{50} \geq 0.84$ $\mu$m (Figure 2, right panel). By transforming the APS aerodynamic diameters to geometric diameters and then applying Mie scattering theory we can use the APS size distributions to calculate $\sigma_{sp,coa}$ for $D_a \geq 1.0$ $\mu$m. This allows us to compare supermicrometer scattering measured by the TSI nephelometers (UH $\sigma_{sp,coa} = \text{UH} \sigma_{sp,coa}$) behind the UH inlet to the supermicrometer scattering size distributions measured behind each inlet. Also, we can then compare supermicrometer scattering size distributions measured behind each inlet to those from the EDW tower distribution. This is a second means of evaluating inter-inlet performance and the inlet’s ability to sample optically relevant supermicrometer aerosols.

Figure 10a shows the linear regression between calculated and measured $\sigma_{sp,coa}$ below 300 m over Rogers dry lake during flights 5, 6, and 8. Figure 10b shows the results from the marine aerosols measured during flights 7 and 8. Once again, the regression intercepts were forced through zero because offsets were all less than 2.0 Mm$^{-1}$.

The mineral dust cases indicate closer agreement between calculated and measured $\sigma_{sp,coa}$ behind the UH inlet compared to either LaRC or UNH. The slope of the regression for the UH APS derived scattering compared to the measured scattering ($\sigma_{sp,tot}$ minus $\sigma_{sp,sub}$) is 0.66. This underestimate could be linked to the assumption that dust particles are spherical. Since dust particles are not spherical but rather angular or fractal in shape they have a higher surface area to mass ratio than spherical particles. This leads to more rapid acceleration in the APS sensing volume and under-sizing. In Figure 10a dashed lines are the results after applying the empirical Reid et al. (2003a) “effective density correction” of 2.0 g cm$^{-3}$ for mineral dusts. Coarse $\sigma_{sp,550}$ is still underestimated by 12% but within measured differences in APS performance (Figure 2), although uncertainties in density, refractive index, and shape factor may also contribute to the difference.
In the marine environment the UH and UNH APS derived supermicrometer scattering is identical within instrument performance differences (Figure 10b). The modified LaRC inlet appears to be losing approximately 50% of the supermicrometer aerosol responsible for light scattering measured behind the UH inlet. This value is consistent with the 45% loss of coarse mode scattering as measured by the Radiance Research nephelometer behind the LaRC inlet.

Comparison of Airborne and Ground-Based Scattering Calculated from APS Size Distributions

Since aerosol scattering efficiency per unit mass is approximately inversely proportional to diameter for supermicrometer sizes, we expect better agreement between values of supermicrometer scattering calculated from the size distributions than agreement between supermicrometer volume (Appendix Table F). In other words, while the small number of large particles lost in the UH and UNH inlets/plumbing account for 67% and 52% of the supermicrometer volume during RF08 Pass #1 (Figure 9a), they should account for a smaller percentage of the supermicrometer scattering.

Figure 9b show the inlets' scattering size distributions for RF08 pass #1 compared to the tower distribution. For RF08 pass #1 supermicrometer scattering behind the UH inlet/plumbing was 88% (14/16 Mm\(^{-1}\)) of that measured at the tower. Scattering behind the UNH inlet/plumbing was 75% (12/16 Mm\(^{-1}\)) of that calculated from the tower size distributions.

These results demonstrate that closure between airborne and ground-based measurements of supermicrometer aerosol volume can be difficult to achieve, potentially increasing uncertainties associated with supermicrometer measurements of aerosol mass and chemistry. Aerosol optical properties and aerosol surface area are less sensitive to large particle losses resulting in better agreement between airborne and ground-based measurements.

Summary

This study was undertaken in order to quantify both the absolute and relative performance of three passive, solid diffuser type inlets aboard the NASA DC-8 research aircraft. The inlets were designed separately and have been used by the University of Hawaii, NASA Langley Research Center and the University of New Hampshire to sample aerosols aboard the NASA P3-B and NASA DC-8 during various field campaigns.

When sampling mineral dust aerosols, \(\sigma_{\text{op, tot}}\) and \(\sigma_{\text{op, mb}}\) measured behind the University of Hawaii's solid diffuser inlet was within 5% of the ground-based measurements in all but one flyby of the EDW ground station. We determined that the outlying case was the result of small-scale enhancements in the local aerosol field due to aircraft activity over the runway complex. In the marine environment, differences between \(\sigma_{\text{op, air}}\) measured behind the UH inlet and those measured at the NOAA/ESRL, Trinidad Head Observatory were less than 16%. Differences between DC-8 and THD measurements of \(\sigma_{\text{op, mb}}\) were larger than \(\sigma_{\text{op, tot}}\) but were still within 30%. No cause could be determined for these relatively large differences although measurements were complicated by high relative humidity (80-95%). Differences in the 50% cut-size of the submicrometer aerodynamic impactors aboard the DC-8 and at THD could also contribute to submicrometer differences especially for coarse sea salt aerosol and if the relative humidity at the impactor plates differs.

Inter-inlet performance was evaluated over the Mojave Desert through an analysis of light scattering as well as supermicrometer aerosol volume and bulk aerosol chemistry. Comparisons of aerosol scattering data recorded over the Mojave Desert indicated that the UH and UNH inlets sampled nearly identically (7% difference) whereas the LaRC inlet failed to pass ~50% of the aerosols responsible for supermicrometer light scattering relative to the UH inlet (see Figure 7a). Evaluations of inlets based on supermicrometer mineral dust volume responsible for light scattering (see Figure 10a) support this finding indicating an 18% difference between the UH and UNH inlets while the LaRC inlet only sampled ~60% of the optically effective aerosol measured by the other two inlets. Filter-based bulk aerosol chemistry measurements (UNH inlet) and aerosol mass calculated from APS aerodynamic size distributions (UH and UNH inlets) were indistinguishable from measurements at the EDW tower assuming a dust density of 2.6 g cm\(^{-3}\) (to shape factor correction) and calcium as 5% of the total dust mass.

In the marine environment, the evaluation of inter-inlet performance was complicated due to the effects of differing instrument relative humidity. After attempting to correct for these effects, estimates of coarse scattering differed by only 13% between the UH and UNH inlets whereas the LaRC inlet failed to pass ~75% of the marine aerosol responsible for supermicrometer light scattering (Figure 7b). Scattering calculated from APS measurements of aerosol volume for the UH and UNH inlets were within APS uncertainty (difference of just 4%) whereas the scattering calculated from distributions behind the LaRC inlet were approximately 50% that measured in the other inlets (Figure 10b).

In the appendix a statistical analysis using the Student's \(t\)-test \((t = t\_{\text{critical}}(\nu, \alpha = \frac{1}{2}))\) is used to evaluate the level of agreement between supermicrometer aerosol aerodynamic volume measured at the EDW tower and supermicrometer aerosol aerodynamic volume measured behind each inlet (Table D). Supermicrometer dust volume measured behind the University of Hawaii's inlet and associated tubing were statistically indistinguishable from those measured at the EDW tower for four of the eight flybys. Behind the University of New Hampshire inlet supermicrometer dust volume was also statistically indistinguishable from that measured on the ground in four of the eight flybys. The modified LaRC inlet performed poorest with supermicrometer dust volume recorded behind the inlet indistinguishable from the ground in only one of the eight flybys.

The mean aerodynamic size distributions from the passes completed under normal operating conditions (i.e., no inlet swapping) were pooled and compared to the corresponding, time-integrated distributions measured at the EDW tower. Based
on these size-resolved results the aerodynamic ($\alpha = 1.0$) 50% passing efficiency ($D_{50, 50}$) of mineral dust for the inlets is determined to be no less than 5.0 and 4.1 $\mu$m for the UH and UNH inlets respectively. However, at the EDW tower few particles were measured beyond ~5 $\mu$m in size potentially indicating that these are conservative estimates of the inlet passing efficiencies. This is also consistent with the results of Huebert et al. (2004) for the silicate mass passing efficiency of the UH inlet. The 50% passing efficiency of the modified LaRC inlet was determined to be 3.6 $\mu$m. The broader shape of the observed efficiency curve is consistent with light scattering and aerosol volumes ~50% those recorded at the EDW tower.

A quantitative determination of the 50% passing efficiency of marine aerosols (i.e., supermicrometer sea-salt) was not possible. Ambient aerosol distributions were computed at 95% relative humidity using a sea salt growth factor of 2.89. In this instance the UH and UNH APS instruments recorded ambient diameters as large as 6–8 $\mu$m although the efficiency at which these particles were sampled remains unknown.

Supermicrometer aerosol scattering calculated from APS size distributions was compared to supermicrometer scattering calculated from size distributions at the EDW tower. At high dust concentrations, supermicrometer scattering ($\alpha_{sp,sc}$) calculated from the aerosol size distributions differed from the tower values by only 12% (27% while inlets were swapped) behind the UH inlet/plumbing despite only measuring 67% (51% while inlets were swapped) of the aerosol volume. The UNH calculated scattering differed from the tower values by 27% (32% while swapped) while measuring only 35% (46% while inlets were swapped) of the aerosol volume. These results illustrate that while sampling supermicrometer aerosol volume through passive inlets can result in significant losses, this has a much smaller impact on aerosol surface area and aerosol optical properties.

Note that the losses evaluated here are the net effect of both the inlet and transfer tubing to the instruments. Losses were highest when inlet swapping had occurred, i.e., when transfer tubing lengths were longest. Estimates from PEH1 suggest that plumbing losses can be on the order of half of all particle losses (Huebert et al. 2004).

CONCLUSIONS

The University of Hawai‘i solid diffuser inlet was shown to effectively pass aerosol particles responsible for better than 95% of total light scattering over the Mojave Desert when compared to identical ground-based measurements at the Edwards Air Force Base air traffic control tower (EDW). In the marine environment total and submicrometer light scattering observed at the aircraft was within 10% and 30% of measurements made at the NOAA/ESRL coastal observatory at Trinidad Head, California (THD).

Over an appropriately scaled integration time, the means of supermicrometer aerosol aerodynamic volume measured behind the UH and UNH inlets were statistically indistinguishable from the pooled means measured at the EDW tower in four of the eight aircraft passes ($\alpha = 0.05$). Periodically swapping sample air between instrument racks necessitated longer transfer tubing between the inlets and the instrumentation. This resulted in enhanced large particle losses and poorer agreement between the airborne and ground-based measurements at high dust concentrations. During lower ambient dust concentrations the aerodynamic particle size at the EDW tower recorded negligible aerosol volume above 5.0 $\mu$m. At these lower dust concentrations inlet swapping had a smaller effect on the results due to the high transmission efficiencies of the UH and the UNH inlets/plumbing in the 3–5 $\mu$m aerodynamic size range.

Based on supermicrometer aerodynamic size distributions, the University of Hawai‘i, NASA Langley and University of New Hampshire inlets have 50% passing efficiency aerodynamic diameters of 5.0, 3.6, and 4.1 $\mu$m, respectively. Thus airborne measurements of aerosol size distributions, their chemical composition, and optical properties can be compared directly to ground or ship-based measurements when dominated by sizes smaller than this.

Using a dust bulk density value of 2.6 g cm$^{-3}$ and ignoring dynamic shape factor considerations (results in a more conservative estimate), the geometric equivalent diameter of these passing efficiencies are 3.1, 2.2, and 2.5 $\mu$m for the inlets. Thus passing efficiencies for the UH and UNH inlets are sufficiently reliable to be comparable with ground-based monitoring standards such as the EPA's$^{x}$ PM$^{2.5}$. However, at higher altitude the ratio of drag forces to inertial forces is reduced. To estimate both the aerodynamic and geometric 50% transmission efficiency diameters at the DC-8 flight ceiling (~12 km) we assume losses are controlled by a phenomenon associated with the particle Stokes number and ignore the effects of fluid compression at high Mach number. The corresponding aerodynamic diameters at 12 km are 3.2, 2.2, and 2.6. Assuming a spherical particle density of 2.6 g cm$^{-3}$ the corresponding geometric diameters are 2.0, 1.4, and 1.6 $\mu$m at 12 km. Incorporating a dynamic shape factor, $\chi$, would tend to increase the geometric diameter that can be effectively sampled but has not been applied.

The DC-8 inlet characterization experiment shows that the NASA Langley small shrouded diffuser inlet does not effectively sample supermicrometer aerosols even after modification to the inlet tip diameter. This confirms the findings of Moore et al. (2004). Therefore, we recommend caution when using aerosol optical properties measured behind the earlier unmodified LaRC inlet aboard the DC-8 during TRACE-P and SOLVE II.

Particle surface area and aerosol scattering are generally dominated by sizes smaller than 4 $\mu$m. The DICE results show that the University of Hawai‘i and University of New Hampshire passive solid diffuser type inlets appear adequate for aerosol sampling objectives aboard the NASA DC-8 during INTEX-NA. However, in environments with more enhanced coarse aerosol such as Asian or Saharan dust storms or the marine boundary

$^x$United States Environmental Protection Agency.
layer under moderate to high winds and high relative humidity, passive inlets will underestimate aerosol volume and, to a lesser extent, light scattering.

While more sophisticated active aerosol inlets are available, their deployment aboard research aircraft involves a larger payload, additional power requirements and post-processing in order to properly account for the size dependent enhancements (Huebert et al., 2004). In contrast the passive diffusers presented here, require no additional space, operators, or power requirements. Past evaluations of active versus passive inlet performance (PELTI) on a lower speed aircraft (NSF/NCAR C-130) showed that the magnitude of corrections needed for particle losses in the solid diffuser inlets at large sizes were comparable to corrections needed for particle enhancements in the Low Turbulence Inlet (LTI). However, direct comparisons to ground based measurements like those presented here were not conducted during PELTI, nor were the comparisons subject to statistical analysis.

REFERENCES


APPENDIX

In the preceding manuscript we evaluated, as a percent difference, the relative agreement between airborne and ground-based measurements of aerosol size distributions and their optical properties. Here we tabulate the results of two-tailed Student’s t-test in order to evaluate whether or not the mean values measured aboard the DC-8 aircraft are statistically indistinguishable (H0) or statistically distinct (H1) from those measured at the ground stations for α = 0.05.

The Student’s t-test requires that the population being tested be normally distributed and that variances are equal. The f-test is used to test for equal variance and in many cases fails. However, with regard to deviations from non-normality the t-test is more robust than the f-test particularly when the test is two-tailed and when the sample population suffers from low sample numbers (Zar 1994). Because our test is two-tailed and suffers from low sample numbers (after pooling the data) and since we do not know if aerosol light scattering/volume is normally distributed in the ambient environment, we feel that the t-test is the best measure of inter-platform agreement even when the data do not meet the f-test criteria. The use of non-parametric rank-sum tests, such as the Mann-Whitney test, did not obviate problems with the two-tailed Student’s t-test.

With regard to low sample numbers we are confronted with the fact that calculated means and variances aboard the DC-8 and at the ground station are not equal in space or time. In order to compare the scattering values or the distributions we must compare them over similar aerosol masses. This is accomplished by using the ratio of the DC-8 true airspeed (TAS) to the wind speeds (WS) measured at the EDW and THD towers. In the manuscript this is referred to as the “integration time” for the ground-based measurements. During DICE this ratio was as low as 9:1 and as high as 60:1. At EDW the aircraft and the ground station data share a common time base of 5-seconds. Scattering data at THD is recorded at 60-second intervals while switching between “Total” and “Submicrometer” scattering every 5 minutes. Thus five 5-second aircraft measurements correspond to between 46 and 301, 5-second samples at the EDW tower but as few as eleven, 1-minute samples at the THD tower. Variability of aerosol properties at the EDW tower is high due to airflow heterogeneity at micrometeorological scales. The occasional sampling of large aerosols results in coefficients of variation at the EDW tower that are higher than those measured...
aboard the aircraft. Consequently, when comparing the aircraft data to the tower data, acceptance of the Students t-test null hypothesis is more easily achieved. To be more accurate in our comparison, variability at the EDW tower should be "smeared" into five "pooled" data points (N_pool as opposed to N_tr in Tables A, B, D, E, and F). The coefficients of variation of the pooled EDW tower means are comparable to those measured aboard the aircraft. This operation is not performed on the THD data set as each data point is already a 1-minute average. The effect of pooling the data is to increase the frequency of acceptance for the t-tests (a test for equal variance) but decreases the number of aircraft passes that meet the t-test criteria (a test for equal means).

Appendix Tables A and B tabulate the results of two-tailed t-tests performed on the TSI model 3563 3-1 nephelometer scattering data during each aircraft pass. In Appendix Table C the mean and standard deviations of the aircraft data collected in the 50–150 meter altitude range during vertical profiles is compared to the EDW and THD tower values over this so-called aircraft "dwell time." Since these results do not compare identical airmass volumes, statistical analysis using the t-tests is not appropriate. Also contained in Appendix Table C are the mean and standard deviations of total and submicrometer light scattering measured at the THD tower during DICE flight 8 and the corresponding data from the 15-minute level leg flown "upwind" of the THD site. Differences between wind speed and wind direction measured at THD and those measured aboard the DC-8 values over the open ocean magnify sampling uncertainties. Therefore we feel a more rigorous statistical analysis is not warranted.

Appendix Table D compares supermicrometer aerosol volume measured behind each inlet by the TSI model 3321 APS. Appendix Table E compares filter-based aerosol chemistry measurements at the EDW tower to those measured behind the UNH inlet aboard the DC-8 as well as calculated mass from APS size distributions. Strictly speaking the filter-based chemistry measurements do not sample equivalent airmass volumes. This is a technical limitation of the technique and we include a statistical analysis for completeness noting that our estimate of dust mass being composed of 5% CaO by weight is the best fit to the data and highly uncertain.

Appendix Table F compares supermicrometer scattering values calculated from the APS aerosol size distributions in order to evaluate how large particle losses affect our ability to calculate aerosol optical properties. Since supermicrometer light scattering was dominated by particles smaller than ~5 µm during DICE and since the 50% passing efficiency of the UNH and UNH inlet is better than 4 µm, there is better relative agreement between airborne and ground-based calculations of light scattering than between measurements of supermicrometer aerosol volume.

**TABLE A**

Student's t-test comparing light scattering (λ = 550 nm) measured aboard the NASA DC-8 behind the University of Hawai’i solid diffuser type inlet to the values measured on the air traffic control tower at Edwards Air Force Base using an omnidirectional inlet during DICE.

<table>
<thead>
<tr>
<th>DICE Flight No.</th>
<th>Platform</th>
<th>ID</th>
<th>N_pool (N_tr)</th>
<th>Mean (Mm⁻¹)</th>
<th>% Difference</th>
<th>Combined¹ t-test</th>
<th>Standard Deviation (Mm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>EDW</td>
<td>Pass #1</td>
<td>5(151)</td>
<td>42.3</td>
<td>1.7</td>
<td>Accept</td>
<td>2.4</td>
</tr>
<tr>
<td></td>
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<td>Pass #2</td>
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</tr>
<tr>
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<td>1.5%</td>
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</tr>
<tr>
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<td>Pass #2</td>
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<td>-2.6%</td>
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</tr>
<tr>
<td></td>
<td>EDW</td>
<td>Pass #1</td>
<td>5(46)</td>
<td>32.2</td>
<td>0.1</td>
<td>Accept</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>Tower</td>
<td>Pass #2</td>
<td>5(46)</td>
<td>35.1</td>
<td>0.8</td>
<td>Accept</td>
<td>-1.0</td>
</tr>
<tr>
<td></td>
<td>UH DC-8</td>
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<td>37.7</td>
<td>17.1%</td>
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<td>6.8</td>
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<tr>
<td></td>
<td>Pass #2</td>
<td>5</td>
<td>35.3</td>
<td>0.7%</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>Pass #1 corr.</td>
<td>3</td>
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<td>3.7%</td>
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<td></td>
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<tr>
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<td>Pass #2 corr.</td>
<td>4</td>
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<td>-3.6%</td>
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<td>1.2</td>
<td></td>
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<tr>
<td></td>
<td>EDW</td>
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<td>49.9</td>
<td>0.8</td>
<td>Accept</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>Tower</td>
<td>Pass #2</td>
<td>5(301)</td>
<td>50.0</td>
<td>1.0</td>
<td>Accept</td>
<td>1.0</td>
</tr>
<tr>
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<td>Pass #3</td>
<td>5(301)</td>
<td>28.5</td>
<td>1.5</td>
<td>Accept</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pass #4</td>
<td>5(301)</td>
<td>26.7</td>
<td>0.8</td>
<td>Accept</td>
<td>0.8</td>
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</tr>
<tr>
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<td>0.9</td>
<td>Accept</td>
<td>0.9</td>
<td></td>
</tr>
<tr>
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<td>Pass #6</td>
<td>5(301)</td>
<td>24.3</td>
<td>1.0</td>
<td>Accept</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
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<td>Inlet</td>
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<td>52.3</td>
<td>5.0%</td>
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<tr>
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<td>0.0%</td>
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<tr>
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<td>Pass #3</td>
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<td>29.1</td>
<td>2.2%</td>
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<td>0.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pass #4</td>
<td>5</td>
<td>26.9</td>
<td>0.7%</td>
<td>Accept</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pass #5</td>
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<td>26.0</td>
<td>2.3%</td>
<td>Accept</td>
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<td></td>
</tr>
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<td></td>
<td>Pass #6</td>
<td>5</td>
<td>24.2</td>
<td>-0.3%</td>
<td>Accept</td>
<td>1.2</td>
<td></td>
</tr>
</tbody>
</table>

¹Computed as the square root of the sum of squares of the standard deviation of the mean and the TSI nephelometer uncertainty (0.4 Mm⁻¹ for a 25 s sample).
TABLE B

Student's t-test comparing light scattering (\( \lambda = 550 \text{ nm} \)) measured aboard the NASA DC-8 behind the University of Hawai'i solid diffuser type inlet to the values measured at the NOAA/CMDL observatory at Trinidad Head California during DICE.

<table>
<thead>
<tr>
<th>DICE Flights</th>
<th>Platform</th>
<th>ID</th>
<th>No.</th>
<th>( N_{\text{ext}} )</th>
<th>Mean (( \text{Mm}^{-1} ))</th>
<th>% Difference</th>
<th>Combined Standard Deviation (( \text{Mm}^{-1} ))</th>
<th>t-test</th>
</tr>
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<tbody>
<tr>
<td>RF07</td>
<td>THD</td>
<td>Total Pass #1</td>
<td>3</td>
<td>10.7</td>
<td></td>
<td></td>
<td>1.2</td>
<td>Accept</td>
</tr>
<tr>
<td></td>
<td>Tower</td>
<td>Total Pass #2</td>
<td>4</td>
<td>9.9</td>
<td></td>
<td></td>
<td>0.5</td>
<td>Accept</td>
</tr>
<tr>
<td></td>
<td>UH DC-8</td>
<td>Total Pass #1</td>
<td>5</td>
<td>10.4</td>
<td>-3.2%</td>
<td>0.5</td>
<td>Accept</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Inlet</td>
<td>Total Pass #2</td>
<td>5</td>
<td>10.7</td>
<td>7.7%</td>
<td>0.5</td>
<td>Accept</td>
<td></td>
</tr>
<tr>
<td></td>
<td>THD</td>
<td>Sub Pass #1</td>
<td>6</td>
<td>9.1</td>
<td></td>
<td></td>
<td>0.8</td>
<td>Accept</td>
</tr>
<tr>
<td></td>
<td>Tower</td>
<td>Sub Pass #2</td>
<td>6</td>
<td>6.2</td>
<td></td>
<td></td>
<td>0.7</td>
<td>Accept</td>
</tr>
<tr>
<td></td>
<td>UH DC-8</td>
<td>Sub Pass #1</td>
<td>5</td>
<td>7.7</td>
<td>-16%</td>
<td>0.6</td>
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</tr>
<tr>
<td></td>
<td>Inlet</td>
<td>Sub Pass #2</td>
<td>5</td>
<td>6.3</td>
<td>0.4%</td>
<td>0.5</td>
<td>Accept</td>
<td></td>
</tr>
<tr>
<td></td>
<td>THD</td>
<td>Total Pass #1</td>
<td>14</td>
<td>23.8</td>
<td></td>
<td></td>
<td>0.3</td>
<td>Accept</td>
</tr>
<tr>
<td></td>
<td>Tower</td>
<td>Total Pass #2</td>
<td>12</td>
<td>23.7</td>
<td></td>
<td></td>
<td>0.3</td>
<td>Accept</td>
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<tr>
<td></td>
<td>UH DC-8</td>
<td>Total Pass #1</td>
<td>11</td>
<td>23.3</td>
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<td></td>
<td>0.6</td>
<td>Accept</td>
</tr>
<tr>
<td>RF08</td>
<td>Inlet</td>
<td>Total Pass #2</td>
<td>5</td>
<td>20.6</td>
<td>-14%</td>
<td>0.5</td>
<td>Reject</td>
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</tr>
<tr>
<td></td>
<td>THD</td>
<td>Total Pass #3</td>
<td>5</td>
<td>21.6</td>
<td>-8.3%</td>
<td>0.5</td>
<td>Reject</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Tower</td>
<td>Total Pass #4</td>
<td>5</td>
<td>20.6</td>
<td>-12%</td>
<td>0.4</td>
<td>Reject</td>
<td></td>
</tr>
<tr>
<td></td>
<td>UH DC-8</td>
<td>Sub Pass #1</td>
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<td>11.5</td>
<td></td>
<td></td>
<td>0.3</td>
<td>Accept</td>
</tr>
<tr>
<td></td>
<td>Inlet</td>
<td>Sub Pass #2</td>
<td>14</td>
<td>11.7</td>
<td></td>
<td></td>
<td>0.3</td>
<td>Accept</td>
</tr>
<tr>
<td></td>
<td>THD</td>
<td>Sub Pass #3</td>
<td>14</td>
<td>12.0</td>
<td></td>
<td></td>
<td>0.4</td>
<td>Accept</td>
</tr>
<tr>
<td></td>
<td>Tower</td>
<td>Sub Pass #4</td>
<td>12</td>
<td>12.4</td>
<td></td>
<td></td>
<td>0.5</td>
<td>Accept</td>
</tr>
<tr>
<td></td>
<td>UH DC-8</td>
<td>Sub Pass #1</td>
<td>5</td>
<td>14.8</td>
<td>29%</td>
<td>0.5</td>
<td>Reject</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Inlet</td>
<td>Sub Pass #2</td>
<td>5</td>
<td>14.0</td>
<td>20%</td>
<td>0.5</td>
<td>Reject</td>
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</tr>
<tr>
<td></td>
<td>THD</td>
<td>Sub Pass #3</td>
<td>5</td>
<td>14.0</td>
<td>17%</td>
<td>0.5</td>
<td>Reject</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Tower</td>
<td>Sub Pass #4</td>
<td>5</td>
<td>14.4</td>
<td>16%</td>
<td>0.6</td>
<td>Reject</td>
<td></td>
</tr>
</tbody>
</table>

TABLE C

Total and submicrometer aerosol light scattering (\( \lambda = 550 \text{ nm} \)) measured behind the UH solid diffuser inlet during vertical profiles compared to the EDW and THD towers. Aircraft means and standard deviations are for all data collected over the 50–150 meter altitude range. Tower means and standard deviations are for the entire aircraft dwell time, i.e. the samples are not equivalent airmass volumes.

<table>
<thead>
<tr>
<th>Regime</th>
<th>Flight</th>
<th>Description</th>
<th>EDW/THD</th>
<th>EDW/THD</th>
<th>EDW/THD</th>
<th>EDW/THD</th>
<th>DC-8</th>
<th>DC-8</th>
<th>Percent difference DC-8: EDW</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Tower ( N_1 )</td>
<td>DC-8 ( N_2 )</td>
<td>mean-( x_1 )</td>
<td>mean-( x_2 )</td>
<td>stdv-( \sigma_1 )</td>
<td>stdv-( \sigma_2 )</td>
<td>DC-8: EDW</td>
</tr>
<tr>
<td>EDW</td>
<td>RF05</td>
<td>Profile</td>
<td>541</td>
<td>163</td>
<td>43</td>
<td>41</td>
<td>2.4</td>
<td>3.6</td>
<td>-5.4%</td>
</tr>
<tr>
<td></td>
<td>RF06</td>
<td>Profile</td>
<td>361</td>
<td>132</td>
<td>34</td>
<td>36</td>
<td>1.9</td>
<td>6.5</td>
<td>7.5%</td>
</tr>
<tr>
<td></td>
<td></td>
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<td>100</td>
<td>34</td>
<td>34</td>
<td>1.9</td>
<td>3.5</td>
<td>1.5%</td>
</tr>
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<td>50</td>
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<td>3.1</td>
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</tr>
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<td>198</td>
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<td>5.1</td>
<td>-15%</td>
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<td>33</td>
<td>186</td>
<td>11</td>
<td>9.9</td>
<td>0.7</td>
<td>0.7</td>
<td>-5.6%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Total-upwind 23:30:30–24:57:35</td>
<td>71</td>
<td>186</td>
<td>12</td>
<td>9.9</td>
<td>1.4</td>
<td>0.7</td>
<td>-16%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Submicron-upwind 23:24:30–24:41:30</td>
<td>39</td>
<td>186</td>
<td>6.3</td>
<td>5.6</td>
<td>0.6</td>
<td>0.6</td>
<td>-11%</td>
</tr>
<tr>
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<td></td>
<td>Submicron-upwind 23:24:30–26:05:30</td>
<td>75</td>
<td>186</td>
<td>6.2</td>
<td>5.6</td>
<td>1.1</td>
<td>0.6</td>
<td>-9.2%</td>
</tr>
<tr>
<td></td>
<td>RF08</td>
<td>Total-profile 18:05:00–18:56:00</td>
<td>27</td>
<td>401</td>
<td>24</td>
<td>25</td>
<td>0.6</td>
<td>2.8</td>
<td>4.8%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Submicron-profile 18:05:00–18:56:00</td>
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<td>401</td>
<td>12</td>
<td>15</td>
<td>0.6</td>
<td>1.3</td>
<td>28%</td>
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</table>
TABLE D
Student's t-test comparing APS aerosol aerodynamic volume measured aboard the NASA DC-8 to the values measured on the air traffic control tower at Edwards Air Force Base during DICE.

<table>
<thead>
<tr>
<th>Flight No.</th>
<th>Platform</th>
<th>ID</th>
<th>N_{pool} (N_{int})</th>
<th>Mean (\mu m^{-3} cm^{-3})</th>
<th>% Difference</th>
<th>Measurement Deviation (\mu m^{-3} cm^{-3})</th>
<th>Ho: \mu_1 = \mu_2</th>
<th>Ha: \mu_1 \neq \mu_2</th>
</tr>
</thead>
<tbody>
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<td>EDW</td>
<td>Pass #1</td>
<td>5(46)</td>
<td>15</td>
<td>1.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Tower</td>
<td>Pass #2</td>
<td>5(46)</td>
<td>19</td>
<td>1.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>UH DC-8</td>
<td>Pass #1</td>
<td>5</td>
<td>15</td>
<td>-0.2%</td>
<td>3.3</td>
<td>Accept</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Inlet</td>
<td>Pass #2</td>
<td>5</td>
<td>18</td>
<td>-9.0%</td>
<td>2.1</td>
<td>Accept</td>
<td></td>
</tr>
<tr>
<td></td>
<td>LaRC DC-8</td>
<td>Pass #1</td>
<td>5</td>
<td>8.1</td>
<td>-47%</td>
<td>3.1</td>
<td>Reject</td>
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<tr>
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<td>Inlet</td>
<td>Pass #2</td>
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<td>5.5</td>
<td>-72%</td>
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<td>Reject</td>
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<td>UNH DC-8</td>
<td>Pass #1</td>
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<td>11</td>
<td>-29%</td>
<td>2.6</td>
<td>Reject</td>
<td></td>
</tr>
<tr>
<td></td>
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<td>10</td>
<td>-46%</td>
<td>1.8</td>
<td>Reject</td>
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<tr>
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<td>EDW</td>
<td>Pass #1</td>
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<td>44</td>
<td>9.2</td>
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</tr>
<tr>
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<td>Tower</td>
<td>Pass #2</td>
<td>5(301)</td>
<td>46</td>
<td>7.9</td>
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<td></td>
<td></td>
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<tr>
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<td>Pass #3</td>
<td>5(301)</td>
<td>10</td>
<td></td>
<td>1.2</td>
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<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pass #4</td>
<td>5(301)</td>
<td>8.9</td>
<td></td>
<td>0.6</td>
<td></td>
<td></td>
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</tr>
<tr>
<td></td>
<td>Pass #5</td>
<td>5(301)</td>
<td>8.4</td>
<td></td>
<td>0.9</td>
<td></td>
<td>Reject</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pass #6</td>
<td>5(301)</td>
<td>8.0</td>
<td></td>
<td>1.1</td>
<td></td>
<td></td>
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</tr>
<tr>
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<td>UH DC-8</td>
<td>Pass #1</td>
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<td>-33%</td>
<td>4.8</td>
<td>Reject</td>
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</tr>
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<td>Inlet</td>
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<td>-49%</td>
<td>1.6</td>
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<td>Pass #3</td>
<td>5</td>
<td>12</td>
<td></td>
<td>23%</td>
<td>1.7</td>
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<td></td>
<td>Pass #4</td>
<td>5</td>
<td>12</td>
<td></td>
<td>29%</td>
<td>2.1</td>
<td>Reject*</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pass #5</td>
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<td>9.8</td>
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<td>16%</td>
<td>3.6</td>
<td>Accept*</td>
<td></td>
</tr>
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<td></td>
<td>Pass #6</td>
<td>5</td>
<td>9.7</td>
<td></td>
<td>21%</td>
<td>3.6</td>
<td>Accept</td>
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</tr>
<tr>
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<td>LaRC DC-8</td>
<td>Pass #1</td>
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<td>18</td>
<td>-60%</td>
<td>4.7</td>
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<td>Inlet</td>
<td>Pass #2</td>
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<td>-65%</td>
<td>4.6</td>
<td>Reject</td>
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<tr>
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<tr>
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<td>UNH DC-8</td>
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<td>7.5</td>
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<td>13%</td>
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<tr>
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<td>Pass #4</td>
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<td>5.5%</td>
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<tr>
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<td>Pass #5</td>
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<td>9.6</td>
<td></td>
<td>14%</td>
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<td>7.5</td>
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<td>-5.3%</td>
<td>1.9</td>
<td>Accept</td>
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</tr>
</tbody>
</table>

*Tower flybys where UH and UNH inlet were swapped.

*Tower flybys where UH and LaRC inlet were swapped.
Filter-based bulk aerosol chemistry measurements at the EDW tower compared to filters behind the UNH inlet aboard the DC-8 and to aerosol mass calculated from APS volume equivalent diameters behind the UH and UNH inlets using a sea salt density of 2.2 g cm\(^{-3}\) and a dust density of 2.6 g cm\(^{-3}\).

### Table E

<table>
<thead>
<tr>
<th>Regime</th>
<th>Flight</th>
<th>Platform</th>
<th>(N_{\text{pool}})</th>
<th>Mean Aerosol Mass ((\mu g \text{ m}^{-3}))</th>
<th>Standard Deviation ((\mu g \text{ m}^{-3}))</th>
<th>(t)-test Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Marine</td>
<td>RF07</td>
<td>DC-8 UNH</td>
<td>3</td>
<td>5.7</td>
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<tr>
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<td></td>
<td>UH APS</td>
<td>3 (242)</td>
<td>5.9</td>
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<tr>
<td></td>
<td></td>
<td>UNH APS</td>
<td>3 (242)</td>
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<td>1.3</td>
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<td>RF08</td>
<td>DC-8 UNH</td>
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<td>4 (332)</td>
<td>14</td>
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<td>12</td>
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<tr>
<td>Desert</td>
<td>RF08</td>
<td>EDW Tower</td>
<td>2</td>
<td>18</td>
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<td>morning</td>
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<td>0.4</td>
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<td></td>
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<td>2 (93)</td>
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<td>15</td>
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</tr>
<tr>
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<td>RF08</td>
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<td>1.1</td>
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<td>1.9</td>
<td>Accept</td>
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<td></td>
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<td>4 (176)</td>
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### Table F

Comparison of EDW Tower APS and DC-8 APS supermicrometer aerodynamic volume and APS derived (\(\lambda = 550 \text{ nm}, m = 1.53 - 0.006i\)) light scattering for both the morning (high dust) and afternoon (low dust) test periods during DICE flight 8.

<table>
<thead>
<tr>
<th>N</th>
<th>Mean</th>
<th>Standard Deviation</th>
<th>Percent Difference</th>
<th>(t)-test Result</th>
<th>(\lambda = 550 \text{ nm}, m = 1.53 - 0.006i) Light Scattering (Mm(^{-1}))</th>
<th>Mean</th>
<th>Standard Deviation</th>
<th>Percent Difference</th>
<th>(t)-test Result</th>
</tr>
</thead>
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<td>5(301)</td>
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<td>9.2</td>
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<td>16</td>
<td>3.0</td>
<td></td>
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<tr>
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<td>5(301)</td>
<td>46</td>
<td>7.9</td>
<td></td>
<td>16</td>
<td>3.3</td>
<td></td>
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<td>5(301)</td>
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</tr>
<tr>
<td></td>
<td>5(301)</td>
<td>8.9</td>
<td>0.6</td>
<td></td>
<td>5.4</td>
<td>1.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5(301)</td>
<td>8.4</td>
<td>0.9</td>
<td></td>
<td>5.1</td>
<td>1.2</td>
<td></td>
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<td></td>
<td>5(301)</td>
<td>8.0</td>
<td>1.1</td>
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<td>1.2</td>
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<td>-33%</td>
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<td>2.2</td>
<td>-12%</td>
<td>Accept</td>
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<tr>
<td></td>
<td>5</td>
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<td>1.6</td>
<td>-49%</td>
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<td>-27%</td>
<td>Reject*</td>
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<td>12</td>
<td>1.7</td>
<td>23%</td>
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<td>0.6</td>
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<td>5</td>
<td>12</td>
<td>2.1</td>
<td>29%</td>
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<td>1.2</td>
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<td>0.8</td>
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<td>3.9</td>
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<td>1.0</td>
<td>1.2%</td>
<td>Accept*</td>
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<td>14%</td>
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<td>3.7</td>
<td>29%</td>
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<td>Accept</td>
<td>4.8</td>
<td>0.5</td>
<td>-1.7%</td>
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</tbody>
</table>

*Tower flybys where UH and UNH inlet were swapped.

*Tower flybys where UH and LaRC inlet were swapped.
Appendix B – Trace gas and aerosol summaries

Table B.1 – Summary of gas and aerosol-phase tracers for Eastern North America
Table B.2 – Summary of gas and aerosol-phase tracers for Mexico and the Gulf
Table B.3 – Summary of gas and aerosol-phase tracers for Hawaii
Table B.4 – Summary of gas and aerosol-phase tracers for Alaska
Table B.5 – Summary of total and submicrometer f(RH) measurements
Table B.6 – Summary of NMD, dry SSA, γT and ambient AOD
Table B.7 – Summary of 3-λ total and submicrometer SSA
### Table B.1a - Water, Nitrogen and Ozone Tracers

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Regime</th>
<th>Class</th>
<th>N</th>
<th>Percentage of LTN Samples</th>
<th>H2O (ppmv)</th>
<th>RH (%)</th>
<th>O3 (ppbv)</th>
<th>HNO3 (ppbv)</th>
<th>NO2 (ppbv)</th>
<th>BrO (RI std m-3)</th>
<th>HNO3/NO2</th>
<th>NO2/HNO3</th>
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<tbody>
<tr>
<td>IA</td>
<td>Clean - medium</td>
<td>60</td>
<td>1.3%</td>
<td>190</td>
<td>34</td>
<td>33</td>
<td>44</td>
<td>169</td>
<td>398</td>
<td>1.5</td>
<td>3.0</td>
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<tr>
<td>UT</td>
<td>BB - medium</td>
<td>137</td>
<td>2.7%</td>
<td>220</td>
<td>34</td>
<td>63</td>
<td>237</td>
<td>167</td>
<td>485</td>
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<tr>
<td>LT</td>
<td>BB - mean</td>
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<td>6.2%</td>
<td>521</td>
<td>81</td>
<td>84</td>
<td>311</td>
<td>720</td>
<td>125</td>
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<tr>
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<td>Arid - median</td>
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<td>321</td>
<td>44</td>
<td>62</td>
<td>233</td>
<td>597</td>
<td>410</td>
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<tr>
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<td>Arid - mean</td>
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<td>8.3%</td>
<td>531</td>
<td>81</td>
<td>84</td>
<td>311</td>
<td>720</td>
<td>125</td>
<td>2.3</td>
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### Table B.1b - Carbon and Refractory Aerosol

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<th>Experiment</th>
<th>Regime</th>
<th>Class</th>
<th>N</th>
<th>Percentage of LTN Samples</th>
<th>CO2 (ppmv)</th>
<th>CH4 (ppbv)</th>
<th>CO (ppbv)</th>
<th>CH2O (ppmv)</th>
<th>Hot CN (# std cm-3)</th>
<th>Tot Abs (# cm-3)</th>
<th>RIN</th>
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<tr>
<td>IA</td>
<td>Clean - medium</td>
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<td>1.764</td>
<td>77</td>
<td>62</td>
<td>531</td>
<td>0.0</td>
<td>5.17</td>
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<td>UT</td>
<td>BB - medium</td>
<td>379.5</td>
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<td>116</td>
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### Table B.1c - Sulfur and Volatile Aerosols

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<th>Regime</th>
<th>Class</th>
<th>N</th>
<th>Percentage of LTN Samples</th>
<th>SO2 (ppmv)</th>
<th>CN &gt; 3 nm (# std cm-3)</th>
<th>CN &gt; 10 nm (# std cm-3)</th>
<th>Total SO4 (ppbv)</th>
<th>Sub-n SO4 (ppbv)</th>
<th>Tot BrO (RI std m-3)</th>
<th>Sub-n BrO (RI std m-3)</th>
<th>SO4/(SO4+SO2)</th>
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<td>BB - medium</td>
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<td>2043</td>
<td>2055</td>
<td>92</td>
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<td>2.6</td>
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<td>0.94</td>
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<td>14610</td>
<td>8119</td>
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<td>1.8</td>
<td>1.8</td>
<td>0.94</td>
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### Table B.2 - Summary of gas and aerosol-phase tracers for Mexico and the Gulf

#### B.2a - Water, Nitrogen and Ozone Tracers

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<th>Experiment</th>
<th>Regime</th>
<th>Class</th>
<th>N</th>
<th>Percentage of UNH mc Samples</th>
<th>H2O (ppmv)</th>
<th>RH (%)</th>
<th>O3 (ppbv)</th>
<th>HNO3 (ppbv)</th>
<th>NOx (ppbv)</th>
<th>N2O (ppbv)</th>
<th>Be7 (fCl std m-3)</th>
<th>HNO3/NOx</th>
<th>NOx/HNO3</th>
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<td>529</td>
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<td>320.8</td>
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#### B.2b - Carbon and Refractory Aerosol

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<th>CO2 (ppmv)</th>
<th>CH4 (ppbv)</th>
<th>CO (ppbv)</th>
<th>CH2O (ppbv)</th>
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<th>Sub Abs (Mm-1)</th>
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#### B.2c - Sulfur and Volatile Aerosols

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<th>Sub-u ssp (Mm-1)</th>
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### Table B.3 - Summary of gas and aerosol-phase tracers for Hawaii

#### B.3a - Water, Nitrogen and Ozone Tracers

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<th>RH (%)</th>
<th>O3 (ppbv)</th>
<th>HNO3 (ppbv)</th>
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<th>N2O (ppbv)</th>
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#### B.3b - Carbon and Refractory Aerosol

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<th>CO (ppbv)</th>
<th>CH2O (ppbv)</th>
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<th>Tot Abs (Mm⁻¹ @ STP)</th>
<th>Sub Abs (Mm⁻¹ @ STP)</th>
<th>RCN Ratio</th>
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#### B.3c - Sulfur and Volatile Aerosols

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<th>CN &gt; 10 nm (# cm⁻³)</th>
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<th>Sub-u SO4 (ppbv)</th>
<th>Total spec (Mm⁻¹)</th>
<th>Sub-u spec (Mm⁻¹)</th>
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### Table B.4 - Summary of gas and aerosol-phase tracers for Alaska

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<th>O3 (ppbv)</th>
<th>HNO3 (pptv)</th>
<th>NOx (pptv)</th>
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#### B.4b - Carbon and Refractory Aerosol

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<th>CH4 (ppmv)</th>
<th>CO (ppbv)</th>
<th>CH2O (pptv)</th>
<th>Hot CN (# std cm-3)</th>
<th>Tot Abs (Mm-1 @ STP)</th>
<th>Sub Abs (Mm-1 @ STP)</th>
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#### B.4c - Sulfur and Volatile Aerosol

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<th>CN &gt; 10 nm (# cm-3)</th>
<th>Total SO4 (pptv)</th>
<th>Sub-u SO4 (pptv)</th>
<th>Total esp (Mm-1)</th>
<th>Sub-u esp (Mm-1)</th>
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Table B.5 - Summary of total and submicrometer f(RH) measurements

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<td>f(80:40)</td>
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<tr>
<td>UT BB mc</td>
<td>11</td>
<td>0.55 (0.07)</td>
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</tr>
<tr>
<td>Anthro mc</td>
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<td></td>
</tr>
<tr>
<td>LT BB (UNHmc)</td>
<td>11</td>
<td>0.44 (0.09)</td>
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</tr>
<tr>
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<td>0.44 (0.09)</td>
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<td>Age 2 (UNHmc)</td>
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<td>1.6</td>
</tr>
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<td>BL Age 1 (UNHmc)</td>
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<td>1.6</td>
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<tr>
<td>Age 2 (UNHmc)</td>
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<td>1.6</td>
</tr>
<tr>
<td>Age 3 (UNHmc)</td>
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<td>0.46 (0.06)</td>
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<td>UT BB mc</td>
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<tr>
<td>Anthro mc</td>
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<td>1.6</td>
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<tr>
<td>Age 2 (UNHalo)</td>
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<td>0.43 (0.10)</td>
<td>1.6</td>
</tr>
<tr>
<td>Age 3 (UNHalo)</td>
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<td>0.46 (0.06)</td>
<td>1.6</td>
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<td>MBL Anthro</td>
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<td>f(80:40)</td>
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<tr>
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<tr>
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<td>0.56 (0.12)</td>
<td>2.2</td>
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<th>Submicrometer</th>
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<td>gamma</td>
<td>f(80:40)</td>
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<td>13</td>
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*Hawaii and Alaska data combined for Student's t-test
Table B.6 - Summary of NMD, dry SSA, γ_T and ambient AOD

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<th>Eastern North America</th>
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<th>NMD (μm)</th>
<th>Dry SSA</th>
<th>γ_T</th>
<th>Ambient AOD</th>
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<td>LOD</td>
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<tr>
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<table>
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<th>Dry SSA</th>
<th>γ_T</th>
<th>Ambient AOD</th>
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<td>1.00</td>
<td>LOD</td>
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<tr>
<td></td>
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<td>Anthro</td>
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<td>0.934 (0.018)</td>
<td>0.32 (0.09)</td>
<td>0.19</td>
</tr>
<tr>
<td></td>
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<td>Anthro</td>
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<table>
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<th>Regime</th>
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<th>Dry SSA</th>
<th>γ_T</th>
<th>Ambient AOD</th>
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<td>LOD</td>
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<tr>
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<td>MBL</td>
<td>Anthro</td>
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<th>Dry SSA</th>
<th>γ_T</th>
<th>Ambient AOD</th>
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<td>LOD</td>
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<tr>
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<td>Anthro</td>
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### Table B.7 - Summary of 3-/5 total and submicrometer SSA

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<td>0.937 (0.042)</td>
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<tr>
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<td>0.957 (0.026)</td>
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</tr>
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<td>LOD</td>
<td>LOD</td>
<td>LOD</td>
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<tr>
<td><strong>LT</strong></td>
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<td>0.953 (0.023)</td>
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<tr>
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<td>0.992 (0.029)</td>
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- Total Age 1 SSA < Age 3 SSA
- Submicron Age 1 SSA < Age 3 SSA
- Total SSA = 1.0; others < 1.0
- All = 1.0
Appendix C – Log-normal fit parameters

Table C.1 – Lognormal fitting statistics for size distributions measured over Eastern North America
Table C.2 – Lognormal fitting statistics for size distributions measured over Mexico and the Gulf of Mexico
Table C.3 – Lognormal fitting statistics for size distributions measured near Hawaii
Table C.4 – Lognormal fitting statistics for size distributions measured near Alaska
Table C.1 - Lognormal fitting statistics for size distributions measured over Eastern North America

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<tr>
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<th>Aitken Mode</th>
<th>Accumulation Mode</th>
<th>Coarse Mode</th>
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<td>V (nmcm⁻³)</td>
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Note: The table includes fitting statistics for size distributions measured over Eastern North America. The columns represent different experiments and regimes with corresponding statistics for Aitken Mode, Accumulation Mode, and Coarse Mode. The statistics include number of counts (# cm⁻³), number mean diameter (NMD), volume mean diameter (VMD), and standard deviation (σ).
Table C.2 - Lognormal fitting statistics for size distributions measured over Mexico and the Gulf of Mexico

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<th>NMD (um)</th>
<th>V (nm² cm⁻³)</th>
<th>VMD (um)</th>
<th>sigma_g (⁻)</th>
<th>N (# cm⁻³)</th>
<th>NMD (um)</th>
<th>V (nm² cm⁻³)</th>
<th>VMD (um)</th>
<th>sigma_g (⁻)</th>
<th>N (# cm⁻³)</th>
<th>NMD (um)</th>
<th>V (nm² cm⁻³)</th>
<th>VMD (um)</th>
<th>sigma_g (⁻)</th>
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<th>Vol. Ratio</th>
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<th>NMD (um)</th>
<th>V (nm² cm⁻³)</th>
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<th>sigma_g (⁻)</th>
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Table C.3 - Lognormal fitting statistics for size distributions measured near Hawaii

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<th>V (mm³ cm⁻³)</th>
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Table C.4 - Lognormal fitting statistics for size distributions measured near Alaska

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<th>NMD (um)</th>
<th>V (mm3 cm-3)</th>
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<th>sigma_g (-)</th>
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|            |        |             |             | 166        | 0.079    | 0.22        | 0.24     | 1.89        |
|            |        |             |             | 433        | 0.074    | 0.297       | 0.30     | 1.98        |
|            |        |             |             | 423        | 0.11     | 1.172       | 0.27     | 1.70        |
|            |        |             |             | 364        | 0.13     | 1.310       | 0.27     | 1.63        |
|            |        |             |             | 332        | 0.13     | 0.993       | 0.24     | 1.56        |

| Heated     |        | STE - median |             |           |          |             |          |             |
|            | IB     | FT          | BB          | 133        | 0.037    | 0.024       | 0.13     | 1.93        |
|            |        | Mixed       |             | 411        | 0.088    | 0.415       | 0.18     | 1.61        |
|            |        | Anthro      |             | 297        | 0.044    | 0.059       | 0.12     | 1.79        |
|            |        |             |             | 339        | 0.048    | 0.138       | 0.16     | 1.94        |
|            |        | Background  |             | 199        | 0.025    | 0.011       | 0.09     | 1.93        |
|            |        | Anthro      |             | 223        | 0.027    | 0.019       | 0.11     | 1.98        |

Ratios

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<th>Class</th>
<th>RON Ratio</th>
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