**AEROSOL MEASUREMENTS DURING THE CENTRAL CHILEAN OROGRAPHIC PRECIPITATION EXPERIMENT**

By

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The Central Chilean Orographic Precipitation Experiment (CCOPE) was a three-month field campaign (June, July and August 2015) that investigated winter rain events. Reported here are analyses of aerosol measurements made at a coastal site (Arauco, Chile) during CCOPE. Data was obtained using a condensation particle counter (CPC) and an aerosol spectrometer (UHSAS). Arauco CPC concentrations are compared to those measured at the NOAA station at coastal Trinidad Head, California (THD). The marine-sector averaged CPC concentration at Arauco is 3457 cm-3 ± 2284 cm-3; at THD the average is1171 cm-3 ± 772 cm-3. Surprisingly, the Arauco concentrations are larger (p < 0.01). In addition, UHSAS measurements were analyzed to determine processes that shaped the ASD at Arauco. Variables analyzed included the fraction of particles smaller than 0.055 μm and moments of the UHSAS-derived aerosol size distributions. There is evidence for both primary particle sources and for new particle formation adding to the aerosol burden in oceanic air as it approaches the coast and advects onshore.

**Section 1: Introduction**

Forecast error due to incomplete understanding of atmospheric aerosols is evident in the predictions of many atmospheric models. An example of this is the predictions of general circulation models (GCMs). These are used to forecast the Earth system’s response to anthropogenic emissions of both aerosols and greenhouse gases. In spite of several decades of GCM development, the effect of anthropogenic aerosols on future climate remains uncertain, particularly when compared to the greater certainty in climate forcing from anthropogenic greenhouse gases (Hansen 2009, their Fig. 10). There are many reasons for this larger uncertainty. Perhaps most significant is the myriad of processes that contribute to the aerosol burden; also significant is the fact that aerosol particles are depleted by clouds and precipitation, which are themselves inhomogeneous in space and time, and that the degree of depletion varies with aerosol type, location and time since emission.

Aerosols influence the Earth’s energy budget by backscattering incoming solar radiation. This is known as the direct effect of aerosols on climate (Forster et al. 2007). Aerosols also perturb the abundance of droplets, drops and ice crystals within clouds. Via these perturbations, known as the indirect effect of aerosols on climate, the backscatter of solar radiation by clouds correlates positively with aerosol abundance (Twomey 1974) and precipitation correlates negatively with aerosol abundance (Albrecht 1989). In their essence, the aerosol direct and indirect effects work to lower the amount of solar energy that is absorbed by the Earth system; thus both of these effects represent a negative climate forcing that opposes the positive forcing (warming) due to anthropogenic greenhouse gases.

Increased understanding of the relationship between aerosols and the direct and indirect effects will improve climate models, and in this way, will improve understanding of how humanity is altering the Earth system (Forster et al. 2007). Natural aerosols (i.e. sea salt, soil dust, and a fraction of the sulfur- and carbon-containing particulate), are significant for cloud processes occurring in regions distant from anthropogenic sources; the cloud processes modulated by natural aerosols are not adequately understood (Yang et al. 2012; de Leeuw et al. 2011). Because of its lower population and lower intensity of aerosol emissions, the Southern Hemisphere is being explored as a region for conducting studies of aerosols and for exploring contrasts with the northern hemisphere (Gras 1995; Yum and Hudson 2004; Yum and Hudson 2005; Bennartz 2007). These investigations can be classified into two types: 1) studies aimed on documenting aerosol properties, and 2) studies aimed at establishing a baseline for climate forcing by aerosols that has occurred since the industrial revolution (e.g., Jiang et al. 2015).

The effect of aerosols on precipitation is a crucial element of forecast accuracy. Other than the demand of society for improved forecasts of precipitation, there is also scientific rationale for improving accuracy. Not only is there a feedback between aerosols and precipitation, but there is also a feedback between the precipitation and the atmospheric wind field. Numerical investigations of these interactions are being conducted at scales that range from models of individual elements of cloud (box models) to models of precipitating weather systems. Generally, these studies demonstrate that an increase in the abundance of aerosol particles decreases the amount of precipitation (Feingold et al. 1999; Feingold et al. 2013; Lebo and Feingold 2014). This is because increased aerosol abundance implies smaller droplets (assuming a fixed mass of condensed liquid), a decelerated rate of rain and snow production, and thus a reduced precipitation efficiency. However, because of accelerated precipitation development due to the presence of giant cloud condensation nuclei (GCCN), the authors of Feingold et al. (1999) state that, “the variable presence of giant cloud condensation nuclei (GCCN) represents yet another uncertainty in estimating the influence of anthropogenic activity on climate.” The Feingold et al. (1999) modeling study showed for a cloud system ingesting the more abundant and smaller anthropogenically-produced aerosol particles, the impact on precipitation is partially negated by the presence of GCCN. This type of compensation is expected for polluted coastal locations where both sea salt aerosol (SSA) and anthropogenic aerosol are intermixed.

Measurements made with a Condensation Particle Counter (CPC), an instrument that reports the concentration of all particles with diameter (*D*; micrometer) larger than ~ 0.01 μm, is the basis for many investigations of aerosol abundance (Brechtel et al. 1998; Birmili et al. 2001; Dall’Osto et al. 2009; Peter et al. 2010; Diesch et al. 2012; Li et al. 2015). These studies also evaluated air parcel back trajectories and used that information to attach a range of CPC concentrations, and thus a characteristic concentration average, to a source region. For example, marine source regions have a lower concentration than continental source regions (Brechtel et al. 1998; Birmili et al. 2001; Peter et al. 2010; Diesch et al. 2012). However, a change in source region is not the only explanation for a changed concentration. For example, Li et al. (2015) found that within the Southern Great Plains, temperature inversions are coincident with enhanced concentrations. This is because inversions trap local particle emissions, and local emissions of particle precursor gases, within an inversion layer.

The air mass classification presented in Table 1 is consistent with the findings of many investigators. The averages presented in Table 1 are rounded to the nearest 1000 cm-3 (coastal continental) and to the nearest 100 cm-3 (remote oceanic). This is because the standard deviation is larger than the average in all of the scenarios analyzed by Diesch et al. (2012), and comparable to (but modestly smaller than) the mid-latitude-marine average presented in Brechtel et al. (1998). Smaller relative variability ( ~ 0.2) is evident in the polar-marine scenario analyzed by Brechtel et al. (1998), but the duration of this polar-marine sampling (Table 1) is only two days.

The aerosol size distribution (ASD), defining aerosol particle number concentration as a function of *D*, is the fundamental aerosol microphysical property. If known, the ASD can be used to calculate three moments of the ASD: 1) size-integrated concentration (*N*), 2) aerosol surface area (*S*), and 3) aerosol volume (*V*).

 (1)

 (2)

 (3)

In Eqs. 1 – 3, the quantity defines the ASD. Two properties are implied by this definition: 1) the group represents the concentration of aerosol particles with diameter between and, and 2) when plotted versus the logarithm of particle diameter, as in Fig. 1, the area under curve represents of the size-integrated concentration[[1]](#footnote-1).

Measurement of an ASD can provide insight into atmospheric processes that went into shaping the distribution. For example, a bimodal ASD (Fig. 1, bottom) can result from cloud processing (Hoppel et al. 1994; Hudson et al. 2015), new particle formation (Petters et al. 2006), and from a mixing of distinct ASD modes characteristic of two air masses (Raes et al. 1997; Hudson et al. 2015). However, attribution is difficult to pin down solely from an ASD measurement and complete understanding requires additional information (e.g., meteorological tracing of the air backwards in time, concurrent measurement of precursor gas concentrations, knowledge of sources in space and time). Further complicating is the possibility of a two-stage or multi-stage process leading to an observed bimodal ASD. In contrast to a bimodal ASD, a unimodal ASD (Fig. 1, top) is often observed in continental air masses with observed sunny conditions or dominated by anticyclonic conditions such as increasing surface pressure (Dall’Osto et al. 2009).

In addition to size-integrated aerosol concentrations, obtained via direct measurement made with a CPC or via measurements of an ASD combined with Eq. 1, the aerosol surface area (*S*, Eq. 2) has received attention. Both Covert et al. (1992) and Clarke et al. (1998) found that the formation of new particles, derived from the condensation of sulfuric acid vapor, is likely to occur if < 10 μm2 cm-3. This was supported by a later study (Petters et al. 2006). All of these investigations demonstrated that there is a link between the occurrence of precipitation and an *S* favorable for new particle formation. This linkage is explained by the fact that rain formation lowers *S*, at least locally, and that this diminishment can be felt over a whole boundary layer given enough time for turbulence to mix the altered property (*S* in this case) uniformly in the vertical.

This study provides analysis of measured aerosol concentrations and measured aerosol size distributions gathered at a coastal site in Chile during the Southern Hemisphere winter (June, July, and August). These ground-based measurements were made during the Chilean Coastal Orographic Precipitation Experiment (CCOPE) of 2015. Motivation for this study is three fold.

**Section 2: Objective**

CCOPE explored relationships between coastal orographic precipitation and meteorology (Massmann et al. 2016) and similarities and differences between CCOPE aerosol properties and those reported in prior studies of coastal areas. The latter topic is the focus of this thesis. This thesis seeks to answer three science questions.

1. How do the mean aerosol concentrations at Arauco compare to those measured at Trinidad Head, CA?
2. What processes can be identified as controlling the ASD at Arauco?
3. Can evidence of sea salt aerosol be identified by correlating the concentration of particles with D > 0.5 μm and sea-surface wind speed?

**Section 3: Measurement Site, Instrumentation and Instrument Calibration**

*3.1 Measurement Site*

During the CCOPE field campaign, a CPC (model 3010, TSI 2000a) and an Ultra High Sensitivity Aerosol Spectrometer (UHSAS) (DMT 2012) were operated in a residence near the coastal city of Arauco (population 35,000), Bío-Bío, Chile (Fig. 2a) (Instituto 2016). Characteristics of the aerosol instruments are provided in Table 2. The aerosol observation site is located at 37.25°S and 73.34°W, 3 km from shore at 55 m MSL. This location will be referred to as the Arauco Site. A meteorological tower at the Arauco Site measured temperature, relative humidity, precipitation, pressure, and horizontal wind.

Aerosol measurements commenced on 29 May 2015. CPC measurements were acquired from 29 May to 14 August. The UHSAS measurements are available from 29 May to 28 June. Aerosol measurements made with the combined systems (CPC and UHSAS), prior to 28 June, provide information about how the ambient particles are distributed as a function of size. A schematic of the aerosol instrument setup at the Arauco Site is provided in Fig. 3.

*3.2 Instrumentation*

At the Arauco Site the ambient aerosol was sampled into the aerosol instruments via a section of copper tube. The volumetric flow rate through the tube (Fig. 3) was 3.4x10-5 m3 s-1 and the length and inner diameter (ID) of the tube were 3 m and 0.003 m, respectively. The Reynolds number (Re) of the tubular flow was 960, well below the critical value (Re = 2300) where the transition from laminar to turbulent flow occurs. Particle transmission efficiencies were evaluated using Eq. 7.29 in Hinds (1999) and results are shown in Table 3. The two larger aerosol particle sizes, D = 0.1 μm and D = 1 μm have a particle transmission efficiency of 99% and while the transmission efficiency is lower for the smallest aerosol particles (D = 0.01 μm), the transmission efficiency is still high at 78 %.

The UHSAS is a single-particle optical scattering spectrometer. It measures scattering produced when aerosol particles are drawn through light emitted by a solid state laser (λ = 1.05 μm). A correction of UHSAS-measured concentrations is needed in environments where the particle sample rate exceeds 3,000 particles per second (DMT 2012). The value 3,000 s-1 was not exceeded in CCOPE and therefore a correction was not applied.

By reference to a calibration table (electronic threshold vs particle diameter; e.g., (Cai et al. 2013), the UHSAS microprocessor converts scattered light pulses to particle size and accumulates the pulses in a 99 channel histogram. Channel widths are logarithmically uniform ( = 0.013) over the full range of the instrument (0.055 < D < 1.0 μm). During CCOPE the UHSAS was configured to sample aerosol at 0.34x10-6 m3 s-1 and to record a count histogram every 10 s. Eq. 4 was used to evaluate the components of the aerosol size distribution (ASD).

 (4)

Here  is the “i th” component of the count histogram, is the aerosol sample flowrate, and = 10 s.

Because the RH at the Arauco Site was often in excess of 80 % (Fig. 4c), particles entering the tube were haze droplets. As these haze droplets transit the tube they experience an increase in temperature, a RH decrease and thereby a decreased D. The lowest relative humidity experienced by a particle is at the point of detection where the aerosol temperature is presumed to be the value measured by the UHSAS. The RH at that point is

 (5)

where is the UHSAS temperature, and and are the ambient RH and temperature respectively. In nearly all of the sampling conducted using the UHSAS, thewas less than 60 % - as seen in Fig. 4d - and this suggests that the particles detected by the UHSAS were partially dried. Partial drying of the particles is supported by calculations (Lewis and Schwartz 2004; their Figure 8) showing that a D = 1.9 μm NaCl haze particle reaches its equilibrium size (D = 1.0 μm) in 0.4 s subsequent to a step-change of RH from 98 % to 80 %. Because 0.4 s is small relative to the average residence time of particles within the inlet tube (0.8 s), it can be assumed that the sampled particles relax to their equilibrium size at  prior to detection.

The CPC counts particles larger than D = 0.01 μm by detecting scattering produced when aerosol particles are drawn through light emitted by a solid state laser (λ = 0.78 μm). Prior to detection, D is increased by at least a factor of 10 via alcohol condensation (TSI 2000a). The aerosol sample flowrate in the CPC is set at 1.7x10-5 m3 s-1 with a critical orifice. The CPC can detect a maximum concentration of 10,000 cm-3. CPC concentrations were recorded once per second during CCOPE.

*3.3 Calibration of Instruments*

Laboratory tests were conducted to evaluate consistency among measurements made with the UHSAS, the CPC, and a Scanning Mobility Particle Scanner (SMPS; TSI 2000b). ASDs

derived using the UHSAS (black) and the SMPS (grey) are shown in Fig. 5a. In this test, the three instruments (UHSAS, CPC and SMPS) were sampling mobility-selected particles with D = 0.075 μm. The mode measured by the UHSAS is close to that reported by the SMPS. Furthermore, size-integrated concentrations reported by the UHSAS, CPC and SMPS are all within 10%. Fig. 5b shows a test with D = 0.71 μm particles. Here the mode measured by the UHSAS agrees with that measured by the SMPS and the concentrations reported by the UHSAS and CPC are within ± 15%. The two-fold larger concentration recorded by the SMPS is a persistent feature of the SMPS measurements made in our laboratory. More research is needed to explain this phenomenon. The plots in Fig. 6a-b summarize all of the lab testing. UHSAS *N* is plotted vs CPC *N* for tests with D < 0.2 μm (Fig. 6a) and for D > 0.2 μm (Fig. 6b). These results show ± 15% agreement between size-integrated concentrations.

**Section 4: Air Mass Classification**

Within the town of Arauco, and within the Arauco region, many burn wood for residential heating especially during winter. Wood Combustion is a significant source of aerosol and trace gas pollution. Another pollution source is the Arauco paper mill located 12 km to the northeast (Fig. 7). When winds were northeasterly, the paper mill likely affected air quality at the Arauco Site. An important component of the mill’s gaseous effluent is sulfur dioxide (SO2). The latter is monitored at the government site at Lota (Ministerio 2015). Distant pollution sources include two cities further to the north, Concepción (60 km; population 224,000) and Santiago (500 km; 5,100,000) (Fig. 2a; Instituto 2016).

*4.1 Air Mass Classification with Wind Direction*

Measured wind directions were used to determine the wind sector classification applied in the analysis of the first research question. The clean and continental classifications used here are based on previous work discussed in section 1 and summarized in Table 1. For the comparisons of CPC concentrations at Arauco and THD (Fig. 2b), local wind measurements were used to classify the CPC measurements as clean sector or as continental sector. The wind direction is an hourly average for both locations. At Arauco, 160° to 290° is the clean sector. At THD, the clean sector is taken to be 250° to 20° east of north (Fig. 8).

*4.2 Air Mass Classification with Trajectories*

In addition to the classifications discussed in the previous section, air parcel trajectories were computed using the HYSPLIT model (NOAA 2016). Trajectories were computed for arrival times (at the Arauco Site) centered on 0, 6, 12, and 18 UTC. The derived trajectories are based on wind fields output to the Global Data Assimilation System (GDAS). The spatial resolution of the wind data is 0.5 degree. Trajectories were classified as marine or continental. Marine trajectories were required to be over the ocean for three days before landfall at Arauco, and with minimal northerly component immediately upwind of Arauco. All other trajectories were classified as continental. There are 22 marine trajectories coincident with availability of UHSAS measurements.

Trajectory altitude is important for determining the presence of SSA particles. Trajectories classified as marine, and having sea-surface origin, were required to have an altitude no larger than 500 m. Of the 22 marine trajectories, 17 classified as marine and sea surface; the five other trajectories have altitudes greater than 500 m. An example of a marine, sea surface trajectory is shown in Fig. 9. For each of the 17, sea surface wind speed was calculated by averaging the speed over a six-hour window ending six hours before the arrival at Arauco. The six-hour window is denoted in the right side of Fig. 9. Aerosol measurements analyzed with the trajectory dataset were acquired over a two-hour window centered on the trajectory arrivals at Arauco.

**Section 5: Analysis Methods**

*5.1 Filtering of the CPC and UHSAS Time Sequences*

For each marine trajectory, a two-hour time sequence, centered on the arrival time, was plotted and analyzed. An example plot is shown in Fig. 10a – c. Fig. 10a shows the sequence of CPC values sampled every second (i.e., 1-s samples here referred to as fast\_CPC), and Fig. 10b shows values sampled every 10 seconds (i.e., 0.1-s samples here referred to as NCPC). This particular example was picked because it exhibits variability (Fig. 10a) that may have been caused by local pollution. Some of this variability was removed via the following procedure.

First, the fast\_CPC values were used to determine, for each 10 s of the sequence, a concentration relative standard deviation (σ / ). Second, if σ /  > 0.02 the datum was discarded. Fig. 10c shows the NCPC sequence after application of the procedure. I refer to the output of the procedure as the filtered NCPC. The filtered NCPC and filtered UHSAS ASDs are used in the analyses presented in sections 6.2 and 6.3. In section 6.1, the fast\_CPC values are

hourly averaged for comparison to the hourly averaged THD CPC data. This is because I wanted to maximize the number of Arauco samples used in each hourly average.

*5.2 Small Particle Fraction*

A derived aerosol property, referred to as the small particle fraction, was formulated with the filtered NCPC and the filtered zeroth moment of the UHSAS ASD (NUHSAS).

 (6)

Because NCPC is the integrated concentration of all particle size categories, and the *NUHSAS* is the concentration of particles larger than 0.055 μm, *F* represents the fraction smaller than 0.055 μm. Assuming particles larger than D = 0.055 μm are not changing, an *F* ~ 0 is an indicator of a net sink having occurred at D < 0.055 μm and an *F* ~ 1 is an indicator of a net source having occurred at D < 0.055 μm. Two monomodal ASDs, one with a mode < 0.055 μm and the other with a mode > 0.055 μm diameter are used to illustrate the concept (Fig. 11a – b). The former has *F* = 0.95 and the latter has *F* = 0.05.

*5.3 Sea Salt Aerosol*

Though a correlation between oceanic wind speed and SSA particle concentration is tenuous, particularly in studies that evaluated the correlation for relatively small particles (e.g., D = 0.15 μm; Berg et al. 1998), an increase of SSA with wind speed is documented in many publications. In their review of the topic, Lewis and Schwartz (2004; herein LS04) classified SSA particle measurements into three size fractions. Their classification scheme uses a particle’s deliquesced wet size, evaluated at 80% relative humidity, as a metric. In field studies conducted at a coastal site, Clarke et al. (2003) demonstrated that particles sizing in the middle of the LS04 small fraction - those with a dry diameter larger than 0.5 μm or a RH = 80% wet diameter larger than 1 μm - were composed of sea salt. The basis for this was measurements made using a continuous-flow particle processing system consisting of a thermal denuder, controlled at 360 o C, followed by an optical particle counter. Within the denuder non-refractory aerosol components were volatilized prior counting and sizing. The only material that did not volatilize was inferred to be marine-derived NaCl (Clarke et al. 2003).

In section 6.3, a size-integrated SSA concentration is derived using UHSAS detections of particles with D > 0.5 μm (ND>0.5). The latter is a factor of two smaller than the RH = 80% diameter corresponding to the LS04 small fraction mentioned above. This is because it is assumed that particle size decreased as the aerosol stream warmed from ambient to the temperature of the UHSAS measurement (section 3.2).

**Section 6: Data Analysis**

*6.1 CPC Concentration Comparisons at the Arauco Site and THD*

 In this section, CPC concentrations measured at the Arauco Site are compared to concentrations measured at THD. The THD dataset spans the years 2002 to 2014 and is comprised of hourly averages. There are 26356 total data points from THD (12964 marine) compared to 1275 data points for Arauco (252 marine). The THD dataset includes contamination from local sources, such as boats in the harbor upwind of that coastal monitoring site (Elizabeth Andrews, private communication 2016); only measurements made during winter (December, January, and February) are compared to the Arauco measurements.

Different sample sizes require a particular statistical comparison. The approach followed here compares the Arauco and THD mean concentrations by applying the Student’s t-distribution method explained by Havlicek and Crain (1988; their equations 10.6 and 10.7). The statistical hypotheses are: A) Null hypothesis: mean concentrations are equal, and B) Alternate hypothesis: the mean concentrations are different.

First, the mean concentrations are compared without considering wind sector. The mean NCPC for Arauco is 3923 cm-3 with a standard deviation (*σ*) of 2669 cm-3. The mean and *σ* at THD are 1088 ± 818 cm-3. Fig. 12 shows the NCPC probability distribution functions (PDF). Most notable is the larger frequency of occurrence of NCPC < 2000 cm-3 at THD. Based on the comparison, I conclude that the Arauco mean is statistically larger than the THD mean (p < 0.01).

Second, before comparing the marine sectors of Arauco and THD, intra-dataset comparisons of the mean concentrations in the marine and continental sectors (section 4.1, Fig. 8) are compared. Fig. 13 shows concentration PDFs for the marine and continental sectors at Arauco. The occurrence of NCPC < 5000 cm-3 is more frequent for the marine sector; however, the occurrence of NCPC > 9000 cm-3 in the continental sector pulls the continental mean up. The marine mean is 3457 cm-3 ± 2284 cm-3, whereas the continental mean is 4041 cm-3 ± 2747 cm-3. Here, I conclude that the continental mean is statistically larger than the marine mean at Arauco (p < 0.01).

Fig. 14 shows the concentration PDFs for the marine and continental sectors at THD. The marine mean is 1171 cm-3 ± 772 cm-3, whereas the continental mean is 1000 ± 852 cm-3. The mean concentrations for the sectors of THD are not significantly different. However, based on the significant difference of the overall concentrations of Arauco and THD, the lack of significant difference is inconsequential.

Third, the marine mean concentrations are compared. The marine mean at Arauco is 3457 cm-3 ± 2284; at THD the average is1171 cm-3 ± 772 cm-3. As seen in Fig. 15, the occurrence of NCPC < 2000 cm-3 is larger at THD compared to Arauco. For the comparison of marine means, I conclude that the Arauco marine mean is larger than the THD marine mean (p < 0.01).

The statistically larger mean concentrations at Arauco, compared to THD, is a surprising result. This finding contradicts satellite studies demonstrating that averaged droplet concentrations within Northern Pacific boundary layer clouds are larger than those in Southern hemispheric clouds of the same type (Bennartz 2007). Bennartz (2007; their figure 5) also evaluated droplet concentrations within subregions. Of the five subregions investigated two were positioned at the eastern margins of the Northern and Southern Pacific basin and with poleward edges that encompass the latitudes of Arauco and THD. For these subregions, the averaged concentrations indicated larger values in the north compared to the south. Bennartz (2007) also commented on “..a strong horizontal gradient with an increase in N toward the coast of South America..” within the Southern Pacific subregion. Based on that comment and the omission of any comment about a coastal gradient within the Northern Pacific subregion one can conclude that the satellite/cloud and ground based/aerosol climatologies are in agreement, i.e., the larger aerosol concentration at Arauco, compared to THD, is consistent with the satellite retrievals showing that the concentration of cloud droplets along the Central Chilean coast are enhanced compared to those along the Northern California coast. Unfortunately, this conclusion is tentative because of the poor spatial resolution of droplet concentrations in Bennartz (2007; their figure 5). A more detailed analysis of the satellite climatology with focus on the winter season is needed to resolve this issue.

*6.2 Processes Controlling the ASD at Arauco*

In this section ASD moments are analyzed with a view toward understanding processes that shaped the ASD at Arauco. Guiding this are papers by Hegg and Kaufman (1998; herein HK98) and van Dingenen et al. (2000; herein VD00). These researchers analyzed correlations of *N* and *V*, slopes of the *N* on *V* regressions and processes inferred to control ASDs in moderately polluted marine air. HK98 based their analysis on airborne sampling conducted over the western Atlantic in air that had advected from the United States. VD00 analyzed a dataset acquired in air that had advected to study sites on Tenerife in the Canary Islands. Both datasets were collected during summer.

HK98 used a passive cavity aerosol spectrometer probe (PCASP) to evaluate *N*, *V* and the N/V ratio*.* Since the UHSAS counts down to a smaller diameter (0.055 μm) than the PCASP (0.12 μm), it is expected that the N/V ratios analyzed here will be larger than those in HK98. The main reason for this is that a smaller lower-limit diameter increases *N* more than *V*, assuming the same ASD. This logic is supported by the studies of VD00. In HK98 the dominant aerosol microphysical processes were new particle formation (NPF) and gas-to-particle conversion (GPC). These produce what is commonly referred to as “secondary” particles; i.e. particles produced in-situ by NPF and whose size is increased by GPC. In HK98 and VD00 little consideration was given to how the ASD was affected by SSA. During winter, when photochemistry is not as active, and sea-surface wind speeds are stronger, the importance of SSA production is expected to increase relative to the secondary processes examined by HK98 and VD00. The three aerosol processes (NPF, GPC and SSA production) are illustrated in Fig. 17.

Interest in the N/V ratio comes from the fact that the ratio is quasi-constant, and can be prognosed, at least in some summertime marine boundary layer settings (VD00), because cloud droplet number concentration is roughly proportional to N/V multiplied by an aerosol mass concentration, and because mass concentration (and thus *V*) is a relatively simple aerosol property to measure. However, this method of predicting droplet concentration requires the assumption that the lower-limit particle size applied in the determination of the N/V ratio is the smallest aerosol dry size activated within a cloud updraft. That minimum dry size has been estimated for summertime marine boundary layer clouds and is approximately 0.1 μm (HK98; VD00).

In addition to the analyses noted above, this section also investigates correlations of *N* and *S* and correlations of the fraction of particles smaller than 0.055 μm (*F*; Eq. 6) and *S*. Taken together, these statistics provide insight into the processes that shape the ASD at Arauco during winter. Throughout this analysis the focus is on two-hour intervals centered on the arrivals of marine trajectories at the Arauco Site. There are 22 arrivals in the dataset (section 4.2); 17 of these are sea-surface marine trajectories and 5 are marine trajectories originating from aloft.

*6.2a Analysis of N/V Ratios*

As in HK98, linear least-squares regression analysis with a model equation of form Y = a·X was used to derive N/V ratios. Moments of the ASD entered into the regressions were evaluated with the lower-limit diameter set at both 0.055 μm and 0.12 μm. The latter allows comparison to N/V ratios in HK98. Table 4 shows the ratios and Pearson correlation coefficients (*r*). With the exception of the 8 June 6 UTC arrival (D > 0.055 μm), all of the correlations are statistically significant at p < 0.01.

As expected from the previous discussion, the mean N/V ratio in the second column of Table 4 (312 ± 251 μm-3; # = 22) is larger than that in HK98 (226 ± 82 μm-3; # = 14). These means are different at p < 0.01 (i.e., the Arauco N/V ratio is larger than HK98’s) and this in spite of the larger variance in the Arauco result. The fourth column has results for Arauco based on the larger lower-limit diameter (D > 0.12 μm). In that comparison, the Arauco mean N/V ratio is smaller than HK98’s (p< 0.01). This result may be indicative of a different process controlling the ASD at Arauco versus that in HK98’s study.

In the previous paragraph it is demonstrated that the mean N/V ratio at Arauco (D > 0.12 μm) is smaller than that in HK98. The setting of their study was different, compared to that at Arauco, and this requires discussion. HK98 conducted an airborne study during summer. The target of HK98’s investigation was air that had advected off the eastern US into the nearshore region of the western Atlantic. Measurements of aerosol used to develop their N/V correlations came from airborne vertical profiling. VD00 also investigated continental outflow, but with ground-based instrumentation. In contrast to both HK98 and VD00, onshore flow (as opposed to continental outflow) during wintertime was the target of this investigation. Onshore flow versus offshore flow may be a factor controlling the N/V ratios in this work versus that in HK98 and VD00. Based on aerosol and trace gas measurements, HK98 concluded that their ASDs were controlled by secondary processes, i.e., NPF and GPC, both involving continentally-derived gaseous precursors (SO2 and organics). These were also active over the eastern Atlantic during collection of the summertime dataset analyzed by VD00. Another difference is that the mixing of free tropospheric and marine boundary layer aerosols thought important for ASDs at Tenerife (VD00) is unlikely to be operating at Arauco because of differences in meteorological and geographic factors. Finally, at Arauco, during winter, oceanic production of SSA is postulated to be dominant. This is investigated in the following two sections.

*6.2b Continental Contamination*

Time sequences of CPC and UHSAS measurements centered on 9 June 0 UTC (9 pm local time) are presented in Fig. 18a – f. This example was selected because its N/V ratio (51 μm-3; fourth column of Table 4) is small in comparison to the HK98 average (226 μm-3) and because of its intermediate N/V correlation coefficient (*r* = 0.81; fifth column of Table 4). In terms of meteorology, winds were light at Arauco and Curanilahue (< 3 m s-1) during this two-hour interval, and the wind direction at Curanilahue was northwesterly. No precipitation was observed at either Arauco or Curanilahue during the two-hour interval. Over the ocean, six hours prior to 9 June 0 UTC, the HYSPLIT wind speed was 8.3 m s-1 and the HYSPLIT direction was westerly (Fig. 9).

In terms of UHSAS measurements (Fig. 18b – d), an obvious feature is the variability in the sequences of NUHSAS (Fig. 18b), *V* (Fig. 18c) and *S* (Fig. 18d). Variation is most evident in the 80 min centered on the trajectory arrival. This interval is punctuated by an aerosol enhancement (23:25 to 00:20 UTC) and an aerosol diminishment (00:20 to 00:33 UTC). Within these periods the N/V ratio varied from 50 μm-3 (enhancement) to 764 μm-3 (diminishment). Can winds over the ocean drive this much aerosol variation, or is a continental source needed to explain the variability? This was addressed by calculating aerosol surface area (*S*; Eqn. 2) for winds that bracket the HYSPLIT-derived value (8.3 m s-1). The basis for the *S* calculation is the *S*-on-U parameterization described in LS04 (their Fig. 22). The calculation indicates that *S* can range from 6 μm2 cm-3 (U = 6.3 m s-1) and 15 μm2 cm-3 (U = 10.3 m s-1). Since the upper-limit of the predicted variation is small compared to the *S* during the enhancement (~ 200 μm2 cm-3; Fig. 18d), and because the wind speed variation applied in the calculation is an order of magnitude larger than the variation in the HYSPLIT-derived wind speed (± 0.2 m s-1), it is concluded that the aerosol enhancement is not due to a wind speed increase over the ocean. Rather, it is conjectured that the enhancement is due to a continental source. This conjecture is consistent with the relatively low wind speeds documented at Arauco and Curanilahue, likely favoring intermingling of marine and continental air, but not complete homogenation of these air masses. Another consistency is the northwesterly flow direction observed at Curanilahue and the fact that this is coterminous with the northern limit of the marine sector (Fig. 8). These results lead me to surmise that continental aerosol was sampled during some of the intervals which, based on the trajectories, should have been purely marine. Contamination, defined with the threshold *S* > 100 μm2 cm-3, was observed during four of the 17 sea-surface trajectories. For each of these, intervals with *S* substantially smaller than 100 μm2 cm-3 were selected. These subintervals, and their N/V ratios, are presented in Table 5.

*6.2c Analysis of N/S Ratios*

Table 6 shows N/S ratios, derived with the lower-limit size thresholds set at D > 0.055 μm, and correlation coefficients. The ratios were derived using linear least-squares regression analysis with a model equation of form Y = a·X. The N/S ratios are larger for D > 0.055 μm, and the *r* values are lower, compared to the penultimate and last columns of the table. This behavior is consistent with the discussion in section 6.2a. All of these correlations are statistically significant at p < 0.01. These positive N/S correlations contradict the negative correlation reported by Clarke (1992), but the contradiction is explicable. Clarke (1992) measured ultrafine particles in a narrow size interval (0.003 μm < D < 0.015 μm). These relatively small particles are produced via NPF. A necessary requirement for NPF is a relatively small *S*. In unpolluted marine air studies the threshold for NPF is approximately *S* = 10 μm2 cm-3 (Covert et al. 1992; Clarke 1992; Clarke et al. 1998; Petters et al. 2006). Conversely, when *S* is larger than 10 μm2 cm-3, the 0.003 to 0.015 μm particles (if produced) are lost via attachment to larger particles. It is because of these two competing processes – NPF source and attachment sink – that a negative N/S correlation was documented by Clarke (1992). In the Arauco data, it is the UHSAS size distributions that were integrated to obtain *N*, *S* and *V*. These moments correlate positively because the UHSAS is sensitive to accumulation mode particles, centered at ~ 0.1 μm, and because these contribute significantly to *N*, *S* and *V* (e.g., Seinfeld and Pandis, 1998; their Fig 7.18 and 7.17).

*6.2d Small Particle Fraction*

As discussed previously, the small particle fraction (*F*, eq. 6) represents the fraction of particles smaller than 0.055 μm. The *F*-on-*S* correlation is investigated in this section. An interesting feature of the relationship between *F* and *S* and is seen in Fig.19d and 19e*.* It is seen that *S* and *F* vary oppositely; hence *S* and *F* are inversely correlated.

Regression statistics for *F* on *S* are presented in Table 7 for the 22 arrivals. Nearly all of these exhibit strong (p < 0.01) negative F/S correlations. Here the fit function has the form *F* = slope\**S* + Y-Intercept. Table 7 shows that the intercepts vary between 0.54 and 0.95 and the slopes vary between -0.0006 and -0.0129 μm-2 cm3. Clearly, the relative variation of the slopes is larger than the relative variation of the intercepts. The last fifth and sixth columns have the interval-averaged surface area (<*S*>) and interval-averaged fraction (<*F*>). With regard to <*S*>, these averages are smaller than that presented in HK98(131 ± 93 μm2 cm-3)and the difference is statistically significant (p < 0.01). This is likely a consequence of the different upper-limit size of the UHSAS, compared to HK98’s PCASP. Also compelling, is the persistence of <*F*> at values typically > 0.6 and this in spite the large variation in the slope. Compensation for large negative slopes comes from their connection to small values of <*S*> (e.g., 5 June 6 UTC, 8 June 12 UTC, and 9 June 6 UTC) and the converse (e.g., 7 June 6 UTC, 9 June 18 UTC and 11 June 6 UTC). Overall, the occurrence of a persistently large <*F*> demonstrates that the Aitken mode portion of the ASD dominates particle concentration.

*6.2e Representation of the ASDs using Lognormal Functions*

The averaged ASDs are made available here so that future investigators can apply them in studies of the Southeastern Pacific region either in modeling (Reddington 2016) or in comparisons with aerosol measurements made in the Southern Pacific region during summer (e.g., Wood et al. 2011). Averaged ASDs for all 22 marine trajectories are presented here. Despite the trajectories’ marine origins, variability is evident in the average ASDs. This variability is not surprising given the variability evident in the two-hour interval shown in Fig. 19.

Eqn. 7.58 from Seinfeld and Pandis (1998) was used to fit the ASDs’ accumulation and coarse modes. Six parameters were derived, the accumulation mode’s concentration, diameter and width, and the coarse mode’s concentration, diameter and width. These are symbolized N1, D1, σ1, N2, D2, and σ2, respectively. Case-specific values and averages are in Table 8. The averaged mode diameters are D1 = 0.10 μm (± 0.02) and D2 = 0.54 μm (± 0.02). These are within a factor of two of the cold-season averages at Cape Grim, Australia (Gras 1995); however, the averaged N1 and averaged N2 are both larger than those at Cape Grim.

Averaged ASDs, variability about the average, and the bi-mode lognormal function (fn) are presented in Fig. 20a – d. From these it is evident that fn underestimates the ASD at diameters between the two modes. However, the ASD concentrations are closely approximated by the bi-mode lognormal function. Overall, the NUHSAS and (N1 + N2) agree within ± 20% (22 cases).

Examination of the individual ASDs (10 s averages) reveals variability that is not obvious in Fig. 20. Although most 10 s ASDs have a dominant accumulation mode (i.e., they are unimodal), bimodality is evinced by a right tail of an Aitken mode with an accumulation mode (5 cases; 5 June 0 UTC, 5 June 6 UTC, 5 June 18 UTC, 8 June 6 UTC, 9 June 6 UTC ) and by an accumulation mode with a coarse mode of comparable amplitude (2 cases; 9 June 0 UTC, 11 June 6 UTC). Larger values of ­*V* and *S* occurred for 9 June 0 UTC and 11 June 6 UTC; also the wind speed measured on the meteorological tower was less than 3 m s-1.

I examined the individual ASDs from the four arrivals that have evidence of continental contamination (section 6.2b). The marine subintervals display the same characteristics as those discussed in the previous paragraph. However, during the polluted periods of *S* > 100 µm2 cm-3, the ASD usually exhibited a mode at ~ 0.5 μm. This characteristic results in higher values of *V* and *S* and correspond to decreases of wind speed on the meteorological tower.

*6.3 Correlation of ND >0.5 and Sea-surface Wind Speed*

As discussed in section 5.3, ND>0.5 represents the concentration of particles larger than 0.5 μm. Even though ND>0.5 is a small fraction of the UHSAS-measured concentration (Fig. 21), these particles disproportionately influence rain development within shallow cloud systems (Feingold et al., 1999). During periods of onshore flow it is expected that particles larger than 0.5 μm originate from SSA production (Clarke et al. 2003). This expectation is explored by analyzing the correlation between ND>0.5 and sea-surface wind speed.

ND>0.5,averaged over the 17 sea-surface trajectory arrivals (section 4.2) is plotted against the sea-surface wind speed in Fig. 22. As in LS04, linear least-squares regression analysis with a model equation of form ln(ND>0.5) = aN⋅U + ln(N0) was used to derive the coefficients aN and N0. The resultant values are aN = 0.41 s m-1, N0 = 0.11 cm-3. Here, the correlation coefficient (r = 0.67) is significant at p < 0.01. Variability evident in these data is also seen in similar studies, such as those presented in LS04. One of the plots from LS04, showing variability within datasets, and variability among datasets, is reproduced in Fig. 23. One of the factors that can contribute to inter-dataset variability is the particle size interval that was deemed to correspond to SSA particles. Of the many possibilities in LS04 (their Table 12), two of the four comparators I picked had a comparable lower-limit diameter at or near 0.5 μm (Table 10), consistent with Clarke et al. (2003), and consistent with the threshold I used to evaluate ND>0.5. In addition, all of the comparators measured particles larger than the maximum detectable by the UHSAS (1 μm). Using the S-on-U parameterization in LS04 (their Fig. 22) it can be shown that the effect of D > 1 μm particles on cumulative concentration is negligible. All of the comparators measured aerosol concentration on ships.

Fig. 23 also demonstrates that intra-dataset variability is large; e.g., at U ~ 10 m s-1 the Parungo et al. values span a factor of three and are larger for measurements made south of 19 ºS. Comparable variability is seen in my dataset (Fig. 22 and Fig. 24). There is considerable discussion of inter- and intra-dataset variability in LS04. Two dominant factors influencing variability are upwind sea-surface wind events, occurring up to several days prior to a measurement, and the removal of particles by precipitation. The latter process resets the SSA concentration to low values. The net result is that wind speed is often poorly correlated with a collocated SSA concentration. I investigated how relative variability in wind speed, either at Arauco or over the sea surface, influence the relative variability of ND>0.5. Neither sea-surface relative wind speed variability nor local relative wind speed variability are factors affecting the variability of ND>0.5. Overall, my ND>0.5-on-U data points and regression line overlap with results from the two comparators (Parungo et al. 1986; O’Dowd and Smith 1993). These findings are demonstrated in Fig. 25.

**Section 7: Conclusions**

This work reports on condensation particle counter (CPC) concentration and aerosol size distribution (ASD) measurements made during winter at a coastal site in the Southern Hemisphere (Arauco, Chile). ASDs were measured using an ultra-high sensitivity aerosol spectrometer (UHSAS).

At Arauco, the marine-sector mean CPC concentration (3457 cm-3) and the sector-independent mean CPC concentration (3923 cm-3) indicate this site classifies more polluted than the coastal marine, but less polluted than the coastal polluted marine criterion (Table 1). At THD, the marine sector and sector-independent averages are 1171 cm-3 and 1088 cm-3, respectively. These are comparable to the coastal marine classification in Table 1. Even smaller winter averages (~ 200 cm-3) are reported for Tasmania (Andreae 2009). This demonstrates that THD should not be classified as a remote marine site. Enhanced CPC concentrations at Arauco, compared to THD, indicate that particle sources are enhanced at Arauco, that particle removal is stronger at THD, or that both of these factors are acting in concert.

Processes influencing the aerosol were probed by analyzing concurrent measurements from the CPC and UHSAS. Emphasis was placed on measurement intervals when a trajectory model indicated on-shore flow at Arauco. The fraction of particles (*F*) that size between the detection lower-limits of the CPC and USHAS (0.01 µm < D < 0.055 µm) were analyzed. The values of <*F*> reported here (Table 7), in excess of 0.4 in all cases, demonstrate that at least 40% of the particles detected by the CPC are smaller than 0.055 μm. Also, an inverse correlation between *F* and *S* is documented(Table 7). It is argued the sub-0.055 μm particles are produced in-situ via NPF and grow to sizes detected by the CPC (D > 0.01 μm) via GPC. There are nine examples of large <*F*> and small <*S*> in Table 7 (5 June 12 UTC; 6 Jun 6 UTC; 6 June 12 UTC; 6 June 18 UTC; 8 June 6 UTC; 8 June 12 UTC; 9 June 0 UTC; 9 June 6 UTC; 10 June 0 UTC). The arrival interval shown in Fig. 19 is representative. This has <NCPC> = 965 cm-3, <*F*> = 0.74, <*V*> = 0.71 μm3 cm-3, <*S*> = 16 μm2 cm-3. The average characteristics of these are presented in the first row of Table 11. Because of the criteria used to select these nine cases, they represent a best estimate of the background marine aerosol at Arauco.

In addition to the background conditions discussed in the previous paragraph, four cases were affected by pollution. This group (7 June 6 UTC, 8 June 18 UTC, 9 June 18 UTC and 10 June 6 UTC) is a subset of the 22 that were classified as marine based on the trajectory model. For these the aerosol measurements demonstrate substantial impact from continental pollution. The criteria used to select these were <*S*> larger than 43 μm2 cm-3 and N/V greater than 390 µm-3. The latter is the N/V ratio reported for aerosol produced by biomass burning (McMeeking 2004; his event I). Table 11 shows the comparison of these large <*S*> cases (bottom row) with the statistics derived for the clean marine cases (first row). When averaged these continentally-contaminated cases have an <NCPC> and an <NUHSAS> which are roughly three and five times larger than the background <NCPC> and an <NUHSAS>, respectively. As discussed in section 4, another plausible reason for these signatures of aerosol pollution is industrially emitted SO2. The latter is readily converted to aerosol number via NPF, and to aerosol surface area and aerosol volume via GPC. Measurements of SO2 at Lota averaged 10 ppbv during June 2015 (Ministerio 2015) which is comparable to the winter average reported for the Ohio River Valley (Shaw and Paur 1983).

 This work has also demonstrated that oceanic emission of SSA is an additional process that shaped the ASD at Arauco. As seen in Fig.22, ND>0.5 and sea surface wind speed are strongly correlated. Because of this correlation, marine flow adduced from the trajectory, and previous work done by Clarke et al. (2003), ND>0.5 is attributed to SSA. This is important because SSA is thought to be a factor which influences precipitation produced by shallow coastal systems (White et al. 2015). Reinforcing this is the modeling study of Feingold et al (1999), which demonstrated that a reasonable concentration of SSA mixed with a range of anthropogenic aerosol concentration can make a non-precipitating stratus cloud precipitate. The larger challenge is assessment of aerosol - precipitation interactions that occur within coastal systems deeper than the stratocumulus modeled by Feingold et al (1999). It is arguable that the low-level aerosol properties described here can impact deeper systems, but a more comprehensive study is needed to address that possibility.

1. By convention, the logarithm in Eqs. 1 – 3 is the decimal logarithm. [↑](#footnote-ref-1)