History of Aerosol-Cloud Interactions Derived from Observations in Mountaintop Clouds in Puerto Rico

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ABSTRACT

Aerosol particles in the atmosphere play a fundamental role in the formation of cloud droplets. Moreover, cloud-processing of aerosols is an important component of the changes observed in aerosol composition and size. In this study we present measurements of the physical and optical properties of interstitial and droplet residual particles in clouds made at a tropical mountain site. The measurements were made with the Aerosol Particle Spectrometer with Polarization Detection (APSPD) that was deployed at the mountaintop observatory of Pico del Este in Puerto Rico, between 25 August and 10 September, 2011 as part of the Puerto Rico African Dust and Cloud Study (PRADACS).

We evaluate the optical signatures and equivalent optical diameters of the sampled aerosol with respect to the origin and meteorological history of the air mass in which the aerosol were embedded. Additionally, the aerosol properties are related to the liquid water content present in the cloud.

The origin of the air mass is the most important factor that modulates the optical signatures, volume size distributions and total volume concentration of the sampled aerosol. Differences in the aerosol volume concentrations were significant (up to a factor of 4) between air masses originating in Africa, the North Atlantic and the South Atlantic. In addition, African aerosols have a much higher ratio of residual to interstitial volume concentration, suggesting that these particles had a higher fraction of cloud condensation nuclei than in the other air masses. Finally, the amount of precipitation along the air mass trajectories impacts the aerosol volume concentration, as does the residence time of the air mass in the moist, oceanic boundary layer, below 500 m.

Keywords: Aerosol optical signatures; African dust; Light Polarization; Cloud processing of aerosols.

BACKGROUND

The symbiosis between aerosol and cloud particles is one of the most important relationships in the atmosphere. In the absence of cloud condensation or ice nuclei (CCN, IN), a relative humidity (RH) in excess of 400% would be required for cloud droplets or ice crystals to form (Pruppacher and Klett, 1998). In contrast, cloud droplets form on CCN when the RH is as little as a fraction of a percent above saturation (100%), i.e., supersaturations of < 1%. Cloud-processing alters the properties of atmospheric aerosols. Some estimates (Pruppacher and Jaenicke, 1995) indicate that on a global average, an atmospheric aerosol particle is processed by a cloud at least three times during its life time. There are multiple pathways by which aerosol particles are either removed or transformed as a result of their interactions with clouds, described in detail by previous studies (i.e., Flossmann et al., 1985, 1987; Flossmann and Pruppacher, 1988; Flossman, 1998). The CCN fraction of aerosol particles experience heterogeneous nucleation during droplet activation modifying the ambient aerosol size distribution. Collection of particles by cloud droplets further changes their concentration. The chemical and physical properties of particles in droplets can change as the soluble part of particles dissolves in cloud water and as atmospheric gases diffuse into droplets and undergo chemical reactions in the aqueous phase (Barth et al., 2000). Evaporation of droplets exposed to dry air by entrainment, results in cloud-processed particles which may have different sizes, shapes or composition than the pre-activated particles. Furthermore, precipitation leads to the irreversible removal of aerosol particles from the atmosphere.

Given the importance of the impact of aerosol and cloud particles on climate, due to direct and indirect effects, it is essential that we thoroughly understand the interactions between aerosols and clouds and the underlying physical
and chemical processes that change composition, number concentration, shape and size. Without this fundamental understanding we cannot adequately represent these processes in climate models and subsequently our forecasts of climate trends will have a high uncertainty, particularly on a regional basis where radiative forcing by aerosols and clouds can dominate over that exerted by well-mixed greenhouse gases.

There have been numerous theoretical studies to analyze the processing of aerosols by clouds (i.e., Flossmann et al., 1985, 1987; Flossmann and Prupacher, 1988; Flossman, 1998). It is a challenge to make measurements from aircraft to validate the theory since cloud lifetimes are short and aircraft can sample only a very small fraction of a cloud. Clouds that develop over hills and mountain-tops are excellent outdoor laboratories where measurements can be made and have lifetimes of more than several hours. The history of the air mass that leads to the cloud formation can usually be identified with back trajectory analysis and finally, measurements can be made at a fixed location over extended periods of time.

One location that has been used frequently for studies of mountain clouds is Pico del Este (PE, Fig. 1) in Puerto Rico (18°18.210’ N, 65° 45.570’ W), at an altitude of 1054 m a.s.l., where a semi-permanent research station is located (Eugster et al., 2006; Allan et al., 2008; Spiegel et al., 2014, Fitzgerald et al., 2015). This location is almost daily in clouds that can sometimes last for several days. The air masses that arrive at this site, carrying the aerosols that produce and are processed by the cloud, are usually from the east of the island and over the ocean. Urban aerosols from the capital city of San Juan are rarely a source of the particles found in these clouds due to the prevailing easterly winds. During the summer and autumn months, air masses frequently originate from the African continent and the particles are mixtures of dust, bioaerosols and carbonaceous aerosols as a result of biomass burning (Spiegel et al., 2014; Fitzgerald, 2015). The location of the research site offers a unique opportunity to study the interaction of aerosols with the mountaintop cloud and the relationship between the processed aerosol properties and the air mass histories. Previous studies that took advantage of these clouds were those by Eugster et al. (2006) who evaluated water flux to the Elfin forest, Allen et al. (2008) who focused on evaluating the importance of organic aerosols, Spiegel et al. (2008) who studied the impact of African dust on cloud microphysical properties, and Fitzgerald et al. (2015) who analyzed the chemical composition of African dust particles.

The measurements reported here are only a subset of those that were made by a large group of scientists and students as part of the Puerto Rico African Dust and Cloud Study (PRADACS), which is described in greater detail in a companion paper (Valle-Díaz et al., 2016). Our study evaluates the physical and optical properties of cloud droplet residuals, i.e., activated and scavenged aerosol particles, and of the interstitial aerosol that were not removed by the cloud droplets. The goal is to identify the factors that are most important in determining the particle properties. In particular, we evaluate the relationships of particle properties with 1) air mass origin and meteorological history, 2) amount of time the air mass was close to the ocean surface and 3) cloud liquid water content (LWC).

Fig. 1. Google Earth image of the island of Puerto Rico and the location of the measurement site at Pico del Este (inset with yellow circle).
MEASUREMENT AND ANALYSIS METHODOLOGY

**Instrumentation**

This study focuses on the comparison of the properties of droplet residual and interstitial aerosol particles. The inlet system used to deliver these two types of aerosols to the instrumentation is described by Allan et al. (2008). The inlet uses an impactor (upper cut-size of 4 µm) to separate water droplets from the air stream such that only non-activated, interstitial particles are sampled. The cloud droplet residuals are produced with a counter-flow virtual impactor (CVI) that has a lower cut-size diameter of 5 µm (Mertes et al., 2005). The CVI removes the interstitial particles, evaporates the water droplets and delivers the residual nuclei to the instrumentation.

The aerosol size distributions of different types of particles (defined by their optical signatures) and the volume concentrations are measured with the Aerosol Particle Spectrometer with Polarization Detection (APSPD), developed by Droplet Measurement Technologies (DMT, Boulder, CO). The APSPD is a ground-based version of the DMT airborne Cloud and Aerosol Spectrometer with Polarization Detection (CAS-POL) described by Glen and Brooks (2013) and a newer instrument, the Cloud Particle Spectrometer with Polarization Detection (CPSPD) that is discussed in detail by Baumgardner et al. (2014). The differences between the APSPD and the other two instruments are highlighted below.

Fig. 2 is an optical schematic of the APSPD. The light scattered by individual particles that pass through the focused laser beam is collected by optics positioned to gather side and backscattered photons. The mangin mirror pair collects the photons over a solid angle from 36° to 144° and two other optical systems collect the backscattered light over solid angles from 147° to 173°. The 680 nm laser is linearly polarized and one of the two backscattering detectors is fitted with a linearly polarized filter oriented so that it collects light scattered with polarization perpendicular to that of the incident laser beam. The particles are introduced to the laser beam with an aerodynamic jet that focuses the particles with dry, particle-free sheath air. The collection angles and aerosol delivery system are different than the CASPOL and CPSPD.

The light scattered at 180° by spherical particles will retain the same angle of polarization as the incident laser polarization but at angles away from 180° some of the scattered photons will have a polarization vector perpendicular to the incident light. Hence, this composite scattered light is considered to be elliptically polarized. Aspherical particles will scatter light that is also elliptically polarized, but much more so than spherical particles. By comparing the scattered light measured by the detector with the polarized filter and by the detector that measures all the backscattered light, the polarization ratio can be derived, a parameter that is related to the complexity of the morphological structure of the particle (Nicolet et al., 2007; Bundke et al., 2008; Nicolet et al., 2010, 2012; Schnaiter et al., 2012).

The equivalent optical diameter (EOD) of the particles is derived from the side scattering signal using Mie Theory (Mie, 1908) to convert the collected light to the diameter of a spherical water droplet (refractive index 1.33) that would have scattered the same measured intensity of light at the same collection angle and laser wavelength. Atmospheric aerosol particles have a wide range of shapes and refractive indices so that an assumption of a spherical water droplet introduces an uncertainty in the derived EOD; however, in the results discussed here, only the changes in the relative size are evaluated and not the absolute diameter of a particle. The nominal diameter range of the APSPD is 0.5 µm to 20 µm.

There are no reference particles at the moment that can be used to calibrate polarimetric instruments like the APSPD, CAS-POL and CPSPD with respect to the magnitude of the polarization ratio relative to the asphericity of a particle. Hence, several laboratory studies have been conducted to evaluate the relative response of these instruments to different types of aspherical particles. Glen and Brooks (2013) employed dust particles of different origins and concluded that there were groups of dust types that could be categorized by their polarization signatures. A similar study was carried...
out with the APSPD using various types of dust, ash collected from the Icelandic volcano, Colorado yellow pine pollen, iron and silicone oxide, hematite and quartz. The dust used in the study was urban (Washington DC), fine (Arizona) and medium (Arizona) dust purchased from the National Institute of Standards and Technology (NIST). The other samples of Australian, Namibian and Azores dust were provided courtesy of Bernadette Weinzierl of the Deutsches Zentrum für Luft und Raumfahrt (DLR) in Oberpfaffenhofen, Germany.

Figs. 3(a) and 3(b) illustrate the differences that arise when comparing the optical signatures from 15 types of minerals, ash and pollen. The polarization ratio is defined here as the signal from the polarization filtered back detector divided by the total backscattering signal. Fig. 3(a) shows that the Australian, Namibian and Azores dusts fall in one group, the ash, urban dust and Arizona dust form another group and the pollen appears to have a trend of its own when plotting the polarization ratio versus the EOD. When displaying the total backscatter versus the polarization signal, the different types begin to separate out more so that there is a greater distinction drawn between them.

Various combinations of the three signals (side, back and polarized scattering) were evaluated to see which ones produced the largest separation with respect to the test particle type, e.g., three combinations can be formed by comparing the total backscattering, polarized scattering and polarization ratio to the EOD. Likewise the polarization ratio can be compared to the backscattered signal. The different combinations are not mutually independent nor do they need to be for the pattern recognition technique that is employed here. As Figs. 3(a) and 3(b) illustrate, the relationships are close to linear and the other combinations that were selected were also sufficiently linear to do a least squares regression fit to each combination for each particle type. In the study reported here the optical signatures of the ambient aerosol particles are derived from the three scattering signals and compared with the linear relationships derived from the test particles. If the ambient particle’s signature falls within one standard deviation of the ensemble least square fit of one of the test particles, the ambient particle is associated with that test particle.

It is important to note, however, that the ambient particle is not necessarily the same type as the test particle since the laboratory tests were far from exhaustive and there are probably many types of atmospheric particles that have similar signatures. Instead, the test particles are labeled with the name of the laboratory particle, followed by the suffix “like”, e.g., “Pollen-like” or “Iron Oxide-like”. If the ambient particle does not match any of the test particle signatures, it is labeled as “No Match”.

Because of the complexity of the atmospheric aerosol population and their associated optical signatures, the results at this time can only be reported qualitatively with no quantitative description related to the actual particle composition. As the database of polarization signatures from different varieties of dust, ash, bioaerosols and other types of particles is expanded, the expectation is that more quantitative analysis will be possible in the future.

The APSPD was installed in an air-conditioned building at the PE research site along with a suite of other aerosol instruments. As described previously, the APSPD sampled air that was delivered to it from the interstitial inlet and the CVI at intervals that were determined by the operator of the day. Due to the length of the sample line, particles larger than 10 µm had a low probability of being measured by the APSPD. The upper size cut-off appeared to be an EOD of approximately 6 µm.

In this study data from the Particle Volume Monitor Model 100 (PVM-100, Gerber Associates) is also used; the PVM-100 measures cloud liquid water content (LWC), droplet surface area and, from these, derives the effective radius, $R_{\text{eff}}$

![Fig. 3.](image-url) A number of different types of dust, bioaerosols and volcanic ash have been measured in the laboratory with the APSPD as shown by their optical signatures in these figures: a) Polarization ratio versus the equivalent optical diameter (EOD) and b) Total backscatter signal versus the polarization ratio. The test particle types are listed in the legend box.
Back Trajectory Analysis and Hypotheses Testing

The origin and history of an air mass will impact the aerosol properties and how they interact with clouds. If the air mass has originated over an industrial area or region of biomass burning, the particle properties would be expected to be quite different than if the air mass originated over the African desert or over the ocean. Likewise, if clouds or precipitation have formed along the path of the air mass before it arrives at the measurement site this will possibly change the properties of the aerosol population from what they were at their origin.

The following hypotheses are put forward to be tested by the analysis of the aerosol and cloud measurements on PE:
1. The particle property metrics will differ depending on air mass origin.
2. The particle property metrics will differ depending on the amount of precipitation during the air mass history.
3. The particle property metrics will differ depending on the number of hours the air mass was in the boundary layer, less than 500 m above the surface.
4. The particle property metrics will differ depending on the amount of LWC in the mountaintop cloud.

The fourth hypothesis is not directly related to the air mass origin, meteorology or history but is a physically reasonable hypothesis given the microphysical processes involved with cloud formation and the chemical and physical processes related to aerosol processing by clouds.

The particle property metrics used are related to the particle types and their volume concentrations in droplet residuals and interstitial aerosol and will be described in greater detail in section 3.0.

The Hybrid Single Particle Lagrangian Integrated Trajectory Model (HYSPLIT) is used to identify the origin and meteorological history of the air masses that arrived at PE during the field program. The HYSPLIT model uses archived meteorological data fields of temperature, humidity, pressure and winds to construct back trajectories that give the three-dimensional position and selected meteorological variables (Draxler and Hess, 1998). For the analysis described below, the HYSPLIT model was run every six hours from August 25 to September 10, 2011. The trajectories were computed going back 10 days in one-hour intervals along with the amount of precipitation, one of the derived meteorological parameters.

Fig. 4 illustrates the two back trajectories per day for the whole measurement period, that have been color-coded by altitude (Fig. 4(a)) and by accumulated rain (Fig. 4(b)). The accumulated rain is derived by summing the hourly precipitation beginning 10 days back. Note that all the air masses are coming only from the East sector, from approximately 45° to 135°. The majority of trajectories are located in the Northern Hemisphere, but a few arrive after crossing the Equator along the coast of Brazil. The air masses coming from the North Atlantic and Africa descend from a higher altitude to reach the research site at PE, whereas those from the southeast have been below 1000 m for several days (Fig. 4(a)). While some of the trajectories coming from Africa and the North Atlantic indicate that the air masses developed precipitation (according to the meteorological fields used by the model), those coming from the south Atlantic have formed precipitation along their track more frequently.

In the analysis discussed in the next section, the air mass origins are identified as Africa, North Atlantic and South Atlantic, based upon examination of the trajectories shown in Fig. 4. Fig. 4(c) shows the accumulated precipitation and time below 500 m, every six hours, over the analysis period from August 25 (day of the year 231) to September 10 (day of the year 253). The colored markers along the top axis of this figure indicate the origins of the air masses. Most of the air masses that have had precipitation forming in them along their trajectory arrived during the first half of the experiment and during the last four days of the project. Likewise, those air masses with accumulated rain also appear to be those that have spent more than a day (24 hours) below 500 m before arriving at PE.

RESULTS

Temporal Evolution of the Particle Physical Properties

The number and volume concentration of all particles measured with the APS, regardless of optical signature, and including both residual and interstitial, are shown as time series in Fig. 5(a), averaged over 10 minute intervals during the period that the instrument was operated. The cloud LWC and effective radius, derived from the PVM-100, and precipitation measured by the weather station (Davis Inc.) are shown for the same time period in Fig. 5(b). The markers between the two panels show when the inlet was turned to the CVI (violet) or to the interstitial (red). The markers along the top axis of Fig. 5(a) show the air mass origin. Note that during days 234 to 236 the equipment was turned off due to the proximity of a tropical cyclone. There is a clear diurnal cycle seen in the concentrations and the LWC during most of the time period. The maximum concentrations occur near midnight, as do the maximum LWC and effective radii. There is no reason to expect the nighttime population of aerosols to be different from those in the daytime so the daily trends most likely are a meteorologically driven phenomenon. Although sometimes the mountain clouds that form at this location are a result of solar heating and convection, more often their formation is driven by vertical velocities caused by the topographic forcing. The wind speed varies quite a bit day to day but almost always reaches maximum velocity near midnight as measured with the anemometer at the research site. Hence, the maximum LWC coincides with the maximum wind and the higher LWC is a reflection of the larger effective radius of the droplets attained through condensational growth.

Fig. 6(a) shows the size distribution of particle volume concentration for the same time period and the precipitation rate (black curve) at the measurement site. The markers between the two panels indicate whether the measurements are interstitial or residual as in Fig. 5 and the other markers along the top axis designate the air mass origin. The daily oscillations that were observed in Fig. 5(a) in the volume concentrations are seen over the whole size range of the
particle size distributions. There is a trend after the break for the tropical storm, from DOY 237 onward, of a shift of the size distribution shape from one that is fairly broad with a peak around 1 µm to a steadily decreasing width and peak around 0.7 µm. During the last two days of measurements the distribution has broadened with the peak volume again around 0.9 µm. There are no noticeable changes in the shape or concentrations of the size distributions associated with the precipitation, i.e., there does not appear to be significant particle removal by inertial scavenging.

**Trends in Optical Signatures**

As discussed previously, the three scattering signals from individual particles are used to categorize the particle with respect to the patterns that have been identified in the laboratory related to specific types of dust, bioaerosols or volcanic ash. The polarization ratio provides a first order indication of the degree of asphericity of the particle population as well as the amount of variation in the composition of the particles, i.e., more aspherical particles with more complex structure will have higher polarization ratios. Fig. 6(b) shows the size distribution of this ratio, indicating a large variability across sizes and time. During the first two days of the experiment, days 231 and 232, the polarization ratio is relatively homogeneous from 0.7 to 2 µm, suggesting that these particles have approximately the same type and composition independent of their size. After the measurement recess caused by the tropical storm (indicated on Fig. 6(a)), the patterns become more inhomogeneous. There is an increase in the polarization ratio for particle sizes between 0.6 and 1 µm on days 238 to 241 and then a decrease over this same size range from days 243.5 to 246. The earlier increase suggests increasing asphericity whereas the latter decrease would be consistent with more quasi-spherical particles. Note from Fig. 4, that during the interval from 238 to 241, the air masses had accumulated rain amounts of over 25 mm whereas almost no precipitation along the trajectories was observed on days 243.5 to 246. The APSPD data set was examined particle by particle to identify how many, if any, of the particles in the PRADACS measurements had optical signatures similar to what were found in the laboratory. Of the 15 types of particles
evaluated in the laboratory, there were only two signatures that were matched in the PRADACS data set: pollen and iron oxide. All the other optical signatures could not be matched and can only be classified as “no match” at this time. Once more laboratory studies are done at DMT and by other groups performing similar studies, a more definitive classification may be possible for these data. For the current study, however, the signatures matching the pollen samples in the laboratory will be referred to as “Pollen-like” (PL), the signatures matching the iron oxide samples in the laboratory as “Iron Oxide-like” (IOL), and all others as “No match” (NM).

**Optical Signatures, Air Mass History and cloud Water Content**

The measurements have been grouped according to air mass history, cloud water content, particle type and whether the particle is a droplet residual or interstitial aerosol. The first stage of the analysis was to compare the volume size distributions, as presented in Figs. 7 and 8, where the conditional variables are air mass origin (Figs. 7(a)–7(c)), number of hours at an altitude below 500 m (Figs. 7(d)–7(f)), accumulated precipitation (Figs. 8(a)–8(c)) and cloud LWC (Figs. 8(d)–8(f)). Note that for the precipitation, altitude and cloud water stratifications, only the air masses with North Atlantic origin are used. This was done because air masses with North Atlantic origin were the most common and also in order to remove any impact that African dust or South Atlantic aerosols might have on the comparison. The solid lines in all figures represent the residual particles and the dashed lines the interstitial. The different colors indicate the three types of particles identified. Table 1 lists the number of minutes of measurements that were used for each of the 12 conditions and in the residual and interstitial categories.

There are clear differences in the aerosol properties as a function of air mass origin as seen in Figs. 7(a)–7(c). The volume size distributions (VSD) of the African origin
residual particles (Fig. 7(a)) are much higher in concentration and the shape of the VSD is much narrower than those found in the residuals in air masses from the other two regions. The three particle types have distinctly different VSDs, e.g., particles associated with the NM type have VSDs always much broader than the other two types and extend out to much larger sizes regardless of air mass origin. A third feature of note is that whereas the interstitial VSDs in Africa (Fig. 7(a)) and South Atlantic (Fig. 7(c)) air masses are much lower in concentration than the residuals, the interstitial and residuals in the North Atlantic air masses (Fig. 7(b)) are nearly equal in concentration.

The VSD are also very sensitive to stratification by the number of hours that the air mass was in the boundary layer below 500 m. The largest differences are seen between the VSDs of particles that were never below 500 m (Fig. 7(d)) compared to those that had spent some time near the surface (Figs. 7(e) and 7(f)). In particular, both the residuals and interstitial concentrations are 2–3 times greater under the former conditions than under the latter. The VSD for NM type particles, for the condition of never at an altitude below 500 m, extends out to larger EODs than for those particles in air masses that spent time near the surface. The relationship between the residual and interstitial VSDs is very different for the three conditions. In Fig. 7(d) the residual and interstitial VSDs for PL and NM are the same while the interstitial is greater than the residual VSD for IOL particles (Fig. 7(d)). In those air masses that were under 500 m less than 24 hours, the interstitial VSDs are a factor or two less in concentration over all sizes than the residual (Fig. 7(e)). In stark contrast to the other conditions, the interstitial VSDs are a factor > 2 times the residual aerosols in those air masses that resided more than 24 hours below 500 m. The logical conclusion from these comparisons is that sedimentation removes a greater fraction of the particles in air masses near the surface than in higher altitude trajectories and that the longer the air mass has been near the surface, the more the hygroscopic particles will be removed. From Fig. 4(c) we see that the air masses that had been near the surface the longest period of time were generally also those that had experienced precipitation. Hence, since precipitation removes aerosols, this correlation suggests that this is the reason that near surface air masses had fewer particles.
Stratifying with respect to accumulated precipitation, shown in Figs. 8(a)–8(c), impacts the volume concentrations and shapes of the VSDs, as well as the relationship of the interstitial to residual concentrations. The VSDs of particles in air masses with little precipitation (Fig. 8(a)) have much higher concentrations than those with precipitation (Figs. 8(b) and 8(c)) and extend to EODs several micrometers larger. In the limited rain VSDs, the interstitial and residual concentrations are the same; however, in those air masses with more than 5 mm of rain along their trajectories, the interstitial particles are in much greater concentration over all sizes. We assume that the formation of precipitation along the air mass trajectory will lead to fewer particles at the point where we measure them as a result of removal by precipitation scavenging. The results support this assumption, and in addition, the increase in interstitial and decrease in the residual particles also supports this assumption as the hygroscopic particles are those that are scavenged by nucleation and subsequently removed by precipitation, leaving more of the hydrophobic, interstitial particles.

The cloud LWC measured at the research site has its greatest impact on the relative distribution of interstitial and residual particles. At very low LWC, $< 0.1$ g m$^{-3}$ (Fig. 8(d)), the residual VSDs are much larger in concentration, over all sizes, for the three types, than the interstitial. This reverses in the case of medium LWC (Fig. 8(e)) when the residual VSDs are substantially less than the interstitial. At larger LWCs (Fig. 8(f)), the interstitial and residual VSDs are approximately equal. Although the volume concentration appears to increase with LWC, this increase occurs over all sizes and types, i.e., the cloud processing does not appear to be either particle size or type specific.

DISCUSSION

From the comparisons displayed in Figs. 7 and 8, it is clear that there are differences in the VSDs that appear to be related to the history of the air masses and the local cloud LWC. In some cases, visual inspection of the VSDs is sufficient to draw a distinction whereas in other cases there are suggestions of differences that need to be further explored with a more quantitative analysis. For this purpose we have chosen the integral of the VSD, i.e., the volume concentrations, as the particle property metric.

In particular, for each condition, we will evaluate relative changes in particle type concentrations, with respect to one another, within residual and interstitial aerosols and assess relative changes in the ratio of residual to total particle concentrations for each type. Figs. 9(a) and 9(b) summarize the volume concentrations by type and conditions and the ratios between the residual and total particle concentrations, respectively.
**Fig. 8.** Similar to Fig. 6 except for conditions of a) accumulated precipitation < 5 mm over the 10 day trajectory, b) < 20 mm, c) > 20 mm, d) cloud LWC < 0.1 g m⁻³, e) 0.1 < LWC < 0.3 g m⁻³ and f) LWC > 0.3 g m⁻³.

**Table 1.** Number of minutes of measurements used in the analysis.

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<th>Condition</th>
<th>Residual</th>
<th>Interstitial</th>
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<td>South Atlantic origin</td>
<td>2070</td>
<td>1530</td>
</tr>
<tr>
<td>Africa origin</td>
<td>2510</td>
<td>2160</td>
</tr>
<tr>
<td>North Atlantic origin</td>
<td>12050</td>
<td>11350</td>
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<tr>
<td>Never &lt; 500 m</td>
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The residual aerosols are proxies for the activated, larger CCN, i.e., although it is possible that some of the residuals are due to inertia scavenging, in general, removal of aerosols by activation and droplet formation is more efficient than collection by Brownian diffusion or collision between a droplet and an aerosol particle (Prupaccher and Klett, 1978). The measured residual aerosols do not represent the complete size spectrum of activated droplets, however, since a large fraction of the activated CCN are smaller than the detection threshold of the APSPD. Interstitial particles in the range measured by the APSPD are either hydrophobic or minimally hygroscopic since they did not activate as cloud droplets. Hence, as we evaluate the relative magnitude of the residual and interstitial volume concentrations we can begin to draw some tentative conclusions about how the air mass history might have altered the relative fraction of CCN and non-CCN.

The NM type aerosols in African air masses have residual concentrations that are four to eight times larger than the NM particles in the other air masses. The volume
concentrations of the other types are also two to three times larger than those in the air masses with other origins. These differences are underscored by the residual to total ratios that are many times larger for all the types in the African air mass compared to similar ratios in the South and North Atlantic cases. This implies that the majority of the particles in the African air masses, by the time they are measured in the PE cloud, have been activated as cloud droplets, or inertially removed by the cloud. The much lower ratios in the South and North Atlantic air masses suggest that a significant fraction of the hygroscopic aerosol particles were likely removed by precipitation prior to arriving at PE.

The very large concentration of NM particles in the African air mass, compared to the other two conditions, suggests that a large fraction of these particles have very different composition and morphology than found in the South or North Atlantic air masses. As previously mentioned, the NM particles are identified by their optical signatures that didn’t match any of the laboratory particles, so they could be a different type of dust than was tested or they could also be other types of organic or inorganic particles, for example. The important point is that they can be identified as different by their optical signature. Fitzgerald et al. (2015) measured the composition of particles in air masses of African origin in the summer of 2010 also at PE and found that a large fraction of them contained alumino-silicate, a type of dust that was not tested in the laboratory. Future studies with the APSPD should include this type of dust to obtain its optical signature and include it in the signature library.

Upon further examination of Fig. 4(c), we observe that there appears to be a rough relationship between the accumulated rain and the hours that an air mass was below 500 m. Comparing the samples when the air mass was never at an altitude below 500 m and those samples that experience precipitation < 5 mm, the residual and interstitial volume concentrations are remarkably similar (Fig. 9(a)), as well as their ratios (Fig. 9(b)). A possible conclusion is that the air masses with little precipitation and those that never passed below 500 m are likely the same. It is reasonable to expect that the air masses that were never below 500 m and those with no precipitation would have higher aerosol loading than those that were near the surface or had more precipitation along their trajectories. The higher humidity near the ocean surface promotes the growth in size of hygroscopic aerosols by deliquescence and subsequently higher terminal velocities. Hence, the more time the air is near the surface, the fewer particles that should arrive at the measurement site. This is what the measurements show for the residual concentrations. The samples that were either never below 500 m or up to less than 24 hours at that
altitude, show decreases in concentrations by factors of two and three across the three particle types. Increasing the time below 500 m further decreases the volume concentration by another 30–50%.

An anomaly that cannot be easily explained is the increase in the ratio of residual to interstitial concentrations for air mass that were below 500 m less than 24 hours. Although this might be a result of the removal of interstitial aerosols by some physical mechanism, it is more likely that the proximity to the ocean surface might have provided an additional hygroscopic aerosols such as sea salt particles generated by wind and/or sulfate particles produced from dimethyl sulfide (DMS).

In the case of precipitation, however, more rain along the trajectory does not lead to fewer particles after the initial decrease from little rain (< 5 mm) to moderate rain < 20 mm. There is actually a slight increase in both the residual and interstitial volume concentrations as the accumulated precipitation increases from < 20 mm to > 20 mm. A more detailed evaluation of the individual trajectories with > 20 mm of precipitation is needed, but beyond the scope of the present study, to better understand why the concentration would increase with increasing accumulated precipitation.

The final condition evaluated is the cloud LWC at the mountaintop site and how it changes in relation to changes in the wind speed and air mass history. The LWC, droplet effective radius (Reff) and wind speed were averaged into the six hour intervals defined by the back trajectories. The LWC is highly correlated with the Reff (r = 0.86, P < 0.01), as shown in Fig. 10(a). The observed high correlation between the LWC and Reff is related to the height of the cloud base with respect to the measurement site. Note that also the LWC is positively correlated with the relative humidity (RH) of the air mass one hour prior to reaching the research site (r = 0.38, P < 0.01) as observed in Fig. 10(b). Furthermore, the RH of the air mass one hour prior to arrival at the research site is also positively correlated with the wind speed at the site (Fig. 10(c)), and is negatively correlated with the altitude of the air mass one hour prior to arrival (Fig. 10(d)). Given that the air masses closest to the surface are those linked to the highest wind speeds at the site, this suggests that the larger RH values of these air masses are a result of increased moisture fluxes from the ocean surface.

In summary, the relationships among the variables shown

![Fig. 10. Dispersion diagrams between a) cloud liquid water content (LWC) and effective radius, b) LWC and relative humidity (RH) of the air mass one hour previously, c) wind speed and RH of the air mass one hour previously and d) air mass RH and altitude one hour before reaching the site. The values r and P in each panel signify the correlation coefficients and their level of significance.](image-url)
in Fig. 10 is consistent with the following scenario: As air rises in a cloud from its base water droplets condense and grow as long as the RH is greater than 100% (supersaturated). Hence, the lower the cloud bases of the mountain cloud with respect to the measurement site, the larger the LWC and the radii of the cloud droplets. While there are no direct measurements of cloud base height, the higher RH in the air masses closest to the surface will result in lower cloud base height as air rises up the mountain, consistent with the correlation between the higher LWC, $R_{eff}$ and air mass RH. Although the research site was in cloud during the majority of the research period, there was a period from the evening of DOY 247 through the afternoon of DOY 248 when there was no cloud (Fig. 5(b)) and when the number and volume concentrations decreased by almost an order of magnitude (Fig. 5(a)). This offered an opportunity to compare the aerosol properties when there was no cloud with those under cloudy conditions. Fig. 11 shows volume concentration size distributions for the three types of aerosols and all types together, comparing spectra from the clear day and the residual and interstitial particles from the cloudy day. Regardless of particle type, the concentration over all sizes is more than an order of magnitude lower on the cloud-free day than during the day with cloud. Whereas the IOL particle spectrum on the cloud free day has fewer large particles than on the cloudy day, the NM size distribution shows a distinctive mode around 3.5 µm that is not seen in the cloud data. The cloud-free distributions show the same trend as the cloud measurements with respect to the NM spectra being the broadest with largest particles and the PL being the narrowest with none having diameters larger than 2 µm. This might suggest that the composition of the particles is similar in both cloud-free and cloudy periods with the same air mass origin. That being said, however, unlike all the other days when the wind speeds varied between 5–10 m s$^{-1}$ throughout the day, during the cloud-free period, the winds were almost calm, never exceeding 2 m s$^{-1}$. It is likely that what we are observing is local, background aerosol particles. Given that the research site is in the middle of a tropical forest, many of the particles are possibly bioaerosol associated with the local vegetation. That being said, since a cloud-free period only occurred once during the project, we cannot state unequivocally that our measurements represent background aerosols.

![Fig. 11. Volume concentration size distributions for a) all particle types, b) iron oxide-like particles, c) pollen-like particles and d) particles that were un-matched to the APS particle library. The three curves in each panel correspond to cloud droplet residuals (blue), interstitial (black) and cloud-free (red), only for air masses originating in Africa.](image-url)
SUMMARY AND CONCLUSIONS

The objective of this study was to evaluate the residual and interstitial particles in the persistent clouds that formed on the mountaintop during a three-week period from August 25 to September 10, 2011, as part of the experiment Puerto Rico African Dust and Cloud Study (PRADACS, http://pradacs.catec.upr.edu/). A new optical sensor, the Aerosol Particle Spectrometer with Polarization Detection (APSPD) was deployed at the mountaintop observatory of Pico del Este (PE) in Puerto Rico to measure the physical and optical properties of these aerosol particles in the size range from 0.5 to 20 µm.

Three types of particles were identified by their optical signatures determined from the polarized light they scattered in the APSPD’s laser beam. Two of the signatures matched test particles of pollen and iron oxide measured in the laboratory and the other signatures are of particle types that remain unidentified. The signatures are related to the particle type that is, in turn, a function of particle composition. The measurements were stratified by the three particle types, their volume size distributions and total volume concentrations, then evaluated under the hypothesized conditions.

Air mass origin was the condition that produced the largest difference in both the volume and the ratio of residual to total particle concentrations. Air masses from Africa produced the largest volume concentrations and residual to total ratios, particularly in particle types that were not matched with a test aerosol. Air masses that spent more than 24 hours below 500 m had lower particle volume concentrations than those that stayed aloft, presumably due to more removal of particles by sedimentation. Likewise, air masses with a history of precipitation formation along their trajectory had much lower volume concentrations than those that had experienced little precipitation. This difference is likely a result of particle removal by precipitation.

The high correlation between LWC and effective radius is a result of the relative humidity of the air masses reaching the site that are positively correlated with wind speed. Higher wind speeds are correlated with air masses that were nearer the site that are positively correlated with wind speed. Higher is a result of the relative humidity of the air masses reaching the ocean one hour prior to reaching the measurement site, leading to larger moister fluxes and lower cloud bases.

The next stage of this study will be to compare the optical signatures with measurements made with an aerosol mass spectrometer that was operated during the same period. More extensive laboratory measurements are also in progress to catalogue a larger library of optical signature that will be used to better quantify measurements by the APSPD and other similar spectrometers that measure polarized light scattering from individual particles.

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REFERENCES


