

University of Puerto Rico
Faculty of Natural Sciences
Department of Environmental Sciences
Rio Piedras, Puerto Rico

**CLOUD AND AEROSOL PROPERTIES
UNDER THE INFLUENCE OF DIFFERENT AIR MASSES**

by

Elvis Torres Delgado

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Olga L. Mayol-Bracero, Ph.D.

Dissertation Director

Chairman

Department of Environmental Sciences

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List of Abbreviations

AAE – absorption Ångström exponent

AE - Aethalometer

AES – atomic emission spectroscopy

Al-CASCSC2 – aluminum Caltech active -strand cloud water collector

ARM – Atmospheric Radiation Measurement

ASO – August, September, and October

ATN - attenuation

BB – biomass burning

BC – black carbon

BCP – Backscatter Cloud Probe

CCN – cloud condensation nuclei

CLAP – Continuous Light Absorption Photometer

CSJ – Cabezas de San Juan

DOC – dissolved organic carbon

DMT – Droplet Measurement Technologies

DN – dissolved nitrogen

ESRL – Earth System Research Lab

EYNF – El Yunque National Forest

GoAmazon– Green Ocean Amazon

HYSPLIT – Hybrid Single-Particle Lagrangian Integrated Trajectory

ICP – inductively coupled plasma

IPCC – Intergovernmental Panel on Climate Change

IN – ice nuclei

LRTAD – long-range transported African dust

LWC – liquid water content

MAAP – Multi-Angle Absorption Photometer

MAC – Mass absorption cross section

MAM – March, April, and May

MAOS – Mobile Aerosol Observing System

NOAA – National Oceanic and Atmospheric Administration

OA – organic acids

PSAP – Particle Soot Absorption Photometer

SMOCC – SMOke, Aerosols, Clouds, rainfall, and Climate

SP2 – Single Particle Soot Photometer

TOC – total organic carbon

TN – total nitrogen

PAS – Photoacoustic Absorption Photometer

PDE – Pico del Este

PM – particulate matter

rBC – refractory Black Carbon

SAE – scattering Ångström exponent

TMCF – Tropical Montane Cloud Forest

USDA – United States Department of Agriculture

USFS – United States Forest Service

Abstract

Aerosols can interact with radiation directly through scattering and absorption and indirectly by serving as cloud condensation nuclei. The uncertainty of how particles and clouds interact with radiation is still high amidst the progress made in recent years, which hinders our current understanding of how these particles affect the Earth's radiation budget. This work aims to reduce this uncertainty by targeting the two most light-absorbing atmospheric particles, mineral dust and black carbon, and study how they interact with radiation, how they serve as cloud condensation nuclei, assessing popular measurement techniques and evaluating their impact in two different tropical forest ecosystems.

Field measurements were carried out in the Caribbean island of Puerto Rico and in the Brazilian Amazon. In Puerto Rico, aerosol-cloud interactions were studied in the tropical montane cloud forest (TMCF) of Pico del Este, which receives consistently during summer months the influence of mineral dust from the Sahara/Sahel region in Africa (i.e., African dust). In Brazil, specifically in the Amazon basin, measurements of black carbon were performed in the city of Manacapuru, an area exposed to the influence of urban and biomass burning pollution.

At Pico del Este, periods of low and high dust influence were identified through the use of aerosol optical properties, and air mass trajectories (HYSPLIT). It was found out that African dust interacts with clouds and produces a higher number of droplets, but the mean droplet effective diameter is not significantly altered. Similarly, the deposition of water and nutrients through water and clouds was studied, and results suggest that rain is

the main mechanism through where water is deposited to the ecosystem over clouds (58-78%). Cloud water presented an enrichment of nutrients over rainwater, suggesting that clouds are more important than rain for supplying TMCFs with nutrients. At the Brazilian Amazon basin, an Aethalometer -the most popular technique for measuring black carbon concentrations through the absorption coefficient- was used and several corrections used to overcome known artefacts for this type of measurements were evaluated. Results suggests that this technique can overestimate the absorption coefficient by a factor of 5 and that the corrections do not agree well among each other.

Biographic Sketch

Mr. Elvis Torres Delgado obtained a Ph. D. degree from the Environmental Sciences department at the University of Puerto Rico. He had previously obtained a B. S. degree in Chemistry from the Chemistry department at the University of Puerto Rico, where he graduated with Magna Cum Laude honors.

As a doctoral student, Mr. Torres Delgado has been awarded with the Louis Stoke Alliance for Minority Participation (LS-AMP) Bridge to the Doctorate fellowship for two years and the Puerto Rico NASA Space Grant Consortium fellowship for three years. He has also worked as a Professor assistant and as an Instrumentation Specialist at the University of Puerto Rico. Besides his thesis project in light absorbing aerosols and aerosol-cloud interactions he participated in four graduate internships at Brookhaven National Laboratory (three consecutive summers) and at the USDA Institute of Tropical Forestry. He also participated in an air quality research project for which he has a publication as a contributing author (Subramanian et al. 2018; Air quality in Puerto Rico in the aftermath of Hurricane Maria: A case study on the use of low-cost air quality monitors. *ACS Earth and Space Chemistry*, 2: 1179-1186). He has also presented his work in several national and international conferences including the prestigious American Geophysical Union (AGU) Fall Meeting, the International Global Atmospheric Chemistry Science (IGAC)Conference and the American Association for Aerosols Research (AAAR) International Aerosol Conference. Education has always been one of his passions and he has volunteered many hours as a science education resource for elementary schools (K-6).

Introduction

The atmosphere is a thin layer of gases that envelops Earth, but it is of outmost importance for maintaining life. It extends from the Earth's surface to about 100 to 140 km in height (Lutgens et al., 2007; Wallace & Hobbs 2006) and is comprised of a mixture of gases and particles. The atmosphere can be fundamentally divided into four layers (troposphere, stratosphere, mesosphere, and thermosphere) based on the relationship of temperature with height. The troposphere, the atmospheric layer closer to the surface, is the most important one with respect to atmospheric particles and weather processes.

Atmospheric particles, also known as aerosols, are particles in solid or liquid state that are suspended in the atmosphere (Steinfeld and Pandis, 2012). These aerosols can come from natural as well as anthropogenic sources, and they play an important role in the Earth's radiative budget, as they can scatter and absorb part of the incoming solar radiation (Steinfeld and Pandis, 2012). Emissions of aerosols can also alter the chemical composition of the atmosphere by undergoing chemical reactions and changing both their chemical and physical properties. Also, these particles can be deposited on the surface, often far from where they are emitted, and have positive or detrimental effects on ecosystems (Jickells et al., 2005; Swap et al., 1992).

Aerosol-Cloud Interactions and Radiation

Particles suspended in the atmosphere can interact directly with the incoming solar radiation by scattering and absorbing it (Butcher & Charlson, 1972). They can also serve

as cloud condensation nuclei, meaning that they can act as a seed in which a cloud droplet is formed, and alter cloud properties (Pruppacher & Klett, 2010). Indirectly, through cloud droplets, aerosols can interact with incoming solar radiation. The interaction of particles with radiation, either directly or indirectly, has implications on the radiative budget and water cycle (Boucher, 2015).

The interaction of aerosols with incoming solar radiation is important for the radiative balance, but also for cloud formation processes. Light absorbing particles alter the radiation balance by absorbing the incoming radiation (Bond et al., 1998) and most of these particles can reemit that energy as heat. The heating of the atmosphere by these particles can affect the vertical temperature profile (Bond et al., 1998) and disrupt circulation, which also affects the water cycle. Both black carbon, a tracer for combustion emissions, and mineral dust, tiny soil particles in the atmosphere, are known for their absorbing potential and are considered to be the most absorbing atmospheric aerosols (Sokolik & Toon, 1999).

Particles in the atmosphere can interact with other particles and gases and change their chemical and physical properties, this is known as aging. Through aging, aerosol properties such as absorption and hygroscopicity can change. Photochemical reactions can also affect these properties. This plays an important role in determining how these particles will affect the radiative budget and the water cycle, as well as their lifetime in the atmosphere.

The latest report of the Intergovernmental Panel on Climate Change (IPCC) shows that, while significant progress has been made, **there is still plenty of uncertainty regarding the impact of aerosols in the radiative budget** (IPCC, Mhyre et al., 2013). **Even more**

uncertainty exists on the effect of aerosols on cloud properties. There has been some consensus with anthropogenic aerosols suppressing precipitation, but there are still mixed results regarding the impacts other particles, such as mineral dust on cloud formation (Rosenfeld et al., 2008).

While the uncertainty of the effects of mineral dust on cloud formation is still large, there has been plenty of research done in the topic (e.g. Rosenfeld et al., 2001; 2008; Yin et al., 2002; DeMott et al., 2003; Spiegel et al., 2014; Raga et al., 2016). However, the findings of these research are sometimes in disagreement. For example, studies have shown that mineral dust can enhance the amount of precipitation (Rosenfeld et al., 2008), while others show that it inhibits precipitation (Rosenfeld et al., 2001; Spiegel et al., 2014).

Recent studies done on the eastern side of the Caribbean island of Puerto Rico performed during the summer period and focusing on long-range transported African dust are clear examples of these disagreements (Spiegel et al., 2014; Raga et al., 2016). Both projects study cloud properties in the tropical montane cloud forest of Pico del Este in El Yunque National Forest, and while Spiegel et al. (2014) suggested that dust was altering cloud properties by increasing the number of cloud droplets but reducing their diameter, Raga et al. (2016) suggested that meteorology played a more important role in cloud formation than the presence or absence of African dust. On a similar line, Denjean et al. (2015), also on the eastern part of Puerto Rico, studied African dust particles in the nature reserve of Cabezas de San Juan and found that most dust particles were externally mixed and thus hydrophobic in nature, suggesting they will be poor cloud condensation nuclei.

Deposition of Atmospheric Particles and Ecosystems

The lifetime of aerosols in the atmosphere is variable and depends on several factors that control how far these particles can travel. Particle size distribution, morphology, and chemical composition are all important in determining the lifetime and effects of aerosols (Boucher, 2015). These particles can be deposited in the surface by dry and wet deposition. Sedimentation is a form of dry deposition and is the process in which a particle is pulled down to the surface by the gravitational force (Boucher, 2015). Particle size plays an important role, as larger heavier particles will be sedimented faster than smaller lighter ones. Wet deposition is the process in which a particle is deposited in the surface by acting as a cloud condensation nuclei, forming a cloud droplet that later falls as a rain droplet (rainout; in-cloud scavenging) or when a particle is below a cloud and ends up being dragged down by a falling rain droplet (washout; below-cloud scavenging). Particle chemical composition, as well as size, are important characteristics that determine their potential to act as cloud condensation nuclei (Pruppacher & Klett, 2010).

Once a particle is airborne it can travel long distances and be deposited to other terrestrial or marine ecosystems through sedimentation, cloud scavenging or wash out. The deposited particles can have detrimental or beneficial effects in the ecosystem. Particles from anthropogenic pollution can reduce the pH of cloud and rainwater, as well as of the soil solution, which can damage the vegetation and produce nutrient leaching (Driscoll et al., 2001). Other particles, like mineral dust, can transport and deposit nutrients in significant quantities that might be beneficial to the ecosystem (Bristow et al., 2010; Swap

et al., 1992). African dust can transport important quantities of nitrogen (Swap et al., 1992) and phosphorus (Pett-Ridge, 2009) to terrestrial ecosystems and iron to marine ecosystems (Jickells et al., 2005), as well as other macro and micronutrients that enhances the productivity of these ecosystems.

Evidence of aerosols travelling from one continent to another has been extensively documented throughout the years. Anthropogenic aerosols and mineral dust crossing from China to the west coast of the United States (Husar et al., 2001), mineral dust traveling from Africa to Europe (Klein et al., 2010; Prodi & Fea, 1979), the Caribbean (Prospero & Mayol-Bracero, 2013), the east coast of the United States (Prospero, 1999) and South America (Swap et al., 1992), and anthropogenic aerosols travelling from the east coast of the United States to the Caribbean (Allan et al., 2008; Gioda et al., 2009; Valle-Díaz et al., 2016) have been documented. However, **the impact of mineral dust on the water and nutrient budgets of tropical montane cloud forests is not well understood.**

Tropical forests

The atmosphere and land surfaces are in constant interaction, so it is intuitive to state that whatever happens in one will alter the other. This is especially true for atmospheric chemistry, as organisms move elements from one to another through different biogeochemical processes, such as respiration. Also, forests are tightly linked to the water cycle (Perry et al., 2008). Tropical forests stand out for their precipitation patterns, high species richness, and elevated rates of nutrient cycling and productivity (Perry et al., 2008).

The Caribbean region hosts 20 of the 600 tropical montane cloud forests (TMCf) in the world (Bubb et al., 2004). These ecosystems are known for being vulnerable to climate change (Lugo & Scatena, 1995), as higher temperatures can alter the cloud base height and circulation and precipitation patterns, affect some of the species it harbors (epiphytes and amphibians), as well as the hydrological cycle. One of those Caribbean TMCfs (Pico del Este) is located in the island of Puerto Rico in El Yunque National Forest, managed by the United States Department of Agriculture (USDA) Forest Service (USFS). Pico del Este has the influence of mineral dust coming from the African continent, impacting cloud chemical (Gioda et al., 2009; Reyes-Rodríguez et al., 2009; Valle-Díaz et al., 2016) and microphysical properties (Raga et al., 2016; Spiegel et al., 2014).

South America is host to the Amazon Rainforest, one of the most important forests in the world. The Amazon is the largest rainforest in the world and hosts about 25% of the world's biodiversity (Dirzo & Raven, 2003). It is also an important place for atmospheric circulation, which affects precipitation in South America (Werth & Avissar, 2002) and is one of the world's largest sources of fresh water (Paratore, 2000). The Amazon is also an important producer of oxygen and remover of carbon and other warming agents from the atmosphere (Paratore, 2000). In the Amazon rainforest slash and burn practices are notorious for agriculture and livestock business. These practices negatively impact the soil and water quality, besides injecting copious amounts of particles to the atmosphere. Introducing particles generated through combustion to the atmosphere poses a threat for human health, as well as affecting weather through their warming potential and disruption

of circulation patterns (Bond et al., 1998). Deposition of these particles on the forest ecosystem also poses a threat for the flora and fauna, as many of these particles are toxic and can lead to changes in soil pH and nutrient leaching (Driscoll et al., 2001).

Thesis Composition

This doctoral thesis is composed of three chapters. First, there is an introduction to atmospheric aerosols and how they can interact with the Earth's radiation budget, influence cloud formation, travel long distances, and influence ecosystem nutrient budgets. Chapter 1 presents a study of mineral dust transported from the African continent to a tropical montane cloud forest (TMCF) in the Caribbean. By identifying periods of low and high dust influence, the potential of dust to act as cloud condensation nuclei, how dust affects cloud properties, and the interaction of dust and clouds with radiation are presented. Chapter 2 takes place as well in the same TMCF in the Caribbean. This chapter presents the impacts of mineral dust transported from Africa on the water and nutrient budget of the TMCF, the importance of rain and cloud water deposition in a place often influenced by both rain and clouds, and the input of nutrients through rain and cloud deposition in periods of low and high dust influence. Finally, Chapter 3 shifts towards black carbon (the most absorbing aerosol in the atmosphere) and one of the most popular techniques for measuring it, the aethalometer. Filter-based measurements of black carbon are known to be biased by several artefacts for which several corrections schemes have been developed. This chapter is based on one-year data collected during a field project in the Brazilian Amazon

rainforest. The long-term data set provided a range of ambient conditions with urban and biomass burning sources of black carbon. We analyze how do the corrections schemes alter the original values, how do they compare to each other, and how do they modify other aerosol properties that are important to quantify the effect these particles have on the Earth's radiative budget. The final part are the concluding remarks and recommendations for future projects.

CHAPTER ONE

DUST PARTICLES AS CLOUD CONDENSATION NUCLEI IN A TROPICAL MONTANE CLOUD FOREST IN THE CARIBBEAN

Abstract

African dust travels thousands of kilometers and can reach the Americas and the Caribbean. Mineral dust particles interact with radiation, by directly scattering and absorbing it, or indirectly by serving as cloud condensation nuclei (CCN) or ice nuclei (IN). These particles can also affect the water budget by altering the normal precipitation patterns of an ecosystem. Mineral dust from the African continent travels thousands of kilometers and can reach the Americas and the Caribbean. As part of the Luquillo Critical Zone Observatory, field campaigns were held during the summers 2013, 2014, and 2015 at Pico del Este, a tropical montane cloud forest in the Caribbean island of Puerto Rico. Cloud microphysical properties, which include liquid water content, droplet concentration, and droplet size, were measured. Using products from models and satellites as well as aerosol optical properties periods of high and low dust influence were identified. Results suggest that African dust acts as a CCN increasing the number of droplets and the liquid water content, but not altering the median droplet diameter. By enhancing the number of cloud droplets, it is expected that the cloud albedo will also increase and thus affect the radiation budget. These results suggest that air mass history before reaching the station such as accumulated precipitation and average altitude might have a more important role in cloud formation at this location than aerosol source.

Introduction

Aerosols play an important role in the Earth's climate. They can directly interact with the incoming solar radiation by scattering and absorbing it (Butcher & Charlson, 1972). They can also indirectly interact with the solar radiation (scattering) by serving as cloud condensation nuclei (CCN) (Pruppacher & Klett, 2010). Large amounts of aerosols that can serve as CCN can increase the number of droplets in a cloud and decrease their diameter, which lengthens their lifetime and increase the cloud albedo (Twomey, 1977; Albrecht, 1989).

Changes in cloud properties and the radiative budget, besides affecting climate, can also affect ecosystems. Increasing the lifetime of a cloud decreases the amount of rain in an area, which alters the water budget. Altering the availability of water can have negative effects in plants and animals that depend on this resource, as well as in human communities. Longer cloud lifetime also increases the cloud albedo, which reflects more radiation out of the Earth and can have both beneficial and detrimental effects on the ecosystems, depending on the area and species affected. Some species can benefit from a reduced direct radiation and an increased diffused radiation, as they can better use the radiation rather than saturate (Gu et al., 2002). However, reducing the incoming solar radiation can reduce photosynthesis (Peri, et al., 2002). An increased albedo can also alter the normal circulation patterns in the vertical column by enhancing light scattering and thus reducing the amount of radiation that reaches the Earth's surface, producing a net cooling effect.

While there has been an increased attention from the scientific community in aerosol-cloud-radiation interaction, a lot of uncertainty in this topic remains (Mhyre et al., 2013). Particularly, understanding the effect of mineral dust in aerosol-cloud-radiation interactions poses a challenge. Dust is understood to both scatter and absorb radiation. It is considered along with black carbon, the most important light absorbing particles in the atmosphere (Sokolik & Toon, 1999). It is also known that dust is a good ice nuclei (DeMott et al., 2003). When it comes to dust acting as a CCN, there is not a clear answer. Some studies have shown that dust is mainly hydrophobic and a poor CCN which impairs precipitation (Rosenfeld et al., 2001). Others have seen that dust acts as a CCN if it has been aged, which seems to be favored if it is mixed with anthropogenic or organic aerosols (Fitzgerald et al., 2015). Dust has also been hypothesized to act as a giant CCN by being a large aerosol itself, and thus producing large cloud droplets that will promote rainfall (Rosenfeld et al., 2008).

In the Caribbean Basin, which is constantly affected by mineral dust emitted from the African continent, studies of aerosol-cloud-radiation interactions are limited. Most of these studies have been done in the island of Puerto Rico. The northeastern part of the island hosts a tropical montane cloud forest (TMCF) known as Pico del Este (PDE). PDE has been an ideal location for several cloud studies, as it is commonly under the influence of clouds. Eugster et al. (2006) studied daily cloud properties as a function of net radiation and saw that denser clouds correlated with less radiation at the surface. Allan et al. (2008) saw that clouds affected by anthropogenic pollution had larger number of droplets with

smaller diameters. A similar observation was seen in Spiegel et al. (2014) but with clouds affected by African dust. In contrast, Raga et al. (2016) saw that meteorology was more important in cloud formation rather than the aerosol source. Cloud chemical properties have also been studied at this location (Weathers et al., 1988; Asbury et al., 1994; Gioda et al., 2008, 2009, 2011, 2013; Reyes-Rodríguez et al., 2009; Valle-Díaz et al., 2016) and have seen an increase in non-sea salt calcium and other crustal and organic components when clouds are influenced by African dust (Valle-Díaz et al., 2016) and an increase in non-sea salt sulfate when under the influence of anthropogenic pollution (Gioda et al., 2009; Valle-Díaz et al., 2016).

The main objective of this study is to measure cloud microphysical properties in a TMCF and help reduce the uncertainty in the current knowledge of mineral dust aerosol-cloud-radiation interactions and the effects this dust can have in the radiation and water budget.

Methodology

Sampling Sites

Measurements were performed at two stations in the Caribbean island of Puerto Rico. The first one is an atmospheric aerosols observatory in the natural reserve of Cabezas de San Juan (CSJ, 18° 23'N, 65°37'W), in the most eastern part of Puerto Rico, in the town of Fajardo. The station is influenced by the northeasterly trade winds most of the time, which makes it a great place to study background aerosols, as the metropolitan area is

located downwind from the station. These winds can carry with them African dust aerosols, which are common during the Northern Hemisphere summer (Prospero & Mayol-Bracero, 2013). Marine aerosols are always present, as the station is close to the ocean. Anthropogenic pollution is also transported from North America by cold fronts, more commonly during the Northern Hemisphere winter and from the nearby islands when the wind direction comes from the southeast, which occasionally can also carry volcanic ash (Allan et al., 2008; Gioda et al., 2009; Valle-Díaz et al., 2016).

The second station is Pico del Este (PDE, 18°16' N, 65°45' W), a cloud observatory in a tropical montane cloud forest in El Yunque National Forest (EYNF), at an elevation of 1051 m asl. PDE is often engulfed in clouds, which makes it a perfect place to study cloud properties without the need of an aircraft. This station is also upwind of the main metropolitan area, thus rarely influenced by local anthropogenic pollution and downwind from the CSJ station, facilitating the study of aerosol-cloud interactions. Vehicle access to the station is limited, minimizing interferences in the samples and data collected. These characteristics allows the study of aerosol-cloud-radiation interactions in this place and eases long-term studies of these properties.

Sampling Campaigns

Sampling campaigns took place in the summers of 2013, 2014, and summer and fall of 2015. Aerosol optical properties were measured at CSJ. The scattering coefficient was measured using a nephelometer (TSI, model 3563) at three different wavelengths (450, 550 and 700 nm). The absorption coefficient was measured using a Continuous Light

Absorption Photometer (CLAP, NOAA) at three different wavelengths (467, 528 and 652 nm) The nephelometer and CLAP were positioned after an impactor with aerodynamic size cuts of 1 and 10 μm (PM1 and PM10). The impactor switched between sizes every six minutes. Since we are mainly interested in the coarse fraction of the aerosol, we used only PM10 data.

In PDE, cloud water samples were collected using an aluminum Caltech active-strand cloud water collector (Al-CASCC2, Demoz et al., 1996). The cloud water sampler was exposed only when there were cloud events. The sampler was rinsed thoroughly with nanopure water and field blanks were collected before each sample. Aliquots of the cloud water sampled were stored in a freezer at $-18\text{ }^{\circ}\text{C}$ until analysis. Ion chromatography (Dionex ICS 1000 with conductivity detection) analysis was used to determine the concentration of water-soluble ions in the samples. The ratio of sodium to calcium cations concentration in sea salt was used to determine the amount of calcium that came from sea salt and the remaining calcium was attributed to non-sea salt sources (Wilson, 1975), mostly crustal.

Cloud microphysical properties were measured using a Backscatter Cloud Probe (BCP, DMT, Beswick et al., 2013). The BCP measures the amount of light backscattered from cloud droplets after being shone with a laser. From the backscattered light intensity and counts, the droplet number, diameter and liquid water content can be calculated.

Weather data was collected at both stations using a Davis VantagePro2 Plus weather station. Total rain, rain rate, wind direction, and wind speed were measured in 15 minutes averaged intervals.

Classification of Periods

To understand the differences between periods where we had high and low dust concentrations, we used aerosol scattering values as a proxy for mineral dust mass load. The average and standard deviation values for the 2013, 2014, and 2015 periods were calculated for the scattering data at 550 nm. We defined scattering values above the average plus the standard deviation as high dust cases and everything below the average minus the standard deviation as low dust cases. Cases where we had consistent high or low values were selected. Air mass trajectories determined using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPPLIT) model (Draxler & Hess, 1998), aerosol optical properties (scattering and absorption coefficients and Ångström exponents), cloud microphysical properties (droplet size distribution and liquid water content), cloud chemical properties (concentration of water-soluble ions) and air mass history (accumulated precipitation and altitude) were analyzed for the selected periods.

Data Quality Assurance

At PDE, BCP data was gathered every second, corrected by wind speed, and reduced to 10-minute averages. A detailed error analysis of the BCP measurements is given by Beswick et al., 2013. However, that error analysis considers a BCP that would be

mounted on an aircraft with an airspeed of 250 m s^{-1} . For this study, the BCP was installed in a wind tunnel with a source of constant airflow and oriented towards the prevailing wind direction. Laboratory tests of different winds speeds measured inside the tunnel showed that this setting enhanced the outside wind speed by a factor of 1.4 inside the tunnel. The average corrected airspeed was $11.2 \pm 1.8 \text{ m s}^{-1}$.

To ensure an uncertainty of 10% or less, a population of 100 particles per sampling interval is needed. While on average, the number concentration of droplets over a 10 m averaging interval was mostly below the 100 particle threshold, the accumulated number concentration exceeded this value when there was the presence of clouds, and thus an uncertainty no larger than 10% in the measurements is expected. No coincidence errors are expected as no measurement of droplet concentration exceeded 500 cm^{-3} .

At CSJ, nephelometer and CLAP data were also gathered at one second intervals and reduced to six-minutes averages. The nephelometer data was corrected for the truncation error (Anderson & Ogren, 1998) and the CLAP data was corrected for enhanced absorption artefacts (Bond et al., 1999; Ogren, 2010). Data from both instruments were adjusted to standard temperature and pressure.

Statistical Analysis

After selecting the data and grouping them as high or low dust cases statistical analyses were performed to see if the differences between them were significant. First, we tested for normal distribution using the Shapiro-Wilk test. Almost all variables for the three

periods were found not to follow a normal distribution. To test for significant differences between low and high dust influenced groups, the non-parametric Mann-Whitney two-tailed test was performed.

Results and Discussion

Air Mass Origin Analysis

Air mass back-trajectory plots at 1051 m asl calculated using the HYSPLIT model show that most of the air masses arriving to PDE during our sampling periods came from the ENE to ESE direction range. This same behavior has been seen by Allan et al. (2008), Raga et al. (2016), and Valle-Díaz et al. (2016). Some of these air masses originated in the Sahara/Sahel region of the African continent and traveled through the Atlantic Ocean and others were originated in the Atlantic Ocean. For the selected periods, 370 trajectories were calculated and analyzed, where 60.5% of them came from the Atlantic and 39.5% from Africa. Because of these, we expect the influenced of marine aerosols in all air masses and African dust influence in those originated in Africa. Anthropogenic pollution from the nearby islands was also expected in air masses that arrived to PDE from the SE, which happened in 29.7% of the analyzed trajectories.

Four air mass trajectories cluster plots are presented in Figure 1.1. Cluster plot A (high dust; summers of 2013 and 2014) shows that most air masses in these periods were originated in the Sahara/Sahel (63%) and traveled through the Atlantic Ocean before

reaching PDE. Cluster plot B (low dust; summers of 2013 and 2014) shows that most air masses in these periods originated in the ocean (82%). Cluster C and D show a similar behavior as clusters A and B, but for the summer and fall 2015. Cluster C (high dust; summer and fall of 2015) shows mainly air masses originating in the Sahara/Sahel (70%) and cluster D (low dust; summer and fall of 2015) shows air masses originating mainly in the Atlantic (96%). The wind direction data agree with the air mass back-trajectories, as periods of high dust influence were dominated by E to ESE wind directions and periods of low dust influence were dominated by ENE to E wind directions. We did not have any trajectories from South America or from North America for these periods as has been previously seen in other studies (Raga et al., 2016; Valle-Díaz et al., 2016), therefore, we expect little contribution from anthropogenic aerosols. However, there might be some anthropogenic aerosol influence, as some air masses pass through the nearby islands southeast of Puerto Rico. This happened in 30% of the analyzed trajectories (31% for high dust influence periods and 29% for low dust influence periods). No volcanic eruptions or ash plumes were reported for the Soufriere Hills volcano at the island of Montserrat from the Montserrat Volcanic Observatory (www.mvo.ms). A total of 48 trajectories were calculated for cluster A, 39 for cluster B, 152 for cluster C and 131 for cluster D.

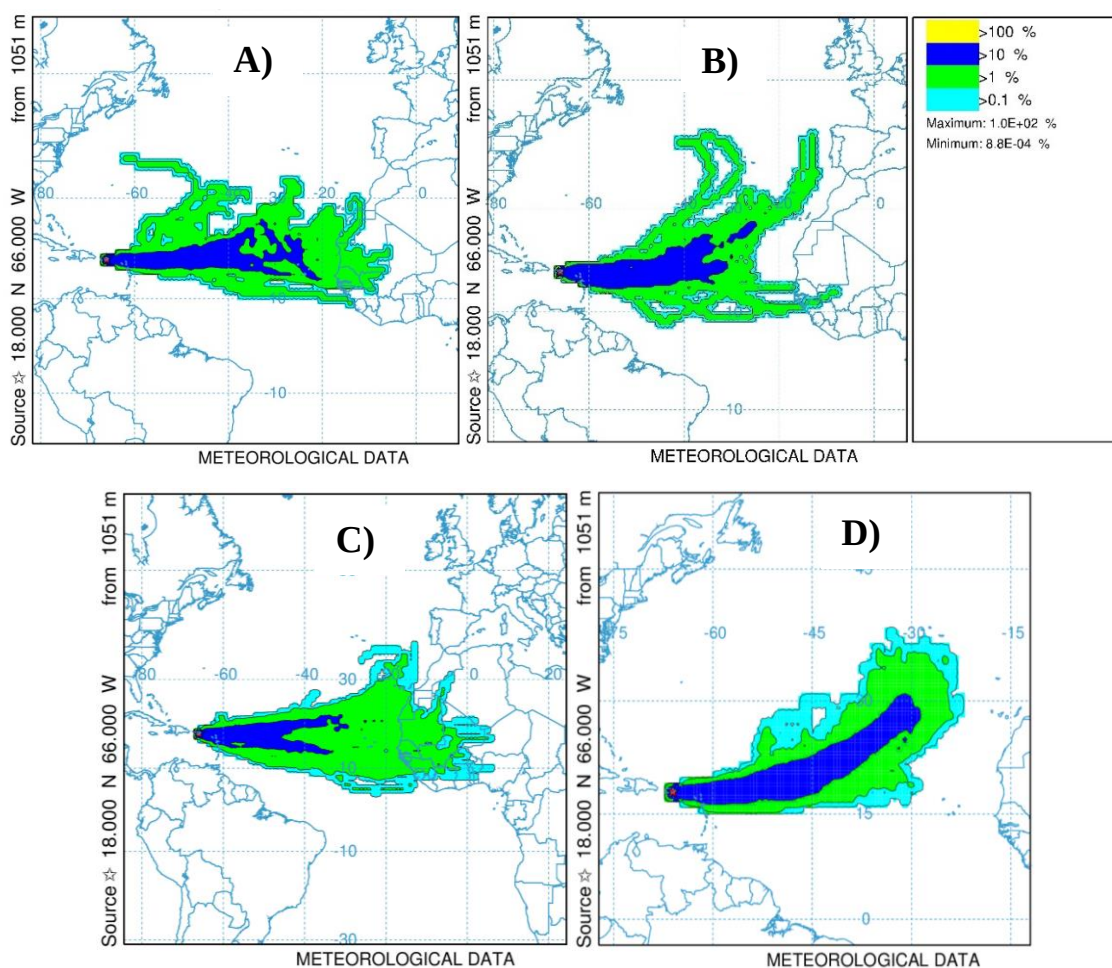
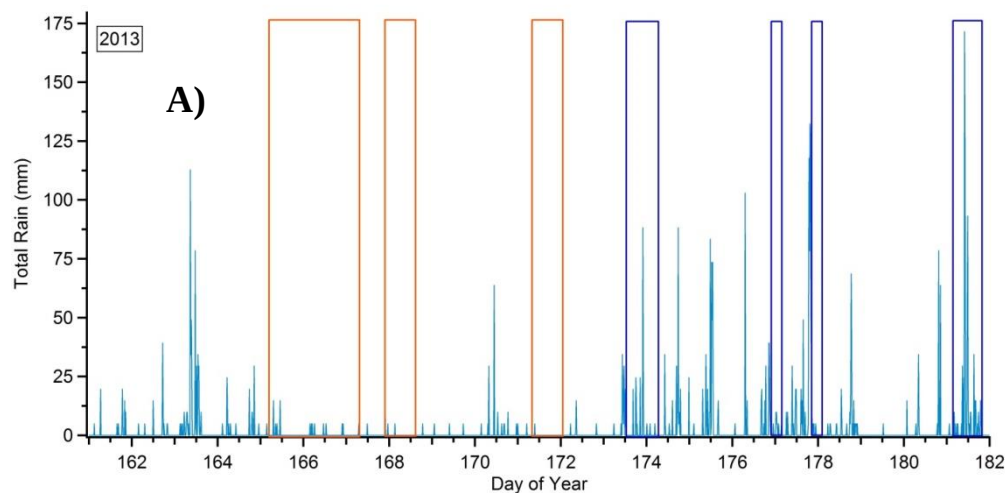


Figure 1.1: HYSPLIT back-trajectory analysis for A) periods with high dust influence for the summers of 2013 and 2014, B) periods with low dust influence for the summers of 2013 and 2014, C) periods with high dust influence for the summer and fall of 2015, and D) periods with low dust influence for summer and fall of 2015. Colors represent the frequency of an air mass to pass through an area in percentage, spanning from the least frequent light cyan to the more frequent dark blue.

Precipitation

Total precipitation was measured at PDE in the summers of 2013 and 2014 (Figure 1.2). There was no precipitation data available for the summer of 2015. Periods of high and low dust influence are identified in both graphs. Periods of high dust influence coincide with periods where there is little precipitation. As well, periods of low dust influence coincide with periods with more precipitation. The main reasons for these are either that precipitation is depositing the African dust particles regardless of their CCN activity or that dust is acting as a CCN and inhibiting precipitation. Raga et al. (2016) argued in their work at PDE that air masses that had precipitation history had less influence of African dust. Spiegel et al. (2014), on the other hand, argued that dust was acting as a CCN and inhibiting precipitation. As seen in Allan et al. (2008), anthropogenic aerosols could also be influencing cloud formation.



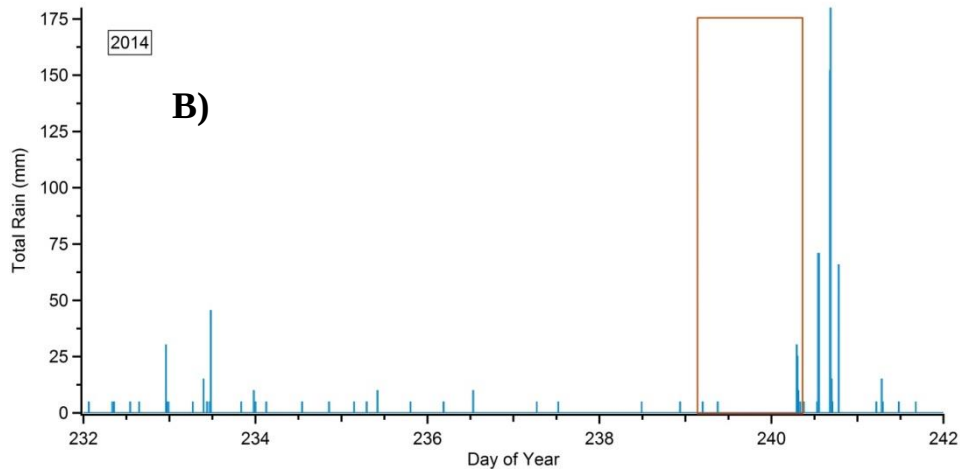


Figure 1.2: Total rain measured at 15 minutes averaged intervals at Pico del Este in the summer of 2013 (A) and 2014 (B). Brown boxes are periods of high dust influence and blue boxes are periods of low dust influence.

Aerosol and Cloud Properties

For the summers of 2013, 2014, and 2015, aerosol scattering and absorption coefficients were measured at CSJ and the scattering and absorption Ångström exponents (SAE, AAE) were calculated. At the same time, cloud droplet number, effective diameter, median volume diameter, liquid water content and size distribution were measured. For 2013, we identified three periods of high dust influence (H1 - H3) and four of low dust influence (L1 - L4) (Figure 1.3). For 2014, we only identified one period of high dust influence (H4) (Figure 1.4). For 2015, we identified twelve high dust influence periods (H5 – H16) and five low dust influence periods (L5 – L9) (Figure 1.5).

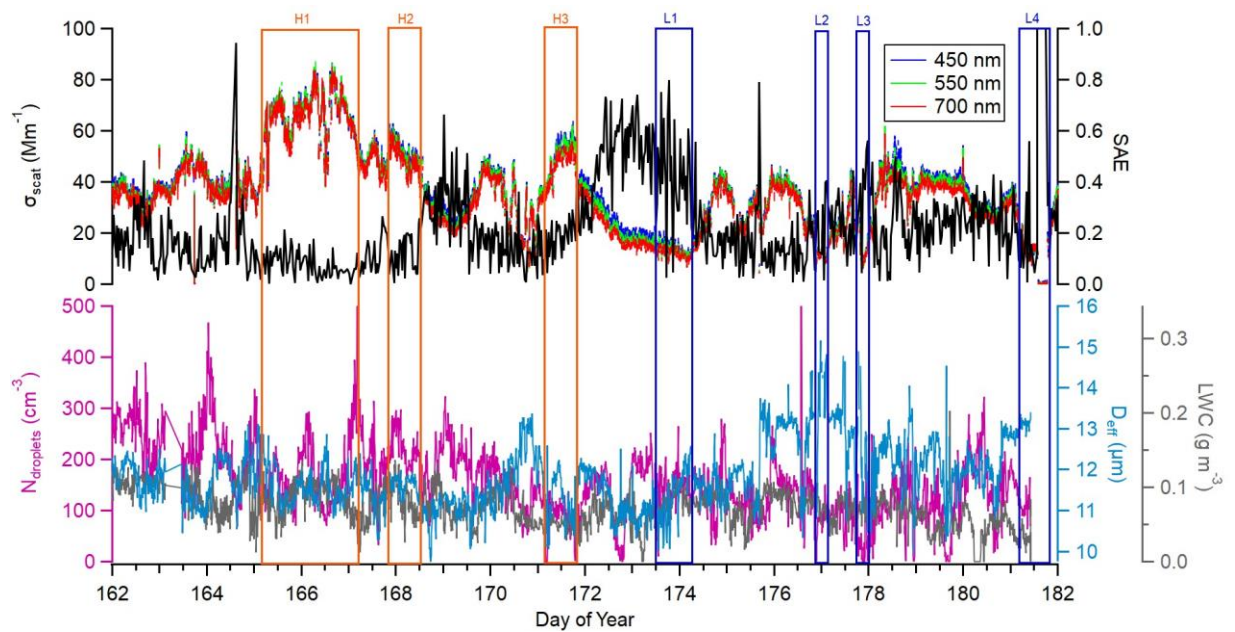


Figure 1.3: Aerosol scattering coefficient and SAE measured at CSJ and cloud microphysical properties measured at Pico del Este in the summer of 2013. The orange squares identify the periods of high dust influence and the blue squares identify the periods of low dust influence.

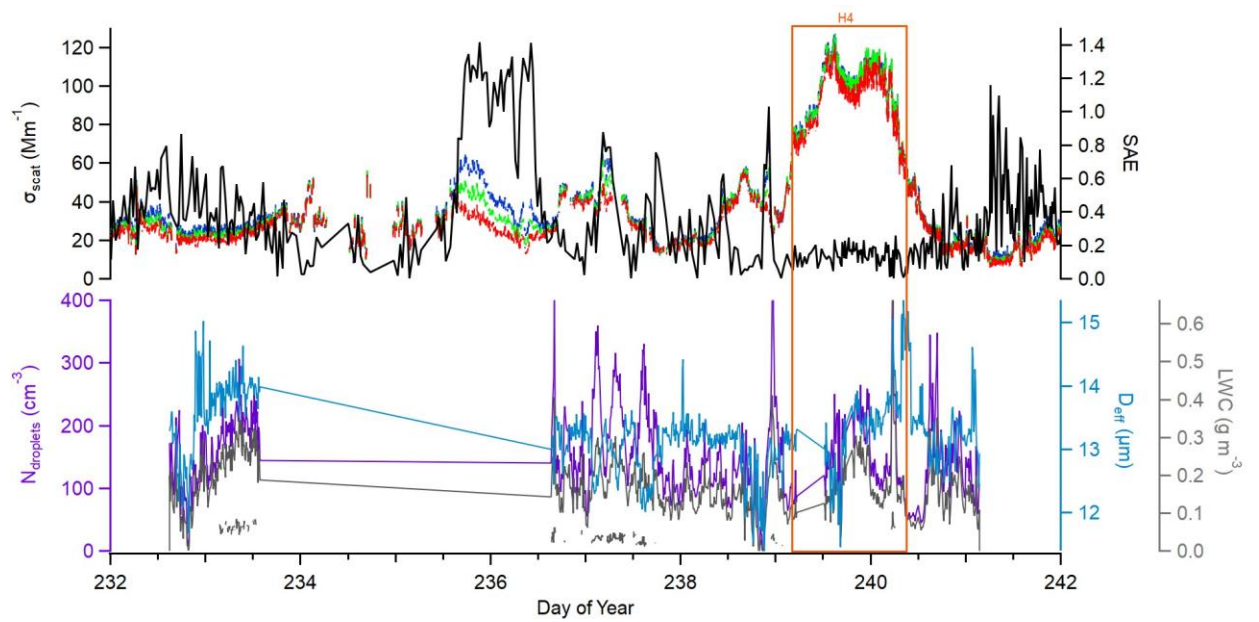


Figure 1.4: Aerosol scattering coefficient and SAE measured at CSJ and cloud microphysical properties measured at Pico del Este in the summer of 2014. The orange square identifies the period of high dust influence.

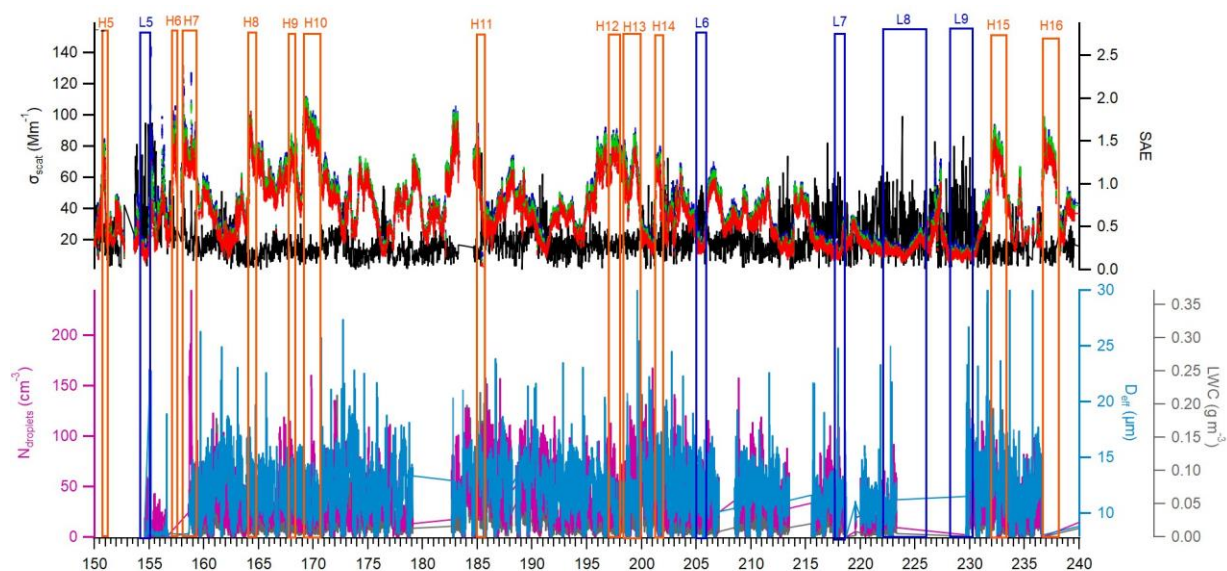


Figure 1.5: Aerosol scattering coefficient and SAE measured at CSJ and cloud microphysical properties measured at Pico del Este in the summer and fall of 2015. The orange square identifies the period of high dust influence and the blue squares identify the periods of low dust influence.

Figure 1.3 shows aerosol scattering coefficient and SAE and cloud droplet number, effective diameter and liquid water content for the summer of 2013. Figures 1.4 and 1.5 show the same parameters for summer 2014 and summer and fall 2015, respectively. Figure 1.3 shows that periods of low dust influence had overall larger diameter sizes and lower number of droplets when compared with periods of high dust influence. However, this pattern is not followed in the high dust influence period identified for the summers of 2014 and 2015. During these periods, the effective diameter had values comparable to the rest of the low dust influenced periods. A key difference is that we are comparing events that happened in different years, where meteorological conditions could have been different

and might have played a crucial role in determining the effect that these variables have in affecting cloud formation.

Figure 1.6 shows box plots for the different aerosol and cloud properties variables studied for high and low dust influence periods. The top four box plots are for aerosol properties, and the bottom four box plots are from cloud properties. Both the scattering and absorption coefficients were considerably higher for high dust influence periods. The SAE was lower for high dust influence periods, which indicates the presence of larger particles than in low dust influence periods. The AAE for high dust periods was usually above two, while on low dust influence periods were usually below two. Both the low SAE and high AAE values confirm the presence of dust in high dust influence periods (Cazorla et al., 2013).

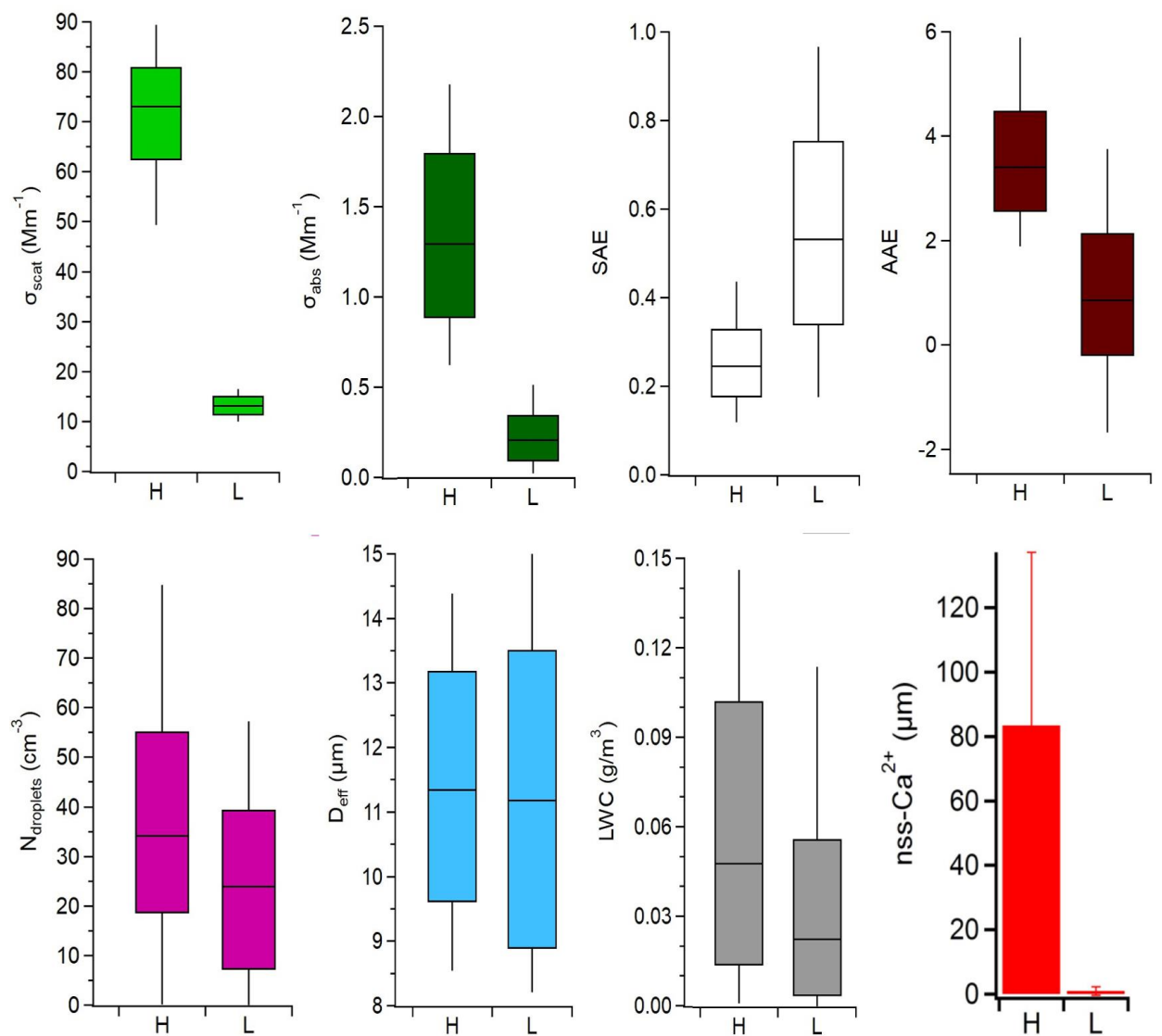


Figure 1.6: Box plots for periods identified as with low and high dust influence for scattering and absorption coefficient, SAE, AAE, droplet concentration, effective diameter, liquid water content and non-sea salt calcium concentration.

The number of droplets was higher in high dust influence periods, which suggests that dust might be acting as a CCN. The effective diameter had a similar median value, but

during low dust influence periods droplets reached larger and smaller diameters than in high dust influence periods. The LWC was higher for high dust influence periods, which makes sense, as we found more droplets and similar diameters. Spiegel et al. (2014) saw an increase in the number of droplets and LWC in dust influenced periods, but a clear decrease in droplet diameter. It is important to point out that our results for summer of 2013 support the findings of Spiegel et al. (2014), but when adding the data from summer 2014 and 2015, this behavior is no longer followed. Including this data, the results are more in the same line as those by Yin et al. (2002), which concluded that mineral dust did not had much effect on maritime clouds and Raga et al. (2016) which suggested that air mass history was most important for cloud formation processes at PDE.

The calcium concentration in cloud water was measured by ion chromatography from cloud water samples collected in the summers of 2013 and 2014. Non-sea salt calcium (nss-Ca^{2+}) in cloud water samples collected in periods with high dust influence was in considerably higher concentration (average of 83 vs 0.97 $\mu\text{eq/L}$) than those taken in low dust influence periods. This further validates the presence of dust in high dust influence periods. A similar finding was previously reported in several other studies (Gioda et al., 2013; Valle-Díaz et al., 2016). It is known that mineral dust contains large amounts of calcium (Scheuvens et al., 2013), so nss-Ca^{2+} can be used as a proxy for mineral dust.

Studied variables for high and low dust influenced periods were statistically analyzed. All variables were tested for normality using the Shappiro-Wilk test. Since most variables did not follow a normal distribution, the non-parametric two sample Mann-

Whitney test was used to test for statistical differences. All the variables showed statistical differences between high and low dust influence periods ($p < 0.001$; $\alpha = 0.05$) and cloud properties derived from the BCP had percent differences higher than the expected uncertainty except for effective and median volume diameter. These results suggest that dust is altering cloud properties. Table 1.1 shows the average and standard deviation of the studied variables for high and low dust influence periods. Table 1.1 along with Figure 1.6 shows that all variables, except effective and median volume diameter, had very distinct values. The average value of the effective diameter and median volume diameter was almost the same.

The increase in the number of cloud droplets in high dust periods suggests that dust aerosols might have an indirect effect on radiation by acting as CCN. A preferential scattering of a wavelength range is not expected, but rather an attenuation of the full spectrum. However, a detailed study of how dust indirect interaction might affect the radiation spectrum is needed to provide better insights in this aspect and to assess the ecological impacts it might have.

Table 1.1: Average and standard deviation for aerosol optical properties and cloud microphysical properties separated for periods of high and low dust influence for the summers of 2013, 2014, 2015 and fall of 2015.

Variable	Period	Average	Standard Deviation
Scattering 550 nm (Mm^{-1})	H	74	18
	L	13	3
Absorption 550 nm (Mm^{-1})	H	1.4	0.6
	L	0.2	0.8
SAE	H	0.2	0.1
	L	0.5	0.4
AAE	H	4	2
	L	1	3
$N_{\text{droplets}} (\text{cm}^{-3})$	H	43	42
	L	28	27
$D_{\text{eff}} (\mu\text{m})$	H	11.5	2.3
	L	11.4	2.7
Median Volume Diameter (μm)	H	12.3	2.2
	L	12.2	2.7
LWC (g m^{-3})	H	0.032	0.037
	L	0.021	0.146

Cloud Droplet Size Distribution

Figure 1.7 shows the cloud droplet size distributions for high and low dust influence periods. Table 1.1 shows the droplet size peak, peak amplitude and peak area results for the best fit of the distributions. Both periods had a bimodal size distribution, which was also seen by Spiegel et al. (2014).

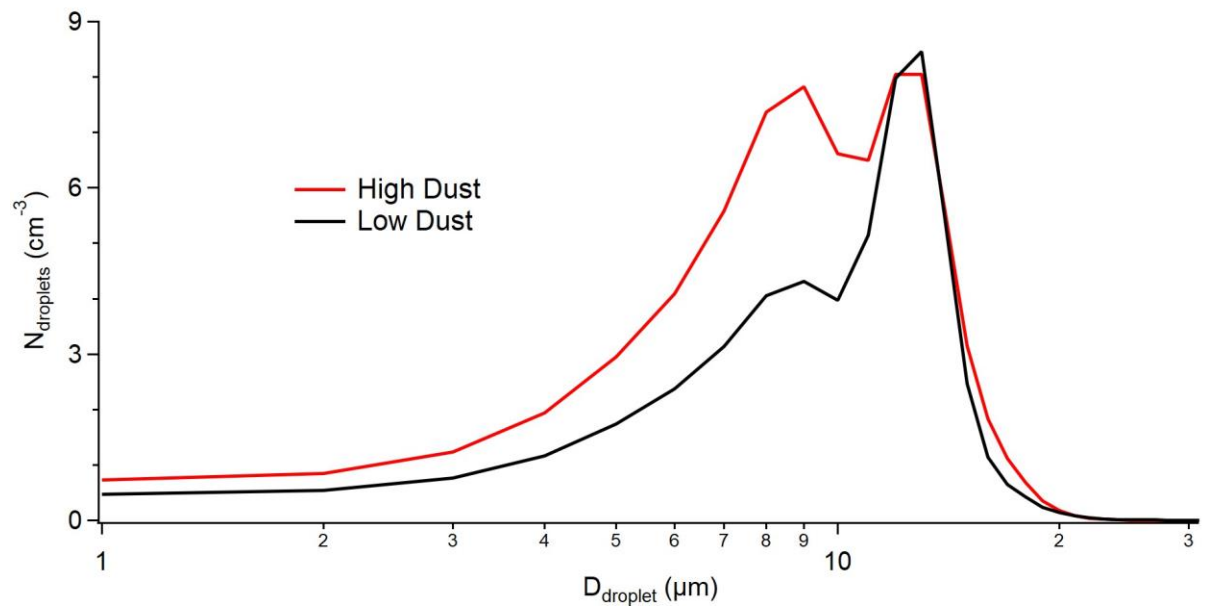


Figure 1.7: Droplet size distribution for high and low dust influence. Red line indicates high dust influence and black line indicates low dust influence.

The periods classified as with high dust influence had a higher peak in the smaller droplet mode (peak 1) than the period classified as with low dust influence. The median diameter for this mode was 8.45 μm for high dust influence periods and 8.41 μm for low dust influence periods. This shows that there is almost no difference in the median size of

both periods. In the larger droplet mode (peak 2), the median diameter was 12.8 μm for high dust influence periods and 12.7 μm for low dust influence periods. These results show that there are minimal differences in the median diameter for low and high dust periods that fall inside the instruments uncertainty.

High dust influence periods had a higher overall number of droplets, as seen in Figure 1.6. This is evidenced in the area of the droplet size distribution peaks shown in Table 1.2. In peak 1, the high dust influence period had an area of 55.7 μm^2 , about 1.8 times the area of low dust influence period, which was 31.6 μm^2 . In peak 2, the high dust influence period had an area of 13.7 μm^2 , and the low dust influence period 19.9 μm^2 . These results suggest that dust preferentially enhances the number of droplets in the smaller size range. The amplitude of the peaks was very close for peak 1 and the same for peak 2. The droplet size distribution is wider for high dust influence periods for all droplet sizes, which alongside with the effective diameter box plot in Figure 1.5 shows that there is an enhancement in the smaller diameter droplets, but also on the larger diameter sizes. These enhancements could be because of dust acting as a CCN, thus creating smaller sized droplets, but improving the chances of collision, thus producing larger droplets by collision and coalescence. A similar behavior was concluded in Yin et al. (2002), where dust coated with sulfate from cloud processing yielded wider size distributions. They argued that the addition of smaller drops competing for the available water vapor counterbalanced the addition of larger particles that would accelerate precipitation.

Table 1.2: Cloud droplet size distribution best-fit parameters for periods of high and low dust influence

Period	D₁ (μm)	Amplitude₁ (μm)	Area₁ (μm²)	D₂ (μm)	Amplitude₂ (μm)	Area₂ (μm²)
High	8.45	0.49	55.7	12.8	0.13	13.7
Low	8.41	0.50	31.6	12.7	0.13	19.9

Air Mass History Analysis

One-hour average of aerosol optical properties and cloud microphysical properties were compared with the corresponding air mass history and meteorological parameters and segregated by air mass origin. Least squares fit linear regression and Pearson correlation coefficient were used to determine the possible relationships among the variables (Figure 1.8). The aerosol optical variables evaluated are the scattering and absorption coefficients and the scattering and absorption Ångström exponents. The cloud microphysical properties evaluated are the droplet number concentration, effective diameter, and liquid water content. The air mass history and meteorological parameter evaluated where the total accumulated rain, accumulated rain during the last 48 hours, hours below 500 m, and the average altitude during the last 6 hours. Pairs with a correlation higher than 0.48 or lower than -0.48 are highlighted in bold in the correlation matrix (Table 1.3).

Table 1.3: Pearson correlation coefficient matrix of aerosol and cloud properties, and air mass history separated by air mass origin. Numbers in bold represent a correlation equal or larger than 0.48 or equal or smaller than -0.48. Values in parenthesis are the precipitation data filtered for values equal to or above 2 mm.

Atlantic

Variables	Scattering	Absorption	SAE	AAE	NC	LWC	ED	Acc Rain	Acc Rain 48h	Hours below 500m	Avg Alt 6h
Scattering	1	-0.06	0.16	0.02	-0.14	0.04	-0.04	-0.43	-0.04 (0.10)	-0.52	0.31
Absorption	-0.06	1	-0.08	0.13	0.25	0.11	0.20	0.04	0.17 (0.04)	0.11	-0.17
SAE	0.16	-0.08	1	-0.10	0.00	0.04	0.02	0.01	-0.04 (-0.17)	0.01	0.05
AAE	0.02	0.13	-0.10	1	0.18	0.09	0.06	0.08	0.17 (-0.15)	0.01	-0.15
NC	-0.14	0.25	0.00	0.18	1	0.74	0.50	0.26	0.43 (0.13)	0.39	-0.71
LWC	0.04	0.11	0.04	0.09	0.74	1	0.611	0.17	0.48 (0.42)	0.14	-0.59
ED	-0.04	0.20	0.02	0.06	0.50	0.61	1	0.26	0.43 (0.30)	0.25	-0.50
Acc Rain	-0.43	0.04	0.01	0.08	0.26	0.17	0.26	1	0.37	0.42	-0.34
Acc Rain 48h	-0.04	0.17	-0.04	0.17	0.43	0.48	0.43	0.37	1	0.14	-0.42
Hours below 500m	-0.52	0.11	0.01	0.01	0.39	0.14	0.25	0.42	0.14	1	-0.53
Avg Alt 6h	0.31	-0.17	0.05	-0.15	-0.71	-0.59	-0.50	-0.36	-0.42	-0.53	1

Africa:

Variables	Scattering	Absorption	SAE	AAE	NC	LWC	ED	Acc Rain	Acc Rain 48h	Hours below 500m	Avg Alt 6h
Scattering	1	-0.04	0.11	0.19	0.33	0.48	-0.19	-0.11	-0.31 (-0.71)	0.49	0.02
Absorption	-0.04	1	0.10	0.01	-0.27	0.14	0.29	0.19	-0.18 (-0.49)	0.05	0.11
SAE	-0.11	-0.10	1	0.10	-0.05	-0.12	-0.37	0.31	0.50 (0.54)	0.15	-0.15
AAE	0.19	0.01	0.10	1	0.22	0.21	-0.008	0.13	0.34 (-0.21)	0.21	-0.28
NC	0.33	-0.27	0.05	0.22	1	0.31	-0.067	-0.13	-0.08 (-0.78)	0.28	0.05
LWC	0.48	0.14	0.12	0.21	0.31	1	0.11	-0.06	-0.10 (-0.68)	0.06	-0.22
ED	-0.19	0.29	0.37	-0.01	-0.07	0.11	1	0.01	-0.07 (0.03)	-0.02	0.20
Acc Rain	-0.11	0.19	0.31	0.13	-0.13	-0.06	0.01	1	0.42	-0.03	-0.10
Acc Rain 48h	-0.31	-0.18	0.50	0.34	-0.08	-0.10	-0.07	0.42	1	0.00	-0.23
Hours below 500m	0.49	0.05	0.15	0.21	0.28	0.06	-0.02	-0.03	0.00	1	0.21
Avg Alt 6h	0.02	0.11	0.15	-0.28	0.05	-0.22	0.20	-0.10	-0.23	0.21	1

For air masses originating in the Atlantic Ocean, which correspond to low dust influence periods, the average altitude six hours before reaching the sampling site negatively correlated with the cloud droplet number concentration ($r^2 = -0.71$), liquid water content ($r^2 = -0.59$), and effective diameter ($r^2 = -0.50$). This suggests that the lower the average altitude of the air mass six hours before arriving, the more favorable the conditions for cloud formation. A possible explanation for this is that these air masses could be picking up aerosols and water vapor from the ocean which will enhance the cloud formation potential. Also, by reaching the station from a lower altitude it is more probable that the air mass will rise because of the topography. The average altitude six hours before reaching the station negatively correlated with the total accumulated rain ($r^2 = -0.36$) and accumulated rain in the last 48 hours ($r^2 = 0.42$), suggesting that the lower the average altitude, the more accumulated rain it will produce and the higher the chance for washing out aerosols, but this correlation was weak and thus this scenario is not expected to be a common occurrence. Accumulated rain in the last 48 hours also had a positive correlation with droplet number concentration ($r^2 = 0.43$), effective diameter ($r^2 = 0.43$), and liquid water content ($r^2 = 0.48$). This result is counterintuitive as it is expected that this rain will reduce the number of aerosols and because of this there will be a lower concentration of cloud droplets. Aerosol removal by rain is not supported by the weak correlations of accumulated rain in the last 48 hours with the scattering ($r^2 = -0.40$) and absorption ($r^2 = 0.17$) coefficients, which are extensive properties.

For air masses originating in Africa, which correspond to high dust influence periods, there was not a good correlation with the average altitude six hours before reaching the sampling site with the cloud microphysical properties. However, this average altitude was often higher than those originating in the Atlantic Ocean. These higher altitudes suggest that these air masses will not be able to pick up water vapor from near the ocean surface and will be drier than those originating in the Atlantic, thus having different conditions for cloud formation processes. A good correlation was found between the number of hours the air mass spent below 500 m and the scattering coefficient ($r^2 = 0.50$), which suggests that these air masses can accumulate aerosols along its path, and the weak correlation with the accumulated rain with the scattering coefficient ($r^2 = -0.3$) suggests that the chances of aerosol removal by rain are small. A good correlation was also found between the accumulated rain and the scattering Ångström exponent ($r^2 = 0.50$), suggesting that in the cases where rain is removing aerosols, it is preferentially removing marine aerosol rather than crustal aerosols that usually have a SAE > 1. A possible explanation is that marine aerosols are more efficient cloud condensation nuclei and more prone to be removed as rain droplets. When the accumulated rain 48 hours before reaching the station is filtered out for values higher than 2 mm of accumulated rain, a clearer trend is revealed for air masses originating in Africa. A strong anti-correlation was found for the scattering ($r^2 = -0.71$) and absorption ($r^2 = -0.49$) coefficients, as well as for the number of droplets ($r^2 = -0.78$) and the liquid water content ($r^2 = -0.68$). This suggests that rain along the air mass path is washing out aerosols and that these aerosols could act as CCN. However, this

filter left only a small amount of data point ($n=7$) and thus only suggests a possible trend and not a firm statement.

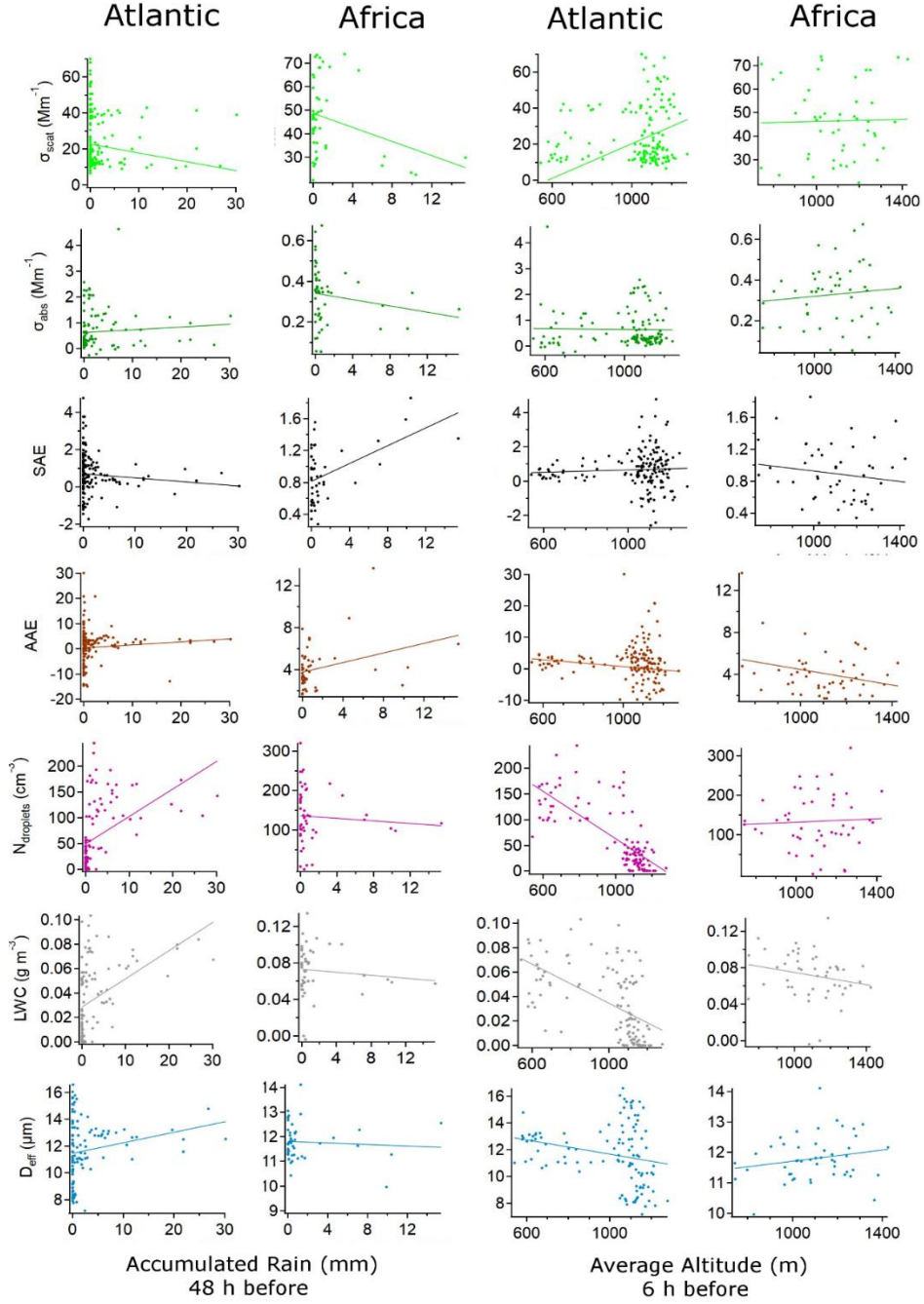


Figure 1.8: Least square fits regression analysis of aerosol and cloud properties as a function of the accumulated rain 48 hours before reaching the station and the average altitude six hours before reaching the station separated by air mass origin.

This analysis of air mass history, meteorology, and aerosol and cloud properties suggests that the more time the air mass spends below the boundary layer and the closer it gets to the surface before reaching the sampling station, the more prone it is to pick up aerosols in its path. Air masses originating in the Atlantic had a lower average altitude before reaching the station, which suggests that these air masses could collect water vapor from near the ocean surface and once they reach the mountain range, it is more probable that they rise and form clouds due to the orographic effect. Air masses that originated in Africa often reached the site from above and this suggests that the cloud formation process for these air masses is different than those that reached the station from below and are influenced by the orographic effect. Accumulated rain along the air mass path was not found to be a dominant aerosol removal mechanism and it seems like it preferentially removes some aerosols over others.

Conclusion

In an effort to reduce the uncertainty in the current knowledge of mineral dust aerosol-cloud-radiation interactions, we held sampling campaigns in the Caribbean island of Puerto Rico in the summers of 2013, 2014, and 2015, which is when Puerto Rico is significantly influenced by long-range transported African dust, as well as in the fall of 2015. Air mass trajectory analysis using the HYSPLIT model, aerosol scattering, absorption, SAE and AAE, cloud droplet size distribution, and precipitation were measured in two sites, a coastal station and a TMCF, both seldom influenced by local activities.

Air mass trajectory analysis showed that for periods classified as with high dust influence, most air masses (69.5%) came from the African continent and might have carried African dust with them through the Atlantic and to the island of Puerto Rico. Of these air masses, 30.5% passed through the nearby southeastern islands, and not much anthropogenic influence is expected from these air masses. In periods classified as with low dust influence, most air masses came from the Atlantic Ocean (95.9%) and 28.8% of the trajectories passed through the nearby islands and could have had the influence of anthropogenic pollution.

Meteorological parameters show that 2013 had more rain events than 2014. Also, the last identified high dust event in summer 2014 was preceded by a long period of little to no rain events, which might have caused an accumulation of mineral dust aerosols. It is also noteworthy that high dust influence events occurred in periods of low rain events, while low dust events periods occurred in periods of high rain events. This leads to the

assumption that dust and rain are tightly coupled, but inconclusive about the dominant mechanism.

Aerosol optical properties were measured and used to identify African dust high and low intensity events. Sixteen high dust influence events and nine low dust influence events were identified. At the same time, cloud microphysical properties were measured. Figure 1.6 shows that, for periods of high dust influence periods, scattering and absorption coefficients, AAE, droplet concentration, LWC, and nss- Ca^{2+} concentrations were higher, and SAE was lower than for periods of low dust influence. Effective diameter showed not much difference between both periods. This leads to the conclusion that mineral dust does act as a CCN, but meteorology seems to have played a more important role in cloud formation.

The air mass history, focused on the average altitude six hours before reaching the station and accumulated precipitation 48 hours before reaching the station, separated by origin was analyzed alongside aerosol and cloud properties. This analysis showed that air masses originating in the Atlantic or Africa have different conditions that will impact the cloud formation processes. Mainly, air masses that came from the Atlantic had lower average altitude before reaching the station, suggesting that this air masses will pick up more water vapor and aerosols from the ocean surface, as well as being more probable to experience orographic ascension and form clouds through this mechanism. Air masses that came from Africa had higher average altitudes before reaching the station, suggesting that they are much less probable to form clouds through the orographic effect and will have

drier conditions. The accumulated rain 48 hours before reaching the station suggest that accumulated precipitation along the air mass path washes out aerosols that could act as a CCN and this effect is much notable in air masses that originate in the African continent.

From the data presented here, we conclude that African dust acts as a CCN and modifies cloud properties by increasing the number of cloud droplets as seen in Spiegel et al. (2014). However, this is not the only variable that affects cloud formation and air mass history also plays an important role, as seen in Raga et al. (2016) and in the results from this study. A detailed study of aerosol-cloud-radiation interactions comprising field measurements and cloud and chemistry modeling is recommended to better understand the ecological impacts that dust might have by indirectly interacting with radiation. As well, a long-term study of dry and wet deposition chemistry is recommended to better understand the contribution of dry deposition of nutrients to this ecosystem if the cloud base continues to rise as a result of climate change and the input of nutrients through wet deposition is reduced.

CHAPTER TWO

WATER AND NUTRIENT DEPOSITION AT A TROPICAL MONTANE CLOUD FOREST INFLUENCED BY AFRICAN DUST

Abstract

Sampling of fog and rainwater chemical properties and fog physical properties took place at a tropical montane cloud forest in Puerto Rico in the Caribbean Basin. This location is often influenced by long-range transported African dust, which can affect the nutrient and water budget of this sensitive ecosystem. Using aerosol physical properties, samples were classified under high or low dust influence and the effects of this dust on the water and nutrient budget were analyzed. From the water deposition studied for fog and rain in 2013, from a total of 2.95 mm day^{-1} , rain contributed 2.29 mm day^{-1} and in 2014, from a total of 1.82 mm day^{-1} , rain contributed 1.05 mm day^{-1} . Hence, rain is the main water contributor to this ecosystem. Deposition of cloud and rainwater was found to be statistically different in days classified with low and high dust influence. Samples analyzed for water-soluble ions, metals, organic carbon, and nitrogen were usually more concentrated in fog water. An enrichment of most of these species was seen in samples under the influence of high dust. The nutrient flux of both fog and rainwater shows that fog water is the main contributor of nutrients to the ecosystem and is enhanced during events of high dust.

Introduction

Tropical montane cloud forests (TMCF) are ecosystems that often contain a high level of endemism and unique species adapted to the frequently water saturated conditions. These ecosystems appear at the elevations of mountains, are constantly exposed to fog and

deposition of fog water (Beiderwieden et al., 2007) and are often places of frequent precipitation. Of the approximately 600 TMCs in the world 20 are in the Caribbean basin one of which is on the island of Puerto Rico (Bubb et al., 2004). TMC, found at altitudes between approximately 1000 and 2400 m asl, are known to be highly vulnerable to changes in precipitation and temperature (Bubb et al., 2004).

Pico del Este (Spanish for East Peak; PDE) is a TMC located in El Yunque National Forest (EYNF), managed by the United States Department of Agriculture (USDA) Forest Service in Puerto Rico. It is the highest peak in the direction of the prevailing winds and has an altitude of 1051 m asl, placing it above the cloud formation level. It is constantly enveloped in clouds, also classified as fog, and has the highest annual precipitation recorded on the island (Murphy and Stallard, 2012). In EYNF, the cloud formation level is at about 600 m (Odum, 1970; Miller et al., 2018).

Fog and precipitation are important sources of water and nutrients in TMCs (Beiderwieden et al., 2007; Bubb et al., 2004). Vegetation in these ecosystems, which are important for the biogeochemical cycle functions in mountainous regions (Beiderwieden et al., 2007; Klemm & Wrzesinsky, 2007) extracts water and nutrients from the fog. Nutrients in fog water are usually more concentrated than those of rainwater (Weathers et al., 1988; Beiderwieden et al., 2007; Vandecar et al., 2015) and even small quantities of fog water can make a large contribution to the nutrient budget.

The Caribbean basin is regularly affected by airborne mineral dust that travels from the African continent during the summer months (Prospero & Lamb, 2003; Prospero &

Mayol-Bracero, 2013b). Long-range transported African dust (LRTAD) has also been documented to reach Europe (Klein et al., 2010; Prodi & Fea, 1979), the east coast of the United States (Prospero, 1999), and South America (Swap, et al., 1992). In addition to direct deposition to surface of plants, aerosol particles can also enter an ecosystem in the inside cloud droplets or raindrops and then deposit nutrients or pollutants to ecosystems. Mineral dust has been shown to provide significant quantities of such nutrients as nitrogen (Swap et al., 1992) and phosphorous (Pett-Ridge, 2009) to terrestrial ecosystems (Bristow, et al., 2010; Swap et al., 1992).

There are studies that show that mineral dust can act as cloud condensation nuclei (CCN) and either aid or hinder cloud formation processes and precipitation (Rosenfeld, et al., 2001). However, the uncertainty about the effects of mineral dust remains high and contradictory results continue appearing from different studies (Rosenfeld et al., 2001, 2008; Spiegel et al., 2014; Raga, et al., 2016). At PDE recent studies have shown that dust can have an indirect effect on radiative forcing when they impact cloud formation (Spiegel et al., 2014) but other studies indicate that meteorology is more important (Raga, et al. 2016), underscoring the need for more research in this area that can lead to better clarification of these processes. If mineral dust has an indirect effect on clouds this could mean a lower water flux from rainfall as liquid water would be distributed in more but smaller droplets, not reaching the necessary size and weight to fall as rain droplets and remaining longer suspended in the atmosphere. In this scenario, an equal flux from fog water could be expected since the liquid water content would be distributed in more

droplets but the vegetation would still be able to collect it through impaction. This could affect the water budget of PDE in the summer months since most of the water is provided by rainwater (Weaver, 1972). If rainwater is decreased then fluxes of fog water could have a higher relative importance on the water budget. Other studies in PDE have shown that anthropogenic air masses reach the island from North America and have an indirect effect on clouds (Allan et al., 2008; Gioda et al., 2011; Valle-Díaz et al., 2016).

Many studies have been done in EYNF characterizing fog and rainwater chemistry (Martens & Harriss, 1973; Weathers et al., 1988; Allan et al., 2008; Asbury, et al., 1994; Gioda et al. 2008, 2009, 2011, 2013; Reyes-Rodríguez, et al., 2009; Medina, et al., 2013; Valle-Díaz et al., 2016; McClintock et al., 2019) and a number of them conclude that LRTAD that reaches the area increases the concentration of several chemical compounds in fog and rainwater (Gioda et al. 2008, 2009, 2011, 2013; Medina, et al., 2013; Valle-Díaz et al., 2016; McClintock et al., 2019). However, none of these studies have simultaneously assessed the nutrient flux of both fog and rainwater and studied the effects of LRTAD on water and nutrients flux, thus establishing a budget for them.

This work seeks to assess the water and nutrient inputs through fog and rainwater in an ecosystem susceptible to weather changes, and to evaluate how mineral dust alters these inputs.

Methodology

Sampling Site

Fog and rain sampling took place at the PDE mountain station (18°16' N, 65°45' W; 1051 m asl), located in EYNF in northeastern Puerto Rico in the Caribbean Basin. Non-convective cloud formation here is normally driven by orographic lifting of warm air currents carrying moisture and aerosols from the ocean, which is about 10 km distance from the station (Brokaw et al., 2012; Murphy & Stallard., 2012; González et al., 2013). While marine aerosols are the most prominent at the station due to its proximity to the ocean, this station can also be influenced by crustal aerosols transported over long distances from the African continent, anthropogenic aerosols carried by cold fronts from eastern United States and local sources such as bioaerosols from the flora around the site. Aerosol physical properties were measured in the Cabezas de San Juan (18° 23' N, 65° 37' W; 60 m asl) atmospheric station located in the most northeastern tip of the island. This station serves as a control station as it is upwind from local aerosol sources and thus rarely influenced by them.

Sample Collection

Fog water samples were collected using an Aluminum Caltech Active Strand Cloud Water Collector version 2 (Al-CASCC2; Demoz, et al., 1996) and rainwater was collected using an amber glass bottle and plastic funnel. A detailed description of the sampling set up is provided by (Valle-Díaz et al., 2016).

Immediately after collection the samples were separated into plastic bottles for ion chromatography and inductively coupled plasma (ICP) analyses and into amber glass bottles for organic carbon and nitrogen analyses. For the analyses of ion chromatography and dissolved organic carbon and nitrogen, samples were filtered using 0.47- μm filters. Samples were frozen at -18°C and later transported to the laboratory for analysis. Samples for ICP analysis were also preserved with about 3 drops of hydrochloric acid. For the sampling period of 2013, a total of 39 fog water samples and 16 rainwater samples were collected.

Chemical Analyses

Water samples were analyzed using ion chromatography and inductively coupled plasma to characterize the inorganic fraction, combustion catalytic oxidation for the organic carbon and chemiluminescence for nitrogen. An ion chromatograph (Dionex ICS 1000) was used to detect the following ions: Na^+ , Ca^{2+} , K^+ , Mg^+ , NH_4^+ , Cl^- , NO_3^- , Br^- , PO_4^{3-} , SO_4^{2-} oxalate, formate, and acetate. Trace metals: Na, Al, Ca, Fe, K, Mg, Mn, P, S were detected using ICP (ICP Model Ciros CCD with optical emission detection) Total and dissolved organic carbon and nitrogen were analyzed using a TOC and TN analyzer (Shimadzu TOC-V CPH coupled with TNM-1).

Online Measurements

Visibility at PDE was measured using a visibility sensor (Belfort Peregrine 6500) placed on a pole at about two meters from the ground facing the predominant wind

direction. Meteorological conditions were monitored at both stations (Davis Vantage Pro 2 weather station) Rain deposition was measured directly with a tipping bucket at 15 minutes intervals, which is part of the weather station. Liquid water content at PDE was calculated from the droplet size distribution determined using a single particle backscattering optical spectrometer (Backscatter Cloud Probe, BCP, DMT).

At CSJ, aerosol scattering and absorption coefficients were measured using an integrating nephelometer (TSI Model 3563) and a Continuous Light Absorption Photometer (CLAP; Ogren et al., 2017), respectively. Both of these instruments measure at three different wavelengths; 450, 550, and 700 nm for the nephelometer; and 467, 528, and 652 nm for the CLAP, allowing an evaluation of aerosol wavelength dependency through the Ångström exponent from which information about air mass origin can be deduced.

Online instruments at both stations were operational from June 10-30, 2013 (20 days of data), from August 20-21 and 24-29, 2014 (8 days of data), from June 3 to August 24, 2014 (73 days of data, 9 days with missing data) and October 2 to December 4, 2015 (63 days of data), from March 2 to April 2, 2015 (21 days of data, 10 days of missing data), and from April 26 to July 10, 2015 (47 days of data, 28 days of missing data).

Sample Classification

The scattering and absorption Ångström exponents were calculated using the regression of the logarithm of scattering and absorption coefficient as a function of the logarithm of wavelength:

$$\ln b_{\text{abs}}(\lambda) = -SAE \ln \lambda + \text{constant} \quad (1)$$

$$\ln b_{\text{abs}}(\lambda) = -AAE \ln \lambda + \text{constant} \quad (2)$$

Using this information, the method developed by Cazorla et al. (2013) was used to classify days with high or low dust influence. This method combines the scattering and absorption Ångström exponents to determine the type of aerosol influence, using a value of $SAE \leq 1$ and $AAE \geq 1.5$ as a threshold for dust dominated aerosols. For more details about the method please refer to Cazorla et al. (2013). The average values of the optical properties for both low and high dust influence are given in Table 2.1. Using this methodology, 23 and 15 fog and rainwater samples were classified as influenced by low and high dust, respectively.

Table 2.1: Average and standard deviation for aerosol optical properties for high and low dust influenced periods

	High Dust		Low Dust	
	Average	Std Dev	Average	Std Dev
Scattering 550 nm (Mm^{-1})	79.2	34.6	47.3	16.5
Absorption 528 nm (Mm^{-1})	0.7	2.66	0.56	4.63
SAE	0.28	0.18	0.35	0.2
AAE	2.9	1.91	0.84	0.26

Back Trajectory Analysis

Air mass backwards trajectories from the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model (Draxler & Hess, 1998) were used to determine the origin of the air masses corresponding to the low and high dust influenced samples.

Data Analysis

The Kolmogorov-Smirnov test was used to decide if a sample followed a normal distribution and all variables showed a non-normal distribution. The non-parametric Mann-Whitney test was used to study statistical significance. Both tests were done using the XLSTAT version 19 and the rest of the data analysis was done using the IGOR Pro software version 8.

Results and Discussion

Estimating fog density through visibility

In cloud forests, visibility has been used to estimate liquid water content (LWC) and cloud density. Eugster et al. (2006) showed that at PDE visibility and LWC had an exponential relationship. In this study, visibility was evaluated as a function of LWC for different periods during the years from 2013 to 2016. The results of Eugster et al. (2006) were confirmed, i.e. an exponential relationship was found (Figure 2.1). We use visibility as a proxy to estimate cloud density using the criteria discussed in Eugster et al. (2006), where visibility that is equal or above 1000 m represents fog-free conditions, a range of

200-1000 m is for light fog, and visibility equal or below 200 m represents dense fog conditions.

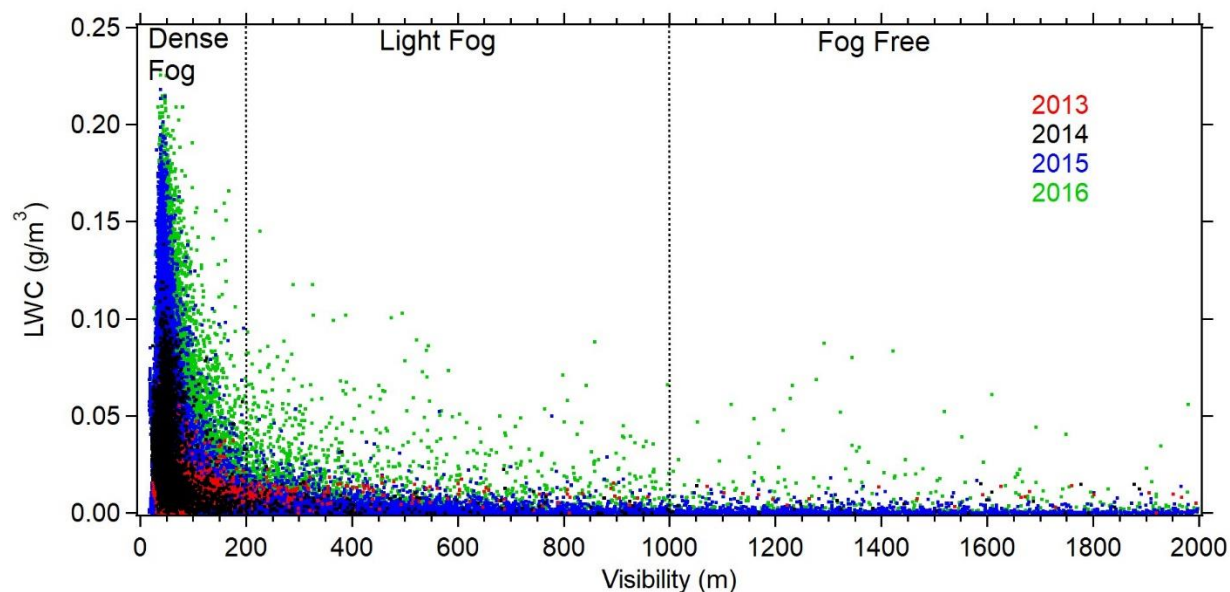


Figure 2.1: Liquid water content as a function of visibility for Pico del Este from various sampling campaigns from 2013 to 2016.

Dense fog conditions, from our visibility measurements, dominated at PDE all the years studied (Figure 2.2). Dense fog represented 98% of fog conditions in 2013, when it had the highest frequency, and 77% in 2016, when it had the lowest frequency. While it may appear that through the years the frequency of dense fog conditions is decreasing and the frequency of light fog and fog-free conditions is increasing, it is important to note that these measurements were not necessarily taken during the same periods of the year and climatic and seasonal patterns could be influencing these results. It is interesting to note that the decrease in frequency of dense fog conditions, as it could also be suggesting a

climate change related environmental issue that has been reported in the literature for EYNF (Van Beusekom et al., 2017; Miller et al., 2018).

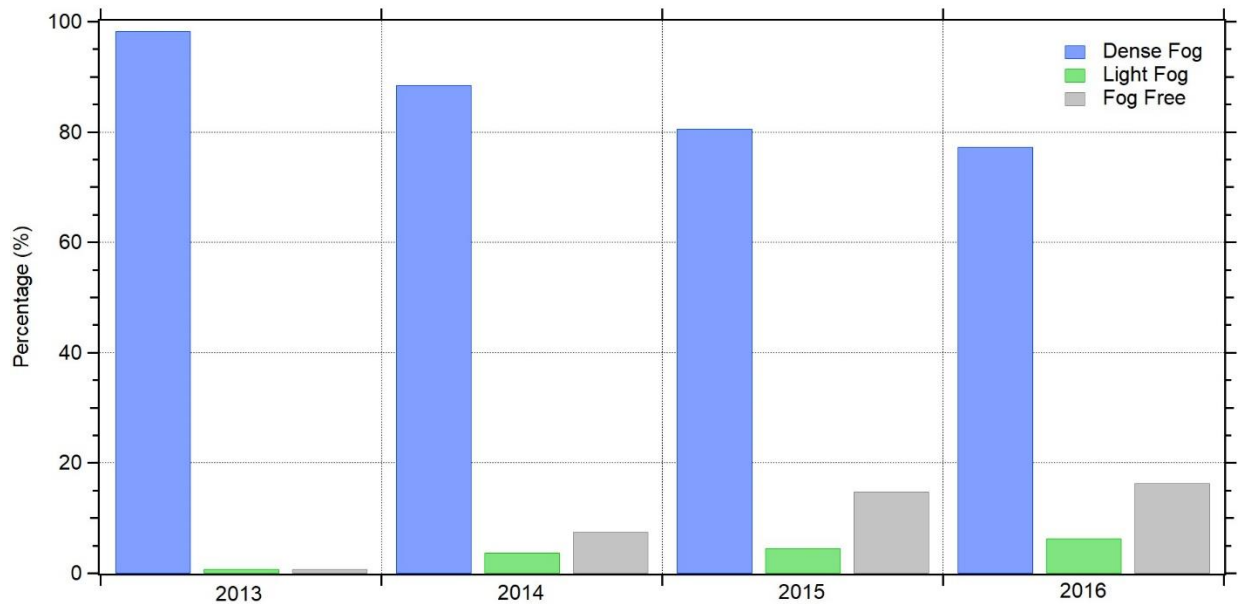


Figure 2.2: Percentage of cloud density at Pico del Este from various sampling campaigns from 2013 to 2016.

Water deposition through fog and rain

Several methods are used to calculate the fog water deposition (Holwerda et al., 2006). The method considered to give the best estimates is the eddy covariance method. This method measures the fog water droplet size distribution and the horizontal and vertical wind components at the same time, allowing to calculate the turbulent flux in the vertical direction, and the gravitational deposition from Stokes' law. The total flux can also be calculated using the horizontal wind component and the LWC. Holwerda et al. (2006)

showed that fog water fluxes determined with the later method correlated well with those determined from the eddy covariance method for rain-free ($r^2 = 0.94$) periods and periods with rain ($r^2 = 0.75$) at PDE. Eugster et al. (2006) developed an equation to determine fog deposition by using LWC based on their results from the eddy covariance method at PDE. Total fog water deposition was determined by multiplying the horizontal windspeed by the fog water LWC using:

$$D_{tot} = U * LWC_{tot} \quad (3)$$

where D_{tot} is the total fog water deposition ($\text{mg m}^{-2} \text{s}^{-1}$), U is the wind speed (m s^{-1}) and LWC_{tot} is the fog water liquid water content (mg m^{-3}). The gravitational deposition was calculated using the Stokes' law approach:

$$D_{sed} = \sum_i V_{s,i} * LWC_i \quad (4)$$

$$V_s = \frac{g d^2 (\rho_{water} - \rho_{air})}{18\eta_{air}} \quad (5)$$

where D_{sed} is the sedimentation or gravitational deposition ($\text{mg m}^{-2} \text{s}^{-1}$), V_s is the sedimentation velocity (m s^{-1}), g is the gravitational acceleration (m s^{-2}), d is the particle diameter (m), ρ is density (kg m^{-3}), and η is the dynamic viscosity ($\text{kg m}^{-1} \text{s}^{-1}$). Total fog water deposition was multiplied by 0.0036 to obtain units of mm/h (Holwerda et al., 2006).

Holwerda et al. (2006) reported an average total fog water flux of 0.73 mm h^{-1} for rain free samples and of 1.83 mm h^{-1} for samples with rain events. From these estimates,

turbulent deposition is the predominant deposition mechanism. Holwerda et al. (2006) estimated that about 8% of the total deposition was due to gravitational deposition. In our estimates, gravitational deposition accounts for less than 0.1% of the deposition (0.06% and 0.09% in 2013 and 2014, respectively). A possible explanation for this is that both studies were not performed in the exact same area or using the same instruments, for which local conditions and instrumental error might be influencing the results.

Fog deposition was also calculated using the equation developed by Eugster et al. (2006):

$$D_{tot} = \exp[(1.23) + (0.327)\ln(LWC_{tot})] \quad (6)$$

Using the fog frequency results determined from visibility, we calculated the daily fog water deposition, only considering the frequency of high fog density. Daily deposition was calculated by multiplying the calculated hourly deposition by 24 and with the percentage of high fog density.

Table 2.2 shows the average results of the two methods (horizontal deposition and equation developed by Eugster et al. (2006)) for determining fog deposition and rainwater deposition. Both methods gave statistically significant results for years 2013 and 2014 ($p < 0.0001$; Mann-Whitney statistical test). While the results we obtained using the method developed by Holwerda et al. (2006) gave similar results as those published in their study, they argument that those values are unrealistically high. The equation developed by Eugster et al. (2006) gave results much more realistic to what is expected at PDE as per results

previously published using the eddy covariance method for estimating fog deposition (Eugster et al., 2006; Holwerda et al., 2006).

Table 2.2: Fog and rainwater hourly and daily deposition for 2013 and 2014 samples.

	Sample Days	Rain Deposition		Fog Deposition (Horizontal)		Fog Deposition (Eugster et al. 2006 best fit)	
		Hourly (mm/h)	Daily (mm/day)	Hourly (mm/h)	Daily (mm/day)	Hourly (mm/h)	Daily (mm/day)
2013	20	0.10	2.3	0.39	9.4	0.03	0.66
2014	9	0.04	1.1	0.67	16	0.03	0.78

It was estimated that for the sampling period of 2013 fog determined with the horizontal deposition method contributed 9.4 mm day^{-1} of water, while with the method developed by Eugster et al. (2006) fog contributed 0.66 mm day^{-1} and rain contributed 2.3 mm day^{-1} . These results indicate that using the horizontal deposition method in 2013 fog would have contributed 80% and with the method developed by Eugster et al. (2006) 22% to the total water deposition. According to Holwerda et al. (2006), fog water deposition is responsible for about 17% (0.78 mm day^{-1}) of the total water deposition at PDE as measured with the eddy covariance method, what puts the estimate from the horizontal deposition method way above that value. For 2014, fog determined with the horizontal deposition method contributed 16.1 mm day^{-1} of water, while with the method developed by Eugster et al. (2006) fog contributed 0.78 mm day^{-1} and rain contributed 1.1 mm day^{-1} .

These values represent a fog contribution of 94% and 43% for the horizontal deposition and Eugster et al. (2006) method, respectively to the total water deposition, again putting the horizontal deposition method way above the expected values (about a 14x factor). While the estimate from the Eugster et al. (2006) method is also above the expected percentage (about a 1.5x factor) for 2014, this year was drier than normal (Torres-González, 2015), which enhances the relative importance of fog water deposition. From these estimates, it can be concluded that rain is the main contributor (57 - 78% of total) of water to the cloud forest and fog represents a smaller fraction (22 - 43%) of all water deposition. We also concluded that the estimates calculated from the Eugster et al. (2006) method are more in harmony with previous studies (Holwerda et al., 2006) than those estimated with the horizontal deposition method. Estimating yearly deposition with this limited data set may not be correct, as fog and rain in this ecosystem are very different throughout the year, so we focused only on the available summer data and refrained from doing a full year estimate.

Sample classification

Calculated backward air mass trajectories were separated by periods of low and high dust influence following the results obtained from the aerosol optical properties. Air masses corresponding to periods identified as with low dust influence had a wider spread of possible origins (Figure 2.3a) rather than those that were classified as with high dust influence, that were more constrained (Figure 2.3b). Air masses classified as with low dust influence suggest that they might have come from the Atlantic Ocean, as well as from close

to the Sahara/Sahel region. Those that were classified as with high dust influence all came from close to the Sahara/Sahel region supporting the constant presence of higher concentrations of African dust.

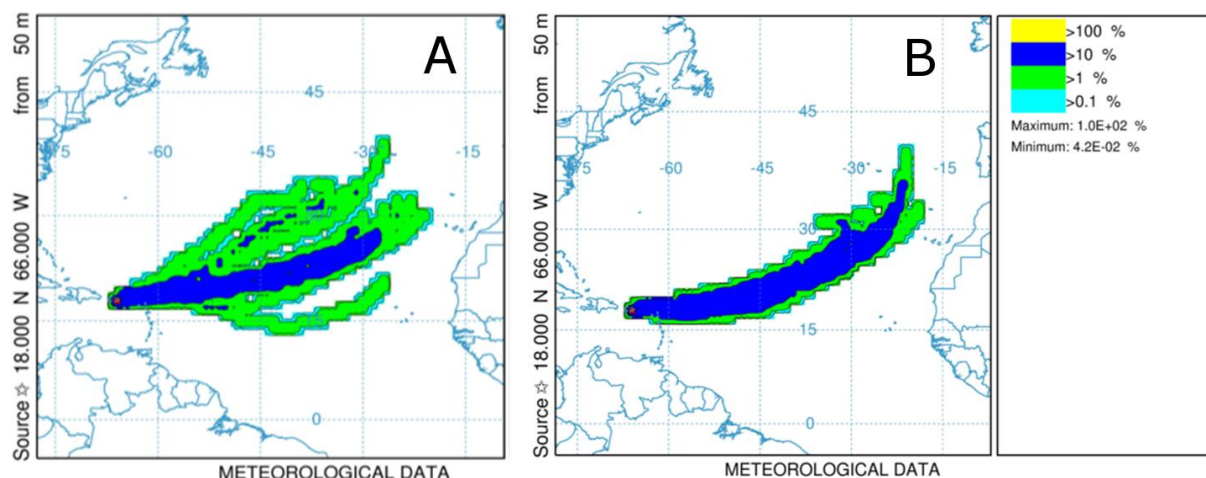


Figure 2.3: Back trajectory analysis for A) periods classified as with low dust influence and B) periods classified as with high dust influence.

Dust influence and water inputs

The Caribbean is influenced by African dust mainly during the summer months (Prospero & Lamb, 2003; Prospero & Mayol-Bracero, 2013), when most of our sampling took place. The effect of mineral dust on cloud physical and chemical properties is still highly uncertain (IPCC; Myhre et al., 2013). Therefore, we were interested in determining water inputs during the periods of high and low dust influence.

Table 2.3 lists the percentage of time when PDE was under the influence of low and dust environments stratified by fog density. In 2013, there was no change in the number of periods with dense fog but there were more fog-free periods and less light fog periods when in high dust influence. During 2014 there were more periods of dense fog when in high dust influence and fewer periods of light and fog free conditions. This does not imply a cause and effect just the conditions as they were that year.

Table 2.3: Percentage of fog occurrence determined from visibility data for 2013 and 2014 separated by periods of high and low dust influence.

	2013		2014	
	Low Dust	High Dust	Low Dust	High Dust
Dense Fog	98%	98%	88%	98%
Light Fog	1%	1%	4%	2%
Fog Free	1%	1%	8%	0%

In 2013, both low and high dust periods had a similar fog water deposition mean value of 0.66 ± 13 and 0.66 ± 17 mm day⁻¹, respectively. Even though the mean values were similar, the Mann-Whitney statistical test showed that the values were statistically different ($p < 0.0001$). Fog deposition, in 2014, was estimated to be 0.78 ± 0.23 mm day⁻¹ for low dust periods and 0.72 ± 0.16 mm day⁻¹ for high dust periods, testing statistically different ($p < 0.0001$). Rainwater fluxes in 2013, during low and high dust periods, were of 3.22 ± 13.3 mm day⁻¹ and 0.60 ± 3.76 mm day⁻¹, respectively. However, in 2014, we found an

opposite behavior, i.e. $0.34 \pm 2.38 \text{ mm day}^{-1}$ and $3.41 \pm 19.9 \text{ mm day}^{-1}$ for low and high dust events, respectively. Rain deposition for periods of low and high dust influence was statistically different for both years, with a $p < 0.0001$ for 2013 and $p = 0.025$ for 2014. These results show that overall, rain provides a larger water flux than fog and that the effect of dust on water flux, which is related to cloud formation and precipitation processes, is not clear for this location and dataset. While most studies in aerosol-cloud interactions suggest mineral dust acting as a cloud condensation nuclei and having an indirect effect on clouds, meaning a reduction of cloud droplet diameter and precipitation and an enhancement of cloud lifetime and reflectivity, these results do not indicate such an effect to be the main factor controlling cloud formation in EYNF. However, to properly assess the effect of mineral dust in clouds at this forest, a detailed study on aerosol-cloud interactions is in order, which is beyond the scope of this study.

Nutrient deposition through fog and rain

Deposition of nutrients through fog and rain was calculated from the ions, trace metals, organic carbon, and nitrogen concentrations. Results for water-soluble ions are shown in Table 2.4 and for trace metals, organic carbon, and nitrogen in Table 2.5. Charge balance for these samples ranged from 0.75 to 1.08, showing that in some cases there were ions that were not seen with these analyses.

Table 2.4: Deposition of water-soluble ions through fog and rainwater.

Ion	Fog (mg/m ²)	Rain (mg/m ²)	Ratio (rain/fog)
Cl ⁻	31.1	7.96	0.26
NO ₃ ⁻	0.60	0.16	0.27
SO ₄ ²⁻	3.00	0.99	0.33
Na ⁺	14.9	4.82	0.32
K ⁺	0.47	0.60	1.28
Mg ⁺	2.26	0.80	0.35
Ca ²⁺	3.02	1.26	0.42
OA	0.16	0.18	1.13
Br ⁻	0.05	0.01	0.20
PO ₄ ³⁻	0.01	0.01	1.00
NH ₄ ⁺	0.51	0.26	0.51

Table 2.5: Deposition of trace metals, organic carbon and nitrogen through fog and rain.

Specie	Fog (mg/m²)	Rain (mg/m²)	Ration (rain/fog)
Al	1.08	0.01	0.01
Ca	3.31	0.02	0.01
Fe	0.63	0	0
K	0.88	0.01	0.01
Mg	2.56	0.01	0
Mn	0	0	0
Na	16.6	0.07	0
P	0.01	0	0
S	2.92	0.02	0.01
TOC	2.61	1.61	0.62
TN	1.19	0.25	0.21
DOC	2.88	0.16	0.07
DN	1.06	0.21	0.20

For water-soluble ions, most species were deposited in higher quantities by fog water, except for potassium, phosphate, and organic acids (Table 2.4). However, concentrations of phosphate and organic acids were very low, so their difference in fog and rainwater might not be as important as what the numbers suggest. For trace metals and for

organic carbon and nitrogen, all species had higher deposition in fog water than in rainwater (Table 2.5). Deposition of other ions such as chloride, nitrate, sulfate, sodium and magnesium were considerably higher in fog water than in rainwater, ranging in percentage difference from 74% to 65%, similar to the differences seen in the average values in Gioda et al. (2011, 2013). The percentage difference for all trace metals was almost 100%, meaning that the deposition of trace metals is mainly driven by fog water and the deposition by rainwater is negligible. For organic carbon and nitrogen, fog water was the main mechanism of deposition, similarly to what the results from Gioda et al. (2011) suggests. Rain had a more significant contribution to the total deposition of carbon and nitrogen than it did with water-soluble ions and trace metals. The deposition of the dissolved fractions was much more favorable through fog water than rainwater.

Dust influence on nutrient deposition

Concentration of water-soluble ions and trace metals in fog and rainwater for the sampling periods of 2013 are shown in Figures 2.4 and 2.5, respectively. These figures show that the concentration of both water-soluble ions and trace metals is higher in periods where there is high dust influence as compared to periods of low dust influence by both fog and rainwater. This is not surprising as it is expected that airborne mineral dust will introduce both ions and trace metals from the parent soil. Concentrations of organic carbon and nitrogen for fog water samples for sampling periods during 2013 are shown in Figure 2.6. Similar to what was seen with the water-soluble ions and trace metals, the

concentrations of total and dissolved organic carbon, as well as those of total and dissolved nitrogen, were higher for periods of high dust influence.

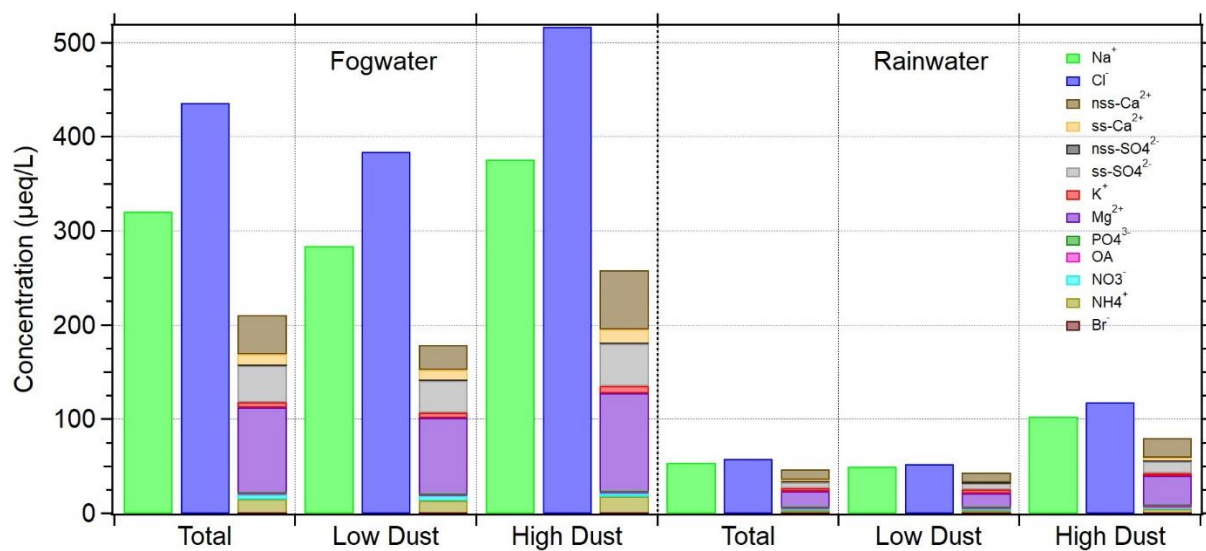


Figure 2.4: Concentration of water-soluble ions for fog and rainwater samples collected during the sampling periods of 2013.

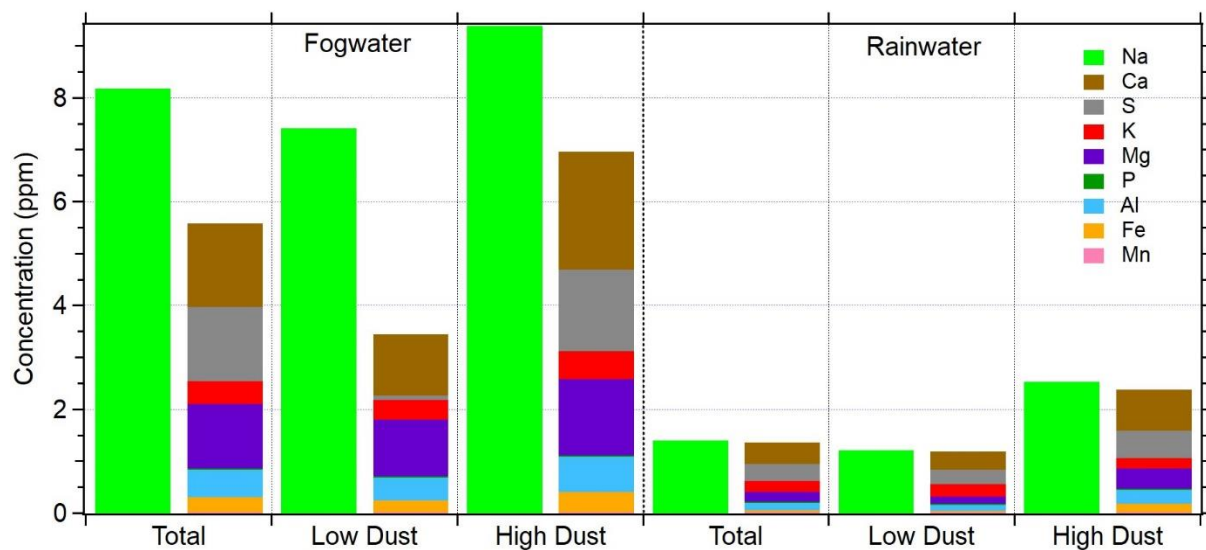


Figure 2.5: Concentration of trace metals for fog and rainwater samples collected during the sampling periods of 2013.

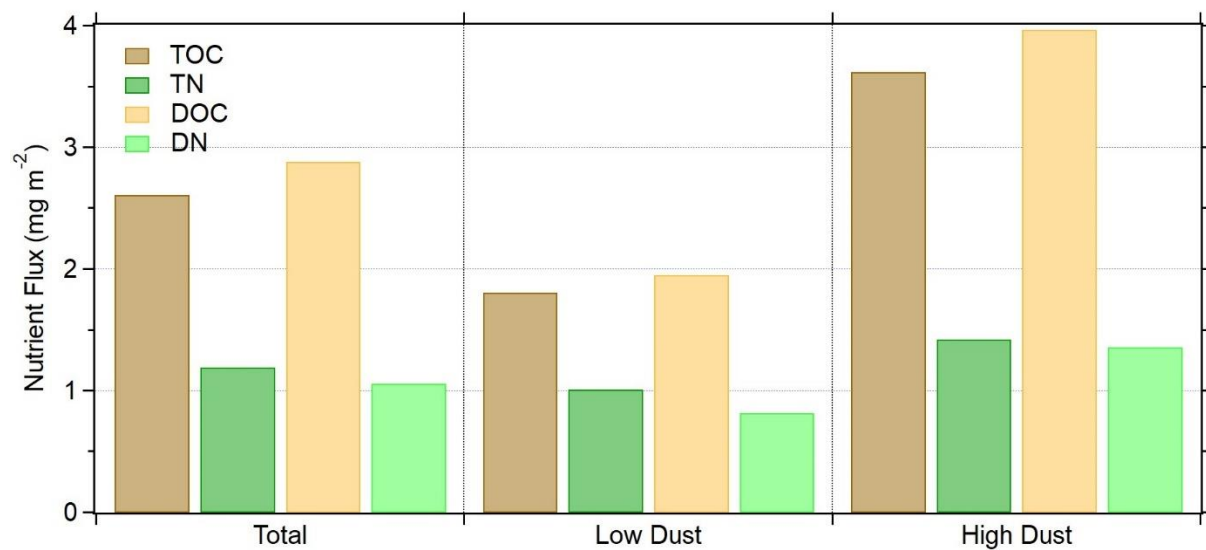


Figure 2.6: Flux of total and dissolved organic carbon and nitrogen for fog water samples collected during the sampling periods of 2013.

The ratios of high dust influence to low dust influence for water-soluble ions show that the concentrations of all ions except organic acids (labeled OA) were higher for samples with high dust influence (Tables 2.6 and 2.7). Calcium, phosphate, and potassium showed the greatest difference for both periods, with a percentage difference equal to or greater than 29%. These three ions are usually found in crustal aerosols. Chloride, sulfate, sodium, and magnesium are the next most enriched ions in high dust influenced samples with a percentage difference around 25 %. It is interesting to note that only magnesium is expected to be from crustal origins, as chloride, sulfate, and sodium are predominant in marine aerosols. For trace metals, it was found that phosphorus was highly enriched in high dust influenced samples, with a percentage difference of 300%, but concentrations of the specie were low. This is an unexpected result as Pett-Ridge (2009) calculated from modeling studies an important yearly contribution of phosphorus to EYNF from long-range transported African dust (LRTAD). Our results do not support the findings in Pett-Ridge (2009), but are in harmony with other experimental studies done in PDE (Valle-Díaz et al., 2016). Calcium, iron, and aluminum were the next more enriched trace metals with a percentage difference ranging from 80 to 45%. The only trace metal that was not enriched in high dust influenced samples was manganese, but the concentrations of this species were the lowest detected. Mann-Whitney statistical tests showed that several of the water-soluble ions and trace metals deposition were statistically different when comparing samples with low and high dust influence, being NO_3^- , Br^- , PO_4^{3-} , NH_4^+ , and OA and Al, Fe, Mn, and S the ones that were not statistically different.

Total and dissolved organic carbon (TOC, DOC) and total and dissolved nitrogen (TN, DN) were also analyzed for cloud samples of 2013 and separated in periods of high and low dust influence (Figure 2.6). All species had higher concentrations in samples with high dust influence, suggesting LRTAD as the likely source. Dissolved organic carbon had the higher enrichment with a 72% difference and total nitrogen had the lowest enrichment with a 14% difference. Only DN deposition was statistically different when comparing low and high dust influenced samples.

Table 2.6: Water-soluble ions for 2013 fog water samples separated by periods of high and low dust influence.

Ion	Low Dust (µeq/L)	High Dust (µeq/L)	High Dust/Low Dust	Percentage Difference
Cl ⁻	384	517	1.35	26%
NO ₃ ⁻	4.82	3.94	0.82	22%
SO ₄ ²⁻	24.7	33.5	1.35	26%
Na ⁺	284	377	1.33	25%
K ⁺	4.97	7.00	1.41	29%
Mg ⁺	81.8	105	1.29	22%
Ca ²⁺	37.8	78.1	2.07	52%
OA	1.47	1.23	0.84	20%
Br ⁻	0.28	0.34	1.21	18%
PO ₄ ³⁻	0.13	0.24	1.85	46%
NH ₄ ⁺	13.5	17.4	1.29	22%

Table 2.7: Trace metals for 2013 fog water samples separated by periods of high and low dust influence.

Metal	Low Dust (ppm)	High Dust (ppm)	Dust/No Dust	Percentage Difference
Al	0.44	0.64	1.45	45%
Ca	1.18	2.12	1.80	80%
Fe	0.25	0.38	1.54	54%
K	0.37	0.50	1.34	34%
Mg	1.12	1.39	1.24	24%
Mn	0.001	0.001	1.00	0%
Na	7.42	8.80	1.19	19%
P	0.002	0.01	4.00	300%
S	1.32	1.58	1.20	20%

Conclusion

Tropical montane cloud forests are unique ecosystems that are home to many species that thrive in these often-saturated conditions. El Yunque National Forest is one of the Caribbean rainforests where these types of ecosystems exist. The Caribbean region is influenced by air masses carrying African dust, which can serve as a nutrient to the ecosystems through wet and dry deposition but can also affect precipitation. Both the water

and nutrient budget are essential to understand the biogeochemical cycle of these ecosystems and small changes in any of them can result in negative consequences for a sensitive ecosystem.

In this study, we show that visibility measurements can be used to estimate the frequency of dense, intermediate and fog free conditions using a method developed in Eugster et al. (2006). Using the relationship between visibility and liquid water content we obtained results similar to those of Eugster et al. (2006) in PDE, supporting the use of visibility measurements to estimate fog density.

The deposition of water through fog and rain at PDE was estimated. In fog water, results showed that the contribution of gravitational deposition is negligible, accounting for less than 0.1% for sampling periods during 2013 and 2014, far from the 8% estimated by Holwerda et al. (2006), and that turbulent deposition is the main deposition mechanism. We also compared two methods for estimating fog water deposition (horizontal deposition and the equation developed by Eugster et al. (2006) and concluded that the horizontal deposition method produced estimates that are unrealistically high for this location and that of Eugster et al. (2006) produced values consistent with what has been previously seen for this location, making the former a good way to estimate fog water deposition if an eddy covariance method cannot be employed.

Results showed that at PDE, rain is the principal mechanism of water deposition, responsible for 78% and 57% of the total deposition for 2013 and 2014, respectively. Water deposition estimates were classified in periods of high and low dust influence and while

the mean deposition value for fog water deposition for both periods was similar, the data set was statistically different. For rainwater deposition, we saw an opposite behavior in both years, with 2013 having a significantly higher water deposition for low dust influence periods and 2014 having a significantly higher deposition for high dust influence events. These results suggest that there are more important factors controlling cloud formation than the type of aerosol, but a detailed microphysical study would be needed to assess that theory.

Nutrient deposition through fog and rainwater was studied in the form of water-soluble ions, trace metal, total and dissolved organic carbon, and total and dissolved nitrogen analyses. While fog was not the major source of water to the ecosystem, it is a major source of nutrients. Most species had higher concentrations in fog water than in rainwater as it has been seen in several studies (e.g. Gioda et al., 2013; Valle-Díaz et al., 2016). The same pattern was followed in the nutrient flux, where fog water had a higher overall nutrient flux in most studied species.

This study suggests that both fog water and rainwater deposition processes are important for this ecosystem. Fog water is a more important process for nutrient deposition in the ecosystem, which mainly occurs from turbulent deposition and rainwater is a more important process for water deposition.

CHAPTER THREE

COMPARISON OF DIFFERENT AETHALOMETER CORRECTION SCHEMES

DURING GOAMAZON 2014/15

Abstract

Black carbon (BC) provides the second largest anthropogenic contribution as a warming agent of Earth's climate, surpassed only by CO₂. The light absorbing properties of BC can also affect atmospheric dynamics: absorption of solar radiation by BC can heat the atmosphere, disrupt circulation, and cool the surface. Filter-based measurements are the most common technique to measure BC concentrations, but they are affected by several artefacts that compromise the quality of the measurements. Correction schemes have been developed to overcome these problems, but their accuracy is still under debate.

Biomass burning (BB) is one of the most important sources of BC and, therefore, of crucial importance in addressing the radiative impact of this aerosol type. As a part of the U.S. Department of Energy-sponsored GoAmazon2014/5 project, an Aethalometer, a nephelometer, and a Single Particle Soot Photometer (SP2) were deployed near Manacapuru, Brazil to study BC emitted from different sources. The station was located in a region where BB events are common yet is also impacted by the anthropogenic plume originating from Manaus, a large city nearby. This work was focused on the periods of March, April, May and August, September, October. This unique setting allows the study of the available correction schemes with urban anthropogenic aerosols and those produced from BB at the forest.

Introduction

Light-absorbing aerosol particles absorb incoming solar radiation, perturbing Earth's radiative balance and affecting atmospheric dynamics and circulation (Bond et al.,

2013; Moosmüller et al., 2009). The most common atmospheric light-absorbing aerosols are black carbon (BC), which is formed by incomplete combustion through anthropogenic activity and biomass burning, and mineral dust (Sokolik & Toon, 1999), which originates by the suspension of soil particles by the wind. Black carbon is an important climate forcer, providing a contribution to radiative forcing of Earth's climate second only to that of CO₂ (Bond et al., 2013; Mhyre & Shindell, 2013). It is considered a short-lived forcer, with a relatively short lifetime in the atmosphere – about a week – before being removed through wet and/or dry deposition (Bond et al., 2013). Because of this short lifetime and the sporadic nature of some of its sources (e.g., biomass burning), BC mass concentration varies greatly, both spatially and temporally. Knowledge of the mass concentration of BC, and the magnitude of its light absorption, is crucial to understanding the role of BC in climate but obtaining accurate values for these quantities can be challenging for different reasons.

Several types of instruments are used to determine aerosol light absorption in the atmosphere. Filter-based instruments are probably the most common, as they are robust, easy to operate, and more economical than instruments that employ other techniques. These properties make them attractive for long-term measurements, for which extensive data records from around the world exist. The Aethalometer (AE) and the Particle Soot Absorption Photometer (PSAP) are the most widely used instruments of this type. Both measure light transmission at several wavelengths through a filter on which aerosol particles are being deposited. When the transmission decreases below a pre-assigned value

(typically ~70%) the filter is changed, or the filter medium is advanced to display a particle-free area.

Filter-based techniques do not measure BC mass concentration directly, but rather infer this quantity through measurements of the attenuation of light through a filter, with an assumption about the relation between the attenuation and the mass concentration. The basic premise of this approach is that the reduction in light intensity is caused only by absorption by BC particles. However, there are a number of effects that complicate accurate inference of BC mass concentrations from these measurements: other absorbing particles may contribute to the reduction in transmission; both BC particles and other particles may scatter light, with several implications; the filter media itself can be the cause of several artefacts; and the dependence of the attenuation on the BC mass concentration varies depending on several factors such as the size distribution of the BC particles or the amount and type of organic substances. To account for some of these effects, various correction schemes have been developed, some of which are specific to the Aethalometer (Weingartner et al., 2003; Arnott, et al., 2005; Schmid et al., 2006; Virkkula et al., 2007; Collaud Coen et al., 2010). However, although these correction schemes are widely used, their accuracy is questionable. While most of these corrections are designed to correct for the same artefacts, they often give different results for the same data set (Collaud Coen et al., 2010; Wang et al., 2016; Laing, et al., 2019). There are also discrepancies as how these corrections are applied. Some of the corrections treat factors as constants over an entire data set, some calculate them at certain time intervals, and some calculate them for each

data point. These different approaches can create differences in the outputs of the corrections.

This manuscript compares various correction schemes that have been proposed for the Aethalometer applied to a dataset that consists of measurements that contain influences from both urban aerosols and biomass burning aerosols. The manuscript is organized as follows. First, the basic operating principles of filter-based measurements and the artefacts associated with these measurements. Next, the Aethalometer is presented and various correction schemes are briefly discussed. The methodology for the comparison, and the sampling site, instrumentation, and data treatment are discussed. Finally, a comparison of the different correction schemes with various aspects of the data, such as the Ångström exponent and mass absorption cross-section, is presented, followed by the conclusions.

Filter-based measurements

The intensity of light $I(\lambda)$ at wavelength λ after penetrating a distance x through a uniform aerosol is related to the initial intensity $I_0(\lambda)$ at this wavelength by the Beer-Lambert law:

$$I(\lambda) = I_0(\lambda) \exp[-b_{\text{ext}}(\lambda)x] \quad (1)$$

where $b_{\text{ext}}(\lambda)$ is defined as the wavelength-dependent aerosol extinction coefficient (it being assumed that the atmospheric contribution to reduction in intensity through both scattering and absorption has already been taken into account), with dimensions of

inverse length. This quantity includes contributions from both scattering and absorption, both of which reduce the incident light intensity, with magnitudes $b_{\text{sca}}(\lambda)$ and $b_{\text{abs}}(\lambda)$, respectively ($b_{\text{ext}} = b_{\text{sca}} + b_{\text{abs}}$). The relative contributions of scattering and absorption to extinction are quantified by the single scattering albedo, $\omega_0(\lambda)$, defined by

$\omega_0(\lambda) = b_{\text{sca}}(\lambda)/b_{\text{ext}}(\lambda)$; for non-absorbing aerosols, for which the scattering and extinction coefficients are equal, $\omega_0 = 1$, whereas an aerosol that contains absorbing particles will have $\omega_0 < 1$.

Filter-based techniques for determination of aerosol light absorption pull an airstream through a filter upon which aerosol particles are deposited and determine the wavelength-dependent light attenuation, defined analogously to the extinction coefficient as

$$ATN(\lambda) = \ln \frac{I_0(\lambda)}{I(\lambda)} \quad (2)$$

where $I(\lambda)$ is the light intensity at wavelength λ after passing through the filter and $I_0(\lambda)$ is the initial light intensity (Weingartner et al., 2003). As particles continually deposit on the filter, the transmitted light intensity decreases with time. For a volume flow rate $\dot{V}$ of aerosol passing through an area A of the filter (called the filter spot area), the attenuation coefficient, with dimensions area per volume (equivalent to inverse distance), is defined by

$$b_{\text{ATN}}(\lambda) = \left(\frac{A}{V} \right) \times \frac{d}{dt} [ATN(\lambda)] \quad (3)$$

although in practice measurements are made at discrete times (designated by subscript n), and the derivative is replaced by a difference over time Δt (Collaud Coen et al., 2010):

$$b_{\text{ATN},n}(\lambda) = \left(\frac{A}{V} \right) \frac{ATN_n(\lambda) - ATN_{n-1}(\lambda)}{\Delta t_n} \quad (4)$$

Were attenuation to result entirely from absorption by BC, then the attenuation coefficient would be equal to the BC aerosol absorption coefficient $b_{\text{abs}}(\lambda)$, a property of the aerosol. However, as noted above, there are several reasons that these two quantities are not equal, and determination of BC aerosol absorption coefficients from light attenuation measurements requires treatment of these artefacts. The primary artefacts are briefly introduced, then the various correction schemes and the means by which they deal with these artefacts are discussed.

Artefacts of Filter-based Measurements

Both absorbing and non-absorbing particles scatter light, and any light that is scattered out of the direction of the beam and not elsewhere detected will result in an apparent attenuation. This artefact is typically accounted for by subtracting a fraction of the aerosol scattering coefficient, $b_{\text{sca}}(\lambda)$, measured by another instrument, from the attenuation coefficient. Particles can also scatter light toward light-absorbing particles, providing additional opportunities for absorption, thus increasing the measured

attenuation. In a similar manner, multiple scattering from filter fibers can provide additional opportunities for light to be absorbed by a light-absorbing aerosol particle. Both of these factors contribute to the measured attenuation coefficient being greater than the actual absorption coefficient. These effects are typically addressed by dividing the attenuation coefficient, after a fraction of the scattering coefficient is subtracted, by a quantity C , which may be wavelength-dependent and is generally greater than unity. Another artefact that affects these measurements is called the filter loading, or shadowing, effect, in which particles initially deposited on a filter are shadowed by those deposited at the top of the filter/particles ensemble. This filter-loading effect, which would result in the attenuation coefficient being less than the absorption coefficient, is usually accounted for by dividing the attenuation coefficient, again after subtraction of a fraction of the scattering coefficient, by a quantity corresponding to the filter loading correction, which is less than unity. While these artefacts can have counteracting effects, it is generally accepted that the net result is to overestimate the aerosol absorption coefficient (Arnott et al. 2005; Schmid et al. 2006; Collaud Coen et al. 2010).

Aethalometer correction schemes

Six correction schemes that have been proposed to convert attenuation coefficients determined by the Aethalometer to aerosol absorption coefficients are used in the comparison presented in this study: one each from Weingartner et al. (2003), Arnott et al. (2005), Schmid et al. (2006), and Virkkula et al. (2007), and two from Collaud Coen et al. (2010). Each of these accounts for the filter-loading effect, and each except that of Virkkula

et al. (2007) accounts for the multiple-scattering effect. A brief description of each correction is presented below.

The Weingartner et al. (2003) correction scheme, is given by

$$b_{\text{abs},n}(\lambda) = \frac{b_{\text{ATN},n}(\lambda)}{C_w \left(1 + \left\{ \frac{1}{1 + [1 - \bar{\omega}_0(\lambda)] a_w(\lambda)} - 1 \right\} \left\{ \frac{\ln[ATN_n(\lambda)] - \ln(10)}{\ln(50) - \ln(10)} \right\} \right)} \quad (5)$$

where ATN_n is the attenuation at time n given as a percent. It was developed using different aerosol types that were generated using two graphite spark generators and a diesel engine, with organic coatings that were formed by adding α -pinene. It is important to note that “attenuation” is used inconsistently by Weingartner et al. (2003): they defined this quantity as in Eq. 1 above, which yields values greater than unity, but used it in their correction scheme as a percent equal to $100\% \times (I_0 - I)/I_0$. Thus, an attenuation stated as 50% would yield an attenuation according to Eq. 1 of $\ln(2)$, or 0.69. The scattering contribution to the attenuation was not directly taken into account in this scheme. The multiple-scattering correction is given by the constant C_w , which was found to be wavelength-independent, with values of 2.14 for urban aerosols and 3.6 for biomass burning aerosols. The filter-loading correction, the term in the second set of curly brackets in Eq. 5, was found to depend on the logarithm of the attenuation (which itself is a logarithm), where 10 and 50 are used as threshold values for the typically lower and higher percent attenuation values, respectively, seen in the instrument after and before a filter change. The average value of the single scattering albedo, $\bar{\omega}_0(\lambda)$, is calculated from values of the attenuation coefficient

at low attenuation and concurrent nephelometer measurements of the scattering coefficient. The quantity $a_w(\lambda)$ is an empirical parameter determined to be 0.87 ± 0.10 at 450 nm and 0.85 ± 0.05 at 660 nm.

The Arnott et al. (2005) correction scheme is given by

$$b_{\text{abs},n}(\lambda) = \frac{b_{\text{ATN},n}(\lambda) - \alpha_A(\lambda)b_{\text{sca},n}(\lambda)}{C_A(\lambda)} \left[1 + \frac{\dot{V}\Delta t}{A\tau_{\alpha,fx}(\lambda)} \sum_{i=1}^{n-1} b_{\text{abs},i}(\lambda) \right]^{1/2} \quad (6)$$

It was developed using laboratory-generated ammonium sulfate and kerosene soot. Particle scattering is taken into account by subtracting from the attenuation coefficient a wavelength-dependent fraction $\alpha_A(\lambda)$ of the light-scattering coefficient determined by a nephelometer, where $\alpha_A(\lambda)$ ranges from 0.0335 at 370 nm to 0.1148 at 950 nm. A wavelength-dependent multiple scattering correction, $C_A(\lambda)$, which ranges from ~ 1.8 at 370 nm to 2.2 at 880 nm, was determined using a radiative transfer model in which the filter was treated as consisting of two layers: an upper layer in which aerosols are uniformly distributed, and a lower layer free of aerosol particles. The filter-loading effect is contained in the term in brackets in Eq. 6, where $\tau_{\alpha,fx}(\lambda)$, the wavelength-dependent filter absorption optical depth determined from laboratory studies, decreases from 0.2736 at 370 nm to 0.1390 at 950 nm. Values of $\alpha_A(\lambda)$, $C_A(\lambda)$, and $\tau_{\alpha,fx}(\lambda)$ at each of the seven Aethalometer wavelengths are listed in Table 1 of Arnott et al. (2005).

The Schmid et al. (2006) correction scheme is given by

$$b_{\text{abs},n}(\lambda) = \frac{b_{\text{ATN},n}(\lambda)}{\left[C_s(\lambda) + \alpha_s \frac{\omega_{0,n}(\lambda)}{1 - \omega_{0,n}(\lambda)} \right] \left(1 + \left\{ \frac{1}{1 + [1 - \omega_{0,n}(\lambda)] m_w(\lambda)} - 1 \right\} \left\{ \frac{\ln[ATN_n(\lambda)] - \ln(10)}{\ln(50) - \ln(10)} \right\} \right)} \quad (6)$$

where ATN_n is expressed as a percent. It is based on the previously published correction schemes of Weingartner et al. (2003) and Arnott et al. (2005), where it adopts the main formula from Weingartner et al. (2003) but includes a particle scattering correction similar to what was done in Arnott et al. (2005) using the single scattering albedo, and adds it to the multiple scattering correction. The scheme was developed using measurements taken during the SMOke aerosols, Clouds, rainfall, and Climate (SMOCC) campaign in Rondonia, Brazil from September to November, 2002, in which biomass burning events sampled, and a Photoacoustic Absorption Photometer (PAS) was used as a reference instrument (Truex & Anderson, 1979). Particle scattering is accounted for using the single-scattering albedo, and the multiple-scattering correction is contained in the wavelength-dependent term $C_s(\lambda)$, which ranges from 4.79 at 450 nm to 6.73 at 950 nm. The filter-loading correction is similar to that of Weingartner et al. (2003).

The Virkkula et al. (2007) correction scheme was designed to be used when scattering data are not available. This scheme, which depends only on measured values and does not contain any parameters, is given by

$$b_{\text{abs},n}(\lambda) = [1 + k_v(\lambda) ATN_n(\lambda)] b_{\text{ATN},n}(\lambda) \quad (7)$$

where k_v , the filter-loading correction, is given by

$$k_V(\lambda) = \frac{b_{\text{ATN},n}(\lambda, t_{i+t, \text{first}}) - b_{\text{ATN},n}(\lambda, t_{i, \text{last}})}{\text{ATN}(\lambda, t_{i, \text{last}})b_{\text{ATN},n}(\lambda, t_{i, \text{last}}) - \text{ATN}(\lambda, t_{i+1, \text{first}})b_{\text{ATN},n}(\lambda, t_{i+1, \text{first}})}. \quad (8)$$

This correction was developed to correct for the lack of continuity in derived absorption coefficients that occurs after a filter change. The quantities $\text{ATN}(\lambda, t_{i+1, \text{first}})$ and $b_{\text{ATN},n}(\lambda, t_{i+1, \text{first}})$ are the first attenuation and attenuation coefficients measured after a filter change (at the given wavelength), and $\text{ATN}(\lambda, t_{i, \text{last}})$ and $b_{\text{ATN},n}(\lambda, t_{i, \text{last}})$ are the last attenuation and attenuation coefficients measured before a filter change (also at that wavelength). The correction was tested on three datasets collected in Helsinki, Finland: two in urban areas and one in a rural area.

Collaud Coen et al. (2010) developed two correction schemes. The first is based on the corrections developed by Arnott et al. (2005):

$$b_{\text{abs},n}(\lambda) = \frac{b_{\text{ATN},n}(\lambda) - \alpha_A(\lambda)\bar{b}_{\text{sca},n}(\lambda)}{C_A(\lambda) \left(1 + \left\{ \frac{1}{1 + m_A(\lambda)[1 - \bar{\omega}_{0,n}(\lambda)]} - 1 \right\} \frac{\text{ATN}_n(\lambda)}{50} \right)} \quad (9)$$

where ATN_n is expressed in percent, $\bar{b}_{\text{sca},n}(\lambda)$ is the aerosol scattering coefficient averaged since the last filter change, and $\bar{\omega}_{0,n}(\lambda)$ is the average single scattering albedo since the last filter change. The other is based on the correction developed by Schmid et al. (2006):

$$b_{\text{abs},n}(\lambda) = \frac{b_{\text{ATN},n}(\lambda)}{\left[C_s(\lambda) + \alpha_s(\lambda) \frac{\bar{\omega}_{0,n}(\lambda)}{1 - \bar{\omega}_{0,n}(\lambda)} \right] \left(1 + \left\{ \frac{1}{1 + m_s(\lambda) [1 - \bar{\omega}_{0,n}(\lambda)]} - 1 \right\} \frac{\text{ATN}_n(\lambda)}{50} \right)}. \quad (10)$$

These corrections, which account for scattering, multiple scattering (through the wavelength-dependent quantities C_A and C_S), and filter loading (through the wavelength-dependent quantities m_A and m_S), were tested on six data sets that had influence from urban, coastal, and biomass burning aerosols, with a collocated Multi-Angle Absorption Photometer (MAAP; Petzold, et al., 2002) used as a reference instrument.

Methodology

Sampling site

As part of the Green Ocean Amazon project (GoAmazon2014/5) sponsored by the U.S. Department of Energy, an Atmospheric Radiation Measurement (ARM) Mobile Aerosol Observing System (MAOS) was deployed at 3° 12' S, 60° 36' W in the state of Amazonas in Brazil, 10 km north of Manacapurú and 70 km west of Manaus, the capital of the Amazonian state. This site receives urban aerosols both from Manacapurú, with just over 90,000 inhabitants, and Manaus, with over two million inhabitants, and biomass burning (BB) aerosols from BB events that are common in and near the state of Amazonas (Martin et al., 2016; Cirino et al., 2018).

The Amazon basin is characterized by its precipitation patterns, divided between the wet season and the dry season (e.g., INMET 2009). These seasons match the movements of the Intertropical Convergence Zone, which are affected by El Niño Southern Oscillation and the Madden-Julian Oscillation (Borges et al., 2018) as well as by the South American low-level jet (Nogués-Paegle & Mo, 1997). The wet season comprises the months from December to February and is characterized by frequent precipitation events (Araujo et al., 2018). The dry season comprises the months of June to August and is distinguished by a considerably lower amount of rainfall (Araujo et al., 2018), accompanied by a notable increase of biomass burning (Martin et al., 2016). Due to data availability, we could not specifically target the dry and wet seasons of 2014; rather we use the measurements taken during March, April, and May (MAM) 2014 as the most representative for the wet season, and measurements taken during August, September, and October (ASO) 2014 as representative of the dry season.

A time series of fires detected in the state of Amazonas by the GOES-13 satellite during 2014, and the corresponding attenuation coefficients determined by the Aethalometer at 520 nm, are shown in Figure 3.1. The number of fires peaks in August, and remains fairly high through September and October, with attenuation coefficients highest during this time period, supporting the period selection. Satellite products were downloaded from <http://www.inpe.br/queimadas/bdqueimadas/>. The GOES-13 satellite identified 159 fires during the MAM period, accounting for 4.4% of the fires detected in 2014, and 2978 in the ASO period, accounting for 81.5% of the fires detected in 2014.

Figure 3.2 shows a map of the Amazon basin for the months of April and August 2014 with the fires detected by the GOES-13 satellite. This shows that fires take place all over the Amazon basin and are much more frequent during the ASO period.

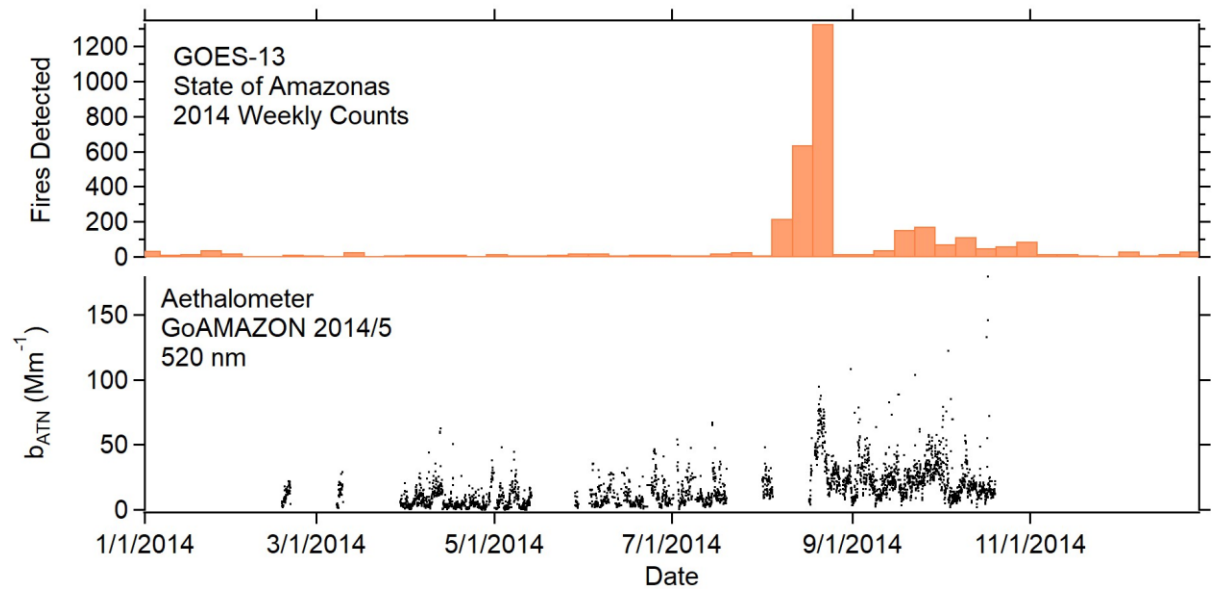


Figure 3.1: Top: Fires detected in the state of Amazonas in 2014 using the GOES 13 satellite. Bars are weekly total fires. Bottom: Aethalometer (AE) uncorrected attenuation coefficient at 520 nm.

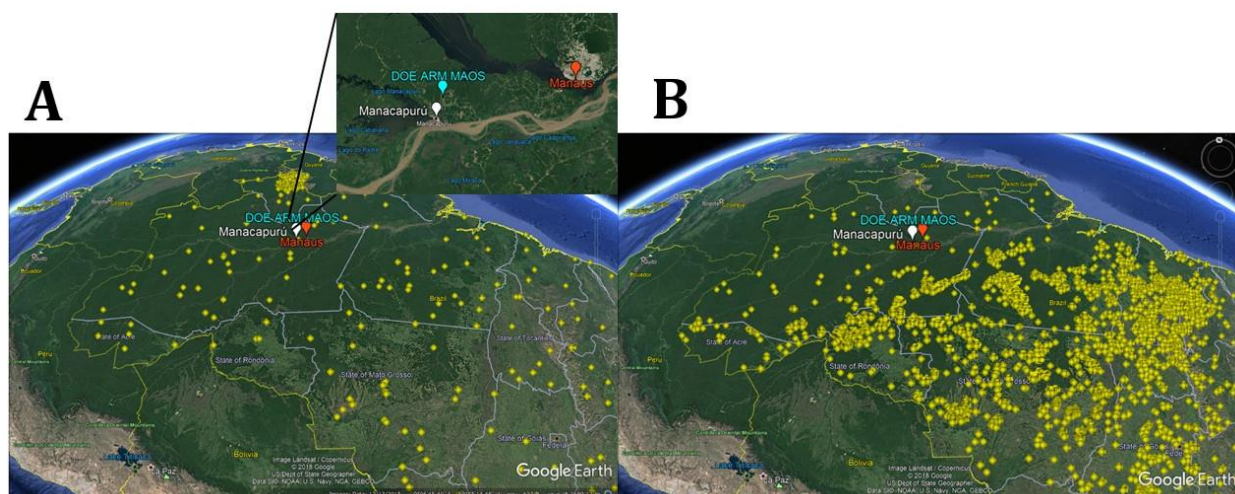


Figure 3.2: Map of Brazil with the location of Manacapuru (white) and the MAOS (blue). Yellow dots represent fires detected by the GOES 13 satellite for A) the month of April 2014, and B) the month of August 2014.
(<http://www.inpe.br/queimadas/bdqueimadas/>).

Instrumentation and data treatment

A number of instruments were deployed inside the MAOS to measure properties of aerosols and gases. Those of particular interest to this investigation were an Aethalometer (AE31; Magee Scientific; Hansen, et al., 1984), an integrating nephelometer (TSI model 3563; Heintzenberg & Charlson, 1996), a Single Particle Soot Photometer (SP2; Droplet Measurement Technologies; Stephens et al., 2003), and a carbon monoxide/water vapor/nitrous oxide (CO/H₂O/N₂O) analyzer (CO-ANALYZER; Los Gatos Research).

The Aethalometer measured the attenuation coefficient using a filter-based technique at seven wavelengths: 370, 430, 470, 520, 565, 700, and 880 nm, as discussed

above. However, the instrument reports results as mass concentrations under the assumption that the reduction in light transmission is caused solely by absorption by BC, and that the absorption coefficient is directly proportional to the BC mass concentration. The ratio of these two quantities, defined as the mass-absorption coefficient, or MAC, is assumed by the manufacturer to be equal to $28.1 \text{ m}^2 \text{ g}^{-1}$ at 520 nm and inversely proportional to the wavelength, as would be the case for particles sufficiently small that light absorption is given by Rayleigh's Law. In this size range, the MAC is given by

$$MAC = \frac{6\pi}{\rho\lambda} \left[-\text{Im} \left(\frac{m^2 - 1}{m^2 + 2} \right) \right] \quad (11)$$

where ρ is the density of the particle and m is the complex index of refraction, resulting in values much smaller than those assumed by the manufacturer. For instance, for typically assumed values of 1.8 g m^{-3} for the density and $1.8 - 0.8i$ for the index of refraction of BC, Eq. 11 yields $5.9 \text{ m}^2 \text{ g}^{-1}$ at 520 nm, and the value for coated particles, which have enhanced absorption, may be up to a factor of two to three greater. The values reported by the Aethalometer, converted to attenuation coefficients using the values for the MAC assumed by the manufacturer at each wavelength, were used in the analysis.

Nephelometer and SP2 data were paired and averaged to 5 minutes intervals to match the Aethalometer time resolution. The nephelometer determined the aerosol light scattering coefficient at three wavelengths: 450, 550, and 700 nm. As only light scattered from $7-170^\circ$ can be detected, a truncation correction was applied following Anderson &

Ogren (1998). The light scattering coefficients were linearly interpolated and extrapolated to match the wavelengths of the Aethalometer. The SP2 determined the masses of individual BC-containing particles using laser-induced incandescence (Baumgardner et al., 2004; Schwarz et al., 2006) in which the particles absorb laser light and heat to near 4000 K, at which temperature they sublime and incandesce. The light emitted from the incandescence is detected and converted to an rBC mass through a calibration curve (where rBC refers to refractory black carbon). The SP2 is also capable of using light scattering to determine the optical diameter of the mixing state (i.e., the relative amount of non-rBC substance) of the rBC particles (Gao et al., 2007; Moteki & Kondo, 2007).

The CO analyzer measured carbon monoxide (CO), water vapor, and nitrous oxide concentrations. The ratio of the CO concentration to the BC mass concentration, indicative of fuel source (Baumgardner et al., 2002; Subramanian et al., 2010), was used to screen the data to avoid biases from a nearby diesel backup power generator, which was operated when the power went off or periodically for maintenance periods. A CO:BC ratio greater than $10 \text{ ng m}^{-3} \text{ ppb}^{-1}$ was assumed to be diesel combustion from the generator, and these data were excluded from this analysis. Corrections schemes for the remaining data were applied using 5-minute data and later all processed data were averaged to hourly intervals.

Comparison of correction schemes

The correction schemes discussed above are compared using several criteria. The slopes of the linear regression lines of the corrected absorption coefficients to the uncorrected ones (i.e., the attenuation coefficients), forced through the origin, quantifies

the magnitudes of the corrections. It is generally accepted that the attenuation coefficients are considerably greater than the true values (Arnott et al., 2005; Schmid et al., 2006; Collaud Coen et al., 2010) driven largely by the values of C , which are typically in the range 2-5. The MAC was calculated from the absorption coefficient and the refractory black carbon and the results were compared by MAC values for urban and biomass burning particles reported in the literature using a thermo/optical technique. The AAE obtained for every correction were compared to each other.

Absorption Ångström exponent

Several filter-based instruments, including both the AE and PSAP, measure attenuation at various wavelengths, providing information on the wavelength dependence of the aerosol absorption coefficient. This dependence is quantified by the absorption Ångström exponent, AAE, defined as the negative of the slope of the linear fit of the logarithm of the aerosol absorption coefficient to the logarithm of the wavelength for measurements taken over a range of wavelengths:

$$\ln b_{\text{abs}}(\lambda) = -AAE \ln \lambda + \text{constant} \quad (11)$$

The AAE characterizes the wavelength dependency of the light absorption and can be used to identify different aerosol types (Bergstrom et al., 2007; Moosmüller, et al., 2011; Andrews, et al., 2017). Values near unity, which indicate a nearly uniform absorption over the range of wavelengths measured, are associated with BC, whereas values greater than ~1.5, which indicate a preferential absorption in the UV-blue region of the spectrum, are

associated with either brown carbon (BrC) from biomass burning or mineral dust (Cazorla et al., 2013).

Results and Discussion

Six corrections schemes were evaluated: those of Weingartner et al. (2003) with $C = 2.14$ (their recommended value for urban aerosols), Weingartner et al. (2003) with $C=3.6$ (their recommended value for biomass burn aerosols); Arnott et al. (2005), Schmid et al. (2006); Virkkula et al. (2007), and two of Collaud Coen et al. (2010): one based on that of Arnott et al. (2005) and one based on that of Schmid et al. (2006). For each, the following quantities are compared: absorption coefficients, which yields an estimate of the magnitude of the corrections; wavelength dependence of the absorption coefficient, absorption coefficient vs. mass concentration, from which values of the MAC were determined, and wavelength dependence of the MAC. Whereas Aethalometer measurements from all wavelengths were used in the analysis, for clarity purposes, in some instances data are presented at only one wavelength, 520 nm, which represents the midpoint of the measurement range of the instrument.

Absorption coefficients

The attenuation and absorption coefficients for the MAM and ASO periods are shown in Figures 3.3A and 3.3B, respectively, for each wavelength. It is clear from these figures that during the ASO period the attenuation and absorption coefficients values are a

factor 2.8 to 4.1 times higher than during the MAM period, as shown previously in Fig. 3.1. This is expected, as this is when most biomass burning events occur. The averages for the MAM and ASO periods for uncorrected absorption coefficient at 520 nm were 7.73 and 24.8 Mm^{-1} , respectively. When looking at the corrections schemes, the corrections from Schmid et al., (2006) and the two from Collaud Coen et al., (2010) provide the most aggressive correction, which ranged from 3.5 to 4.8 times lower absorption coefficient values for both periods.

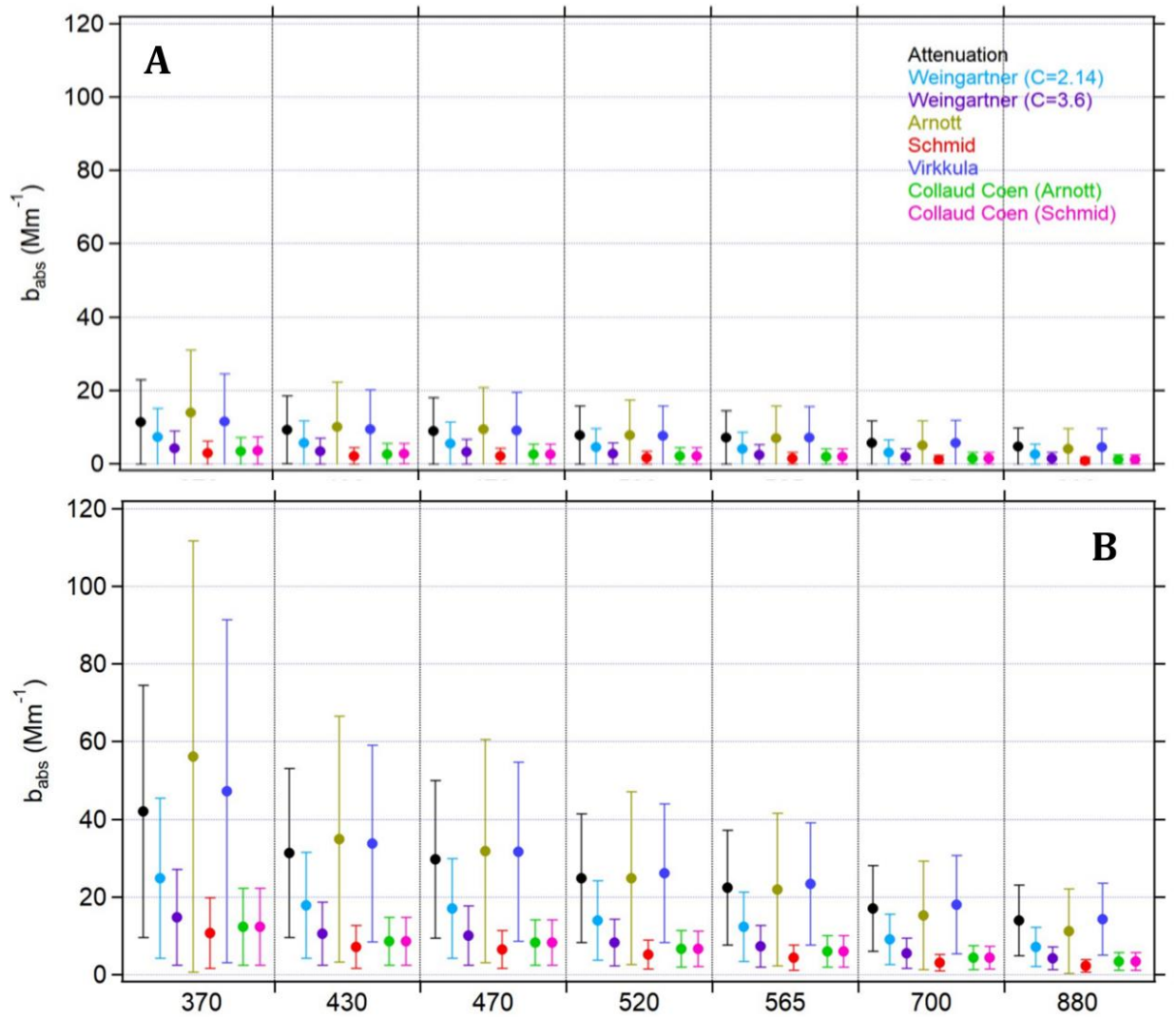


Figure 3.3: Attenuation and absorption coefficient as a function of wavelength for the A) MAM period of 2014 and B) the ASO period of 2014.

The linear regressions of the absorption coefficients at 520 nm for each correction scheme to the attenuation coefficient, forced through the origin, are shown in Figure 3.4. The slopes of this regressions quantify how much each correction alters the attenuation

value. The correction schemes of Schmid et al. (2006) and the two of Collaud Coen et al. (2010) are seen to be the most aggressive, represented by the lower slopes, with values of 0.22, 0.27 and 0.28, respectively (the last two fall on top of each other on the plot). The correction schemes of Arnott et al. (2005) and Virkkula et al., (2007) yielded slopes greater than unity, although with a large amount of scatter. However, as it is generally accepted that the filter-based attenuation measurements (i.e., uncorrected) are considerably greater than the absorption (i.e., true) values (Arnott et al., 2005; Schmid et al., 2006; Collaud Coen et al., 2010), the high values of the slopes suggests that this correction algorithm is not accurate.

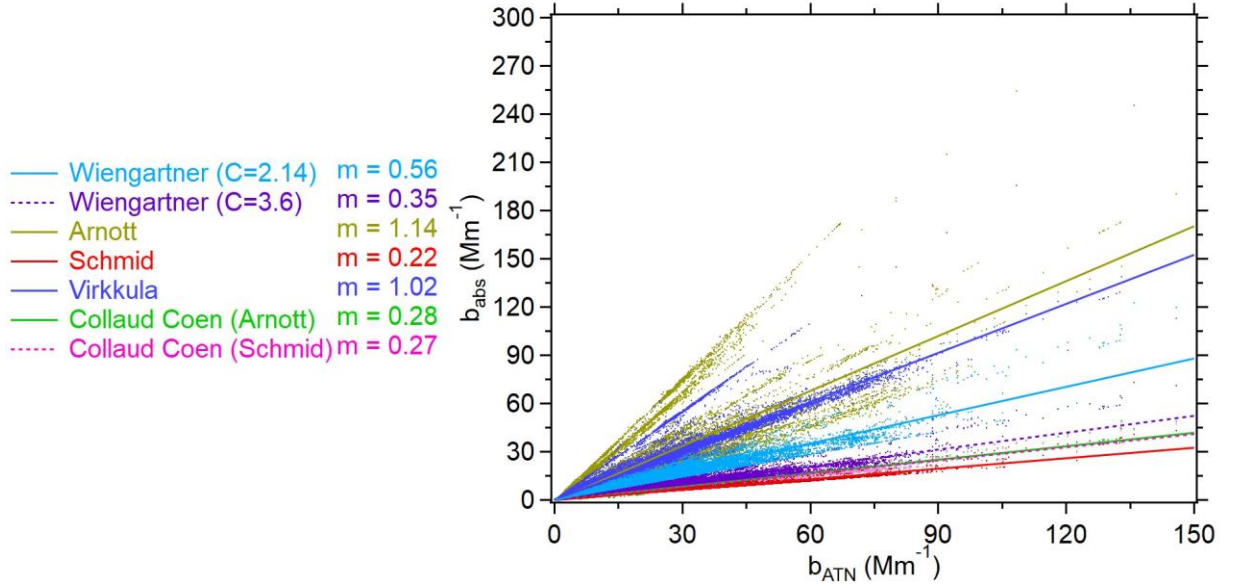


Figure 3.4: Absorption coefficients determined using each of the correction schemes vs. the attenuation coefficient at 520 nm, with least-squares fit lines forced through the origin.

The absorption coefficients determined with the Arnott et al. (2005) and Virkkula et al. (2007) algorithms had standard deviations of 9.6 and 8.1 for the MAM period and of 22.4 and 17.9 for the ASO period at 520 nm, respectively, and this behavior can also be seen in Figures 3.3A and 3.3B. In contrast, the range of the standard deviation for the rest of the corrections at 520 nm goes from 1.77 to 4.99 for the MAM period and from 3.72 to 10.2 in the ASO period. The Schmid et al. (2006) correction scheme produced the lowest absorption coefficients, the averages of which for the MAM and ASO periods were 1.66 and 5.13 Mm^{-1} , respectively, as well as the lowest standard deviations. A difference of 79% was found between the uncorrected absorption coefficient and the corrected one using Schmid et al. (2006) correction scheme for both periods.

The Arnott et al. (2005) correction exhibits the strongest wavelength dependence (Fig. 3.5A and 3.5B). At 370 nm, this correction gave the higher average results and the higher spread for both periods, while at 880 nm, the average value goes below the uncorrected values and the ones corrected through the Virkkula et al. (2007) correction. A possible explanation for this behavior is that this correction takes light scattering directly into account while others do it through the single scattering albedo, which can introduce more error as well as more wavelength dependence.

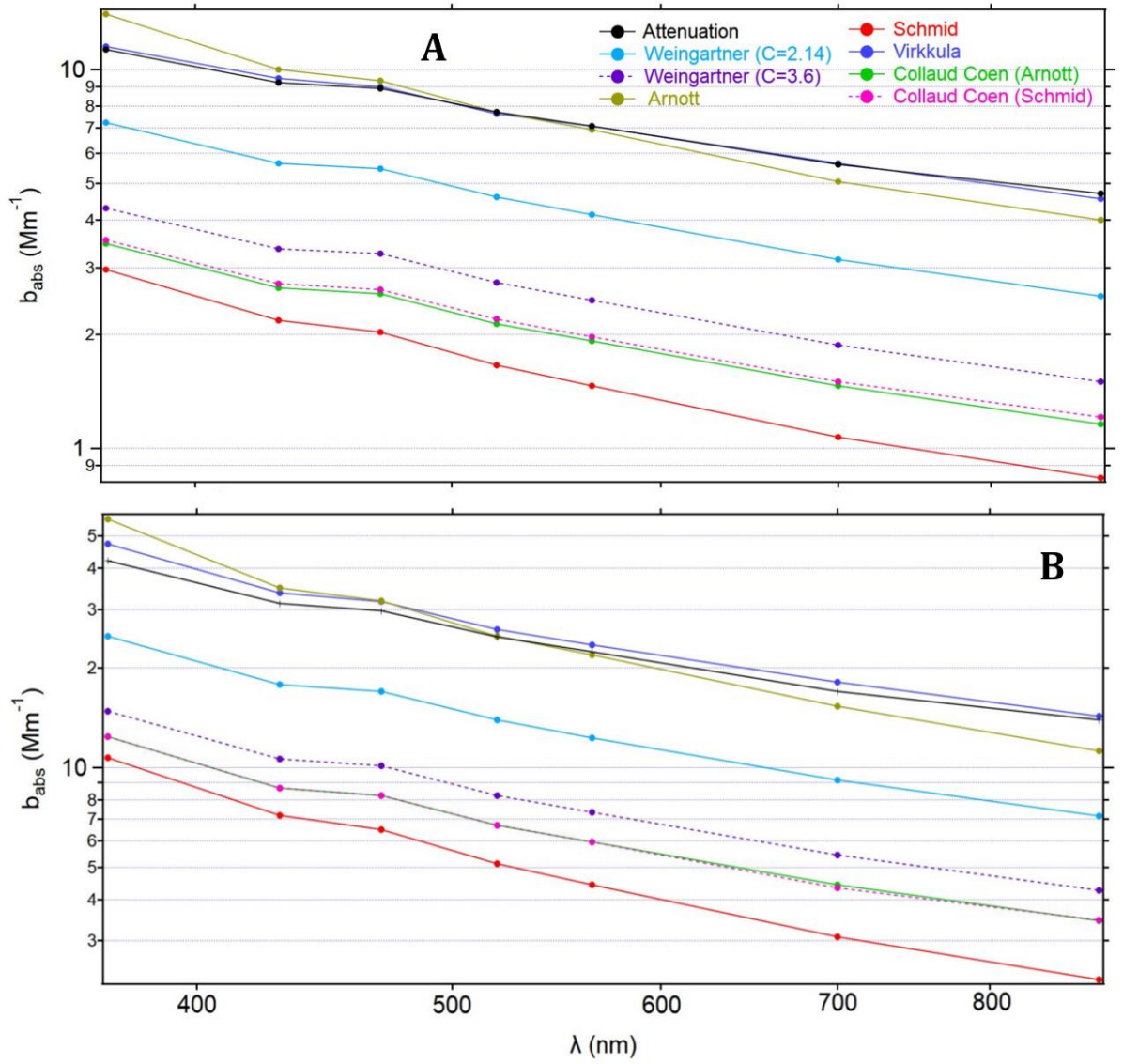


Figure 3.5: Logarithm of the attenuation coefficient and absorption coefficients calculated using each of the correction schemes as a function of the logarithm of the wavelength for A) the MAM period of 2014 and B) the ASO period of 2014.

Absorption Ångström exponent (AAE)

When comparing the AAE obtained from uncorrected absorption coefficient values with that obtained from corrected values, some corrections drastically changed the AAE from its uncorrected value, which complicates assessing the possible aerosol composition. The results for the AAE calculated from each correction for the MAM and ASO periods are shown in Figure 3.6A and 3.6B, respectively. The correction schemes of Arnott et al. (2005) and Schmid et al. (2006) yielded the greatest changes in AAE, with increases of 34% and 29% for the MAM period and 30% and 28% for the ASO period, respectively. The Virkkula et al. (2007) correction scheme yielded little change in the AAE (6% for the MAM period and 3% for the ASO period), and the Weingartner et al. (2003) and Collaud Coen et al. (2010) based on Schmid et al. (2006) schemes resulted only in a slight increase: 13% and 14% for the MAM period and 9% and 12% for the ASO period, respectively. The Arnott et al. (2005) and the Schmid et al. (2006) are wavelength dependent corrections and this will affect the AAE. While the Collaud Coen et al. (2010) corrections are also wavelength dependent, they purposely tried not to modify the AAE much with their algorithm. Large modifications of the AAE are undesired because of the lack of reference instruments to measure this property, as well as some theoretical considerations about the low relative importance of the factors that could alter this wavelength dependence described in Collaud Coen et al. (2010). A similar result was reported in Collaud Coen et al. 2010, where they saw that the corrections from Arnott et al. 2005 and Schmid et al. 2006 produced significant changes in the AAE.

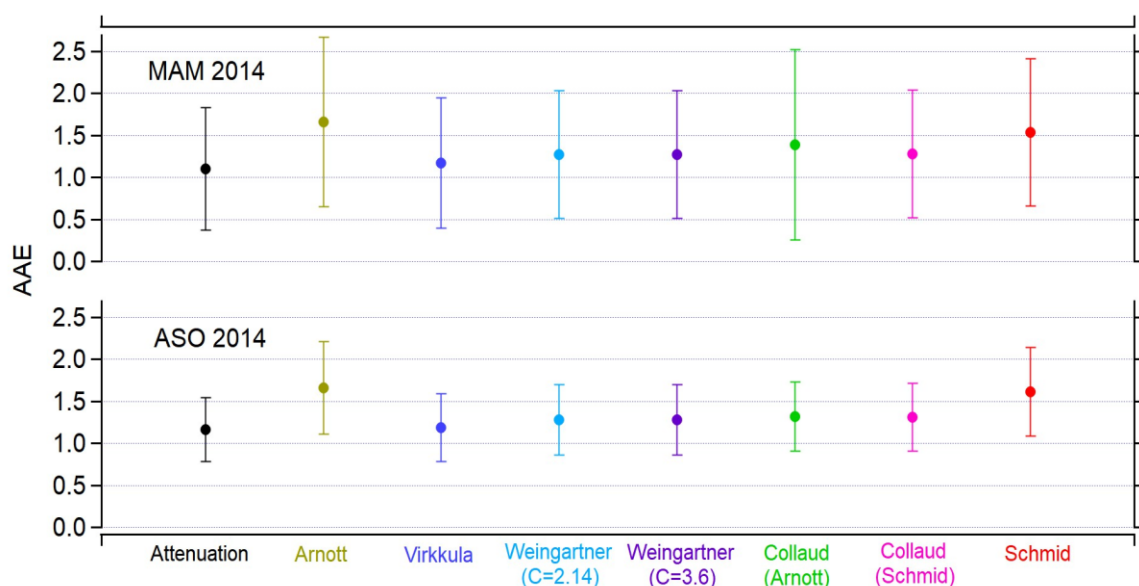


Figure 3.6: Absorption Ångström exponent (AAE) determined from the linear fit of the logarithm on the absorption coefficient as a function of the logarithm on the wavelength for corrected and uncorrected absorption coefficients determined with the Aethalometer. Top half of the graph corresponds to the MAM period, and bottom half to the ASO period of 2014.

The standard deviation for the AAE of all corrections was larger in the MAM period than the ASO period, opposite to what was seen in the absorption coefficient values. A possible explanation for this is that during the MAM period, when the absorption coefficients were lower, there is a mix of aerosol sources, being them urban, vegetation, and biomass burning, resulting in a larger range of AAE values, while at the ASO period, when concentrations are larger, it is mainly biomass burning, resulting in a narrower range of AAE values.

Mass absorption cross section

The mass absorption cross section (MAC) is defined as the absorption coefficient per unit mass at a given wavelength, and is determined by the slope of the regression line of absorption coefficient vs. rBC mass concentration, forced through the origin (Fig. 3.7). Figure 3.7 shows that most absorption coefficients have a large amount of spread when plotted as a function of the rBC mass concentration. One of the reasons for this could be due to the natural variability that exists in filter-based instruments, which can be accentuated by some of the corrections. Another possible explanation is that there could be a mix of aerosol sources, which will all have different MACs. The two corrections from Collaud Coen et al. (2010) and the one from Schmid et al. (2006), which were the most aggressive, resulted in the least amount of spread. This can also be seen in the standard deviations presented in Figures 3.8A and 3.8B.

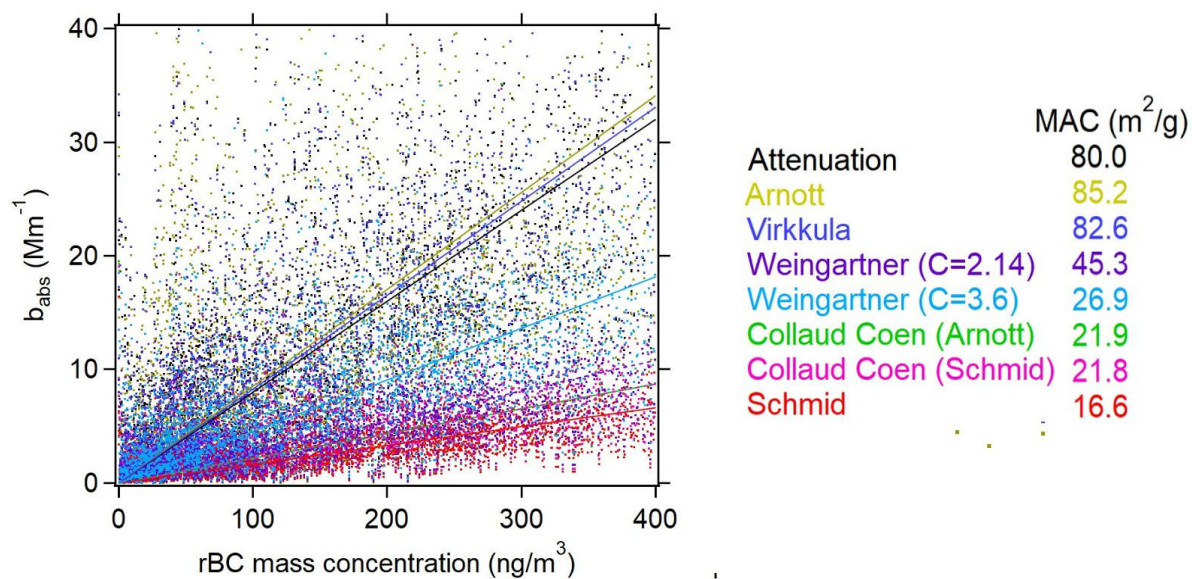


Figure 3.7: Absorption coefficient at 520 nm as a function of rBC mass concentration determined by the SP2. MAC values at 520 nm are calculated from the slopes of the regression lines of absorption coefficient against rBC mass concentration, forced through the origin.

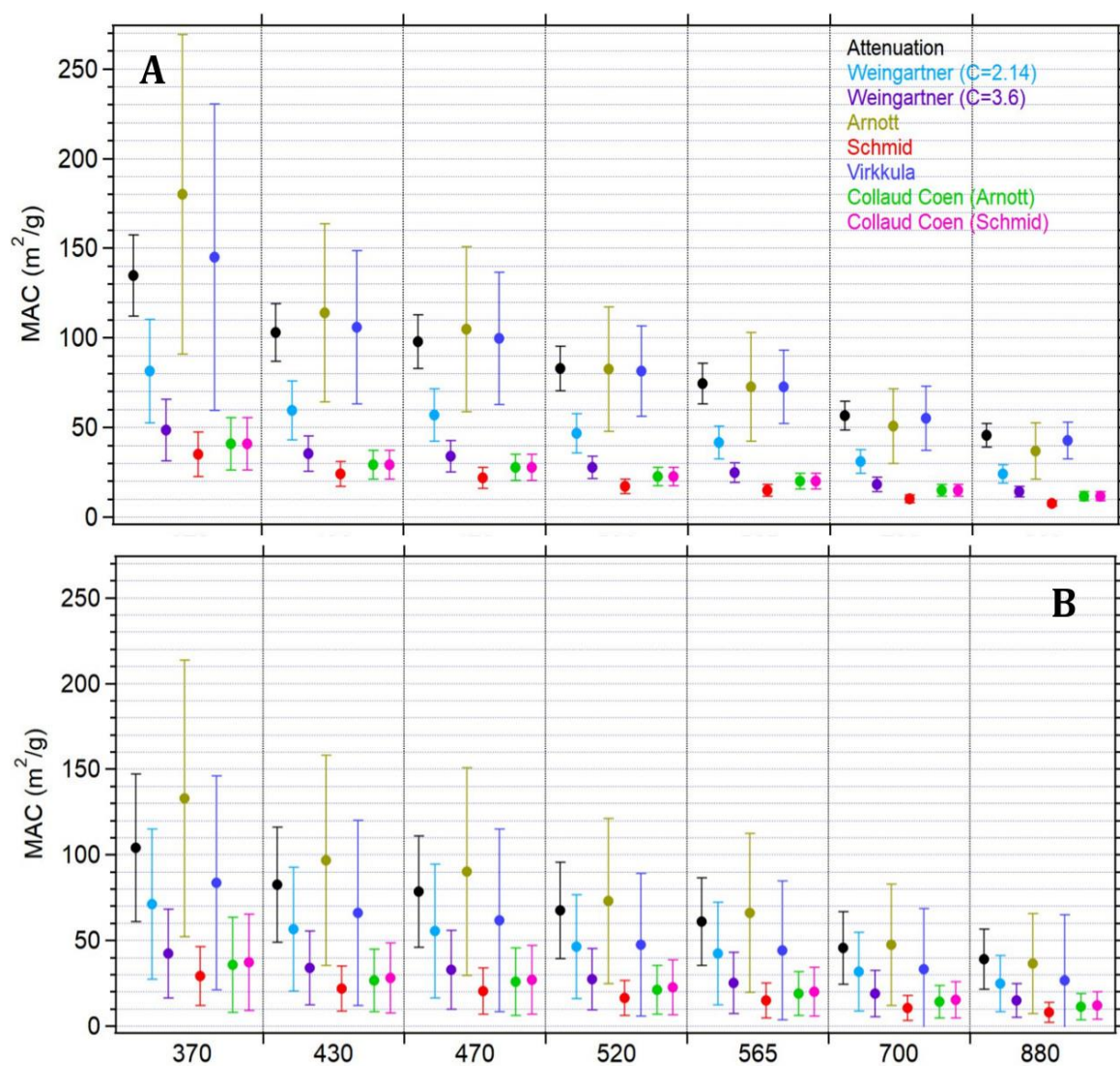


Figure 3.8: Mass absorption cross-section (MAC) as a function of wavelength for A) the MAM period of 2014 and B) ASO period of 2014 calculated from the uncorrected and corrected absorption coefficients determined with the Aethalometer and the rBC mass concentration determined with the SP2.

Values for the MAC were generally higher for the ASO period than for the MAM period, but most of the correction schemes did not yield much difference in the MACs between periods. Figures 3.8A and 3.8B show the MAC calculated for every wavelength for uncorrected and corrected absorption coefficient values for the MAM and ASO periods, respectively, and Figures 3.9A and 3.9B show the natural logarithm of the MAC as a function of the natural logarithm of the wavelength for the MAM and ASO periods, respectively. As could be seen for the absorption coefficient values, the correction from Arnott et al. (2005) exhibited the strongest dependence on wavelength, and the higher spread in values, as well as giving some corrected values above the range of the uncorrected values. The correction from Schmid et al. (2006) generally resulted in the lowest MAC values for both periods at all wavelengths.

Literature values for the MAC of BC at 550 nm determined using a Particle Soot Absorption Photometer (PSAP) and an EC/OC thermo-optical technique range from 10.5 to 15.1 m²/g (Nordmann et al., 2013), with values for coated BC particles being about 1.5 times greater than for uncoated particles (Flanner, et al., 2007), resulting in a range from 10.5 to 22.7 m²/g for data sets that have anthropogenic and biomass burning influence. Most of the correction schemes applied to the GoAmazon data yielded values that are considerably greater than this range; only the two corrections by Collaud Coen et al. (2010) and that of Schmid et al. (2006) gave results that are in the expected range based on previous studies on thermal techniques. This suggests that all other corrections, as well as the uncorrected absorption coefficient values, are overestimated.

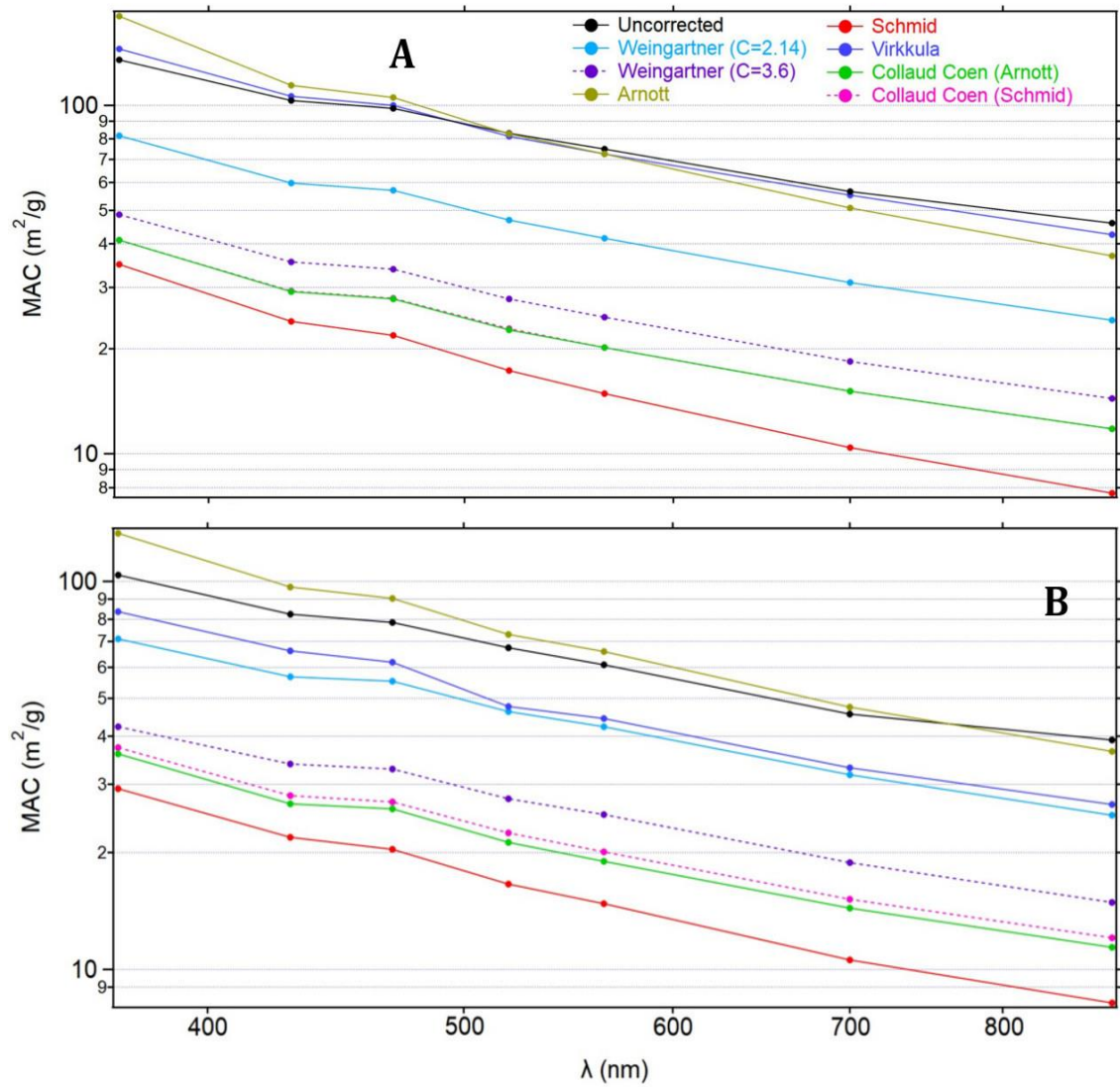


Figure 3.9: Logarithm of the mass absorption cross-section (MAC) as a function of the logarithm of the wavelength for A) the MAM period of 2014 and B) the ASO period of 2014 calculated from the uncorrected and corrected absorption coefficients determined with the Aethalometer and the rBC mass concentration determined with the SP2.

Conclusion

Several correction schemes for the Aethalometer were employed and compared using data from the GoAmazon 2014/15 field project. These schemes exhibited large differences in the absorption coefficient, MAC and AAE. Some resulted in little change, while others reduced the absorption coefficient by a factor of nearly 5. While there was an evident difference in the absorption coefficient values for both periods, differences in the corrections between periods were not found, suggesting these corrections are not source or seasonal dependent. Only three of the correction schemes resulted in calculated MAC values that were in the range reported in the literature: the Schmid et al. (2006) and the two of Collaud Coen et al. (2010). The different correction schemes resulted in increases in the MAC at 520 nm up to a factor of 4.4. The AAE was modified by all corrections. Corrections from Arnott et al. (2005) and Schmid et al. (2006) resulted in the largest differences from the uncorrected, with a difference of 0.56 and 0.51-0.53, respectively, and corrections from Weingartner et al. (2003) and Collaud Coen et al. (2010) based on Schmid et al. (2003) only caused about 0.18-0.21 units difference. Like in the case of the absorption coefficient, after applying the corrections schemes, the changes in the MAC and AAE were about the same for both periods, also suggesting that the corrections are not seasonal dependent. The correction scheme from Collaud Coen et al. (2010) based on the correction from Schmid et al. (2006) is the correction that performed best, as it reduced the absorption coefficient to a reasonable range, it produced MAC values inside the range seen in other studies, and it only slightly modified the AAE from its original value.

Concluding Remarks

This study presents the effects of the two most light absorbing aerosols on the environment (black carbon and mineral dust), particularly on the Earth's radiative balance. These effects were studied through the indirect effect of aerosols in clouds, cloud formation processes, and measurements of the concentration of light absorbing aerosols. Results of this study supports the findings that light absorbing aerosols can absorb radiation and heat the atmosphere, but the quantification of this effect is still a challenge. Also, results show that mineral dust particles can act as a cloud condensation nuclei and have a counteracting effect by creating more cloud droplets, thus increasing the cloud's surface area and blocking the incoming solar radiation and having a net cooling effect.

The results presented in Chapter 1 with the data obtained from several sampling campaigns at Pico del Este in El Yunque National Forest shows that African dust particles can act as cloud condensation nuclei and alter cloud properties. Through the combination of optical properties and air mass trajectory analysis periods of high and low dust influence were identified. Periods of high dust influence had a larger amount of cloud droplets as well as of liquid water content than periods of low dust influence, but similar droplet sizes. This suggests that mineral dust will have an indirect effect in the radiative balance by scattering radiation as a cloud droplet but will not have a negative impact on the lifetime of the cloud. It was also found that meteorology and air mass history play an important role in cloud formation on this site.

The effect of mineral dust on the nutrient and water budget of a tropical montane cloud forest was presented on Chapter 2. The water and nutrient deposition through fog and rainwater with emphasis in periods of high and low dust influence was studied. Results suggest that water deposition through rain is more important for the water budget than fog, but nutrient deposition through fog is more important than nutrient deposition through rain. Also, results suggest that there are more important factors controlling cloud formation processes rather than aerosol type, such as meteorology. Nutrient deposition on high dust influenced samples was greater than in low dust influenced samples, suggesting that dust is an important nutrient source for this ecosystem.

Chapter 3 presents a study where different corrections schemes for measuring absorption coefficient using an Aethalometer are tested using a data set collected in the GoAmazon 2014/15 field campaign in the Amazon rainforest. The results point out the wide differences yielded by the different correction schemes available for this technique and how they affect the mass absorption cross section estimates. The mass absorption cross section of an aerosol is a fundamental property to be considered when estimating its effect on the Earth's radiative balance by radiation transfer models, which requires accurate measurements to reduce model uncertainty and have a clearer picture of its effect.

Through this work it was shown that both mineral dust and black carbon influence Earth's radiative budget. While mineral dust can interact directly with radiation, it was shown that it can also indirectly interact with it through cloud droplets and reduce the amount of radiation that reaches the surface. However, we did not find clear evidence of it

hindering precipitation, but it does serve as a nutrient source for ecosystems. In the case of black carbon, while there is consensus about its light absorbing characteristics, there is still the need for accurate estimates of its absorbing potential. The use of correction schemes for a popular techniques gives access to big data sets collected over the years at diverse environments around the world, but the differences in these corrections, as well as the requisites for their implementation, are still challenging.

Further longer-term studies are required to keep reducing the uncertainties of light absorbing particles in our changing environment.

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