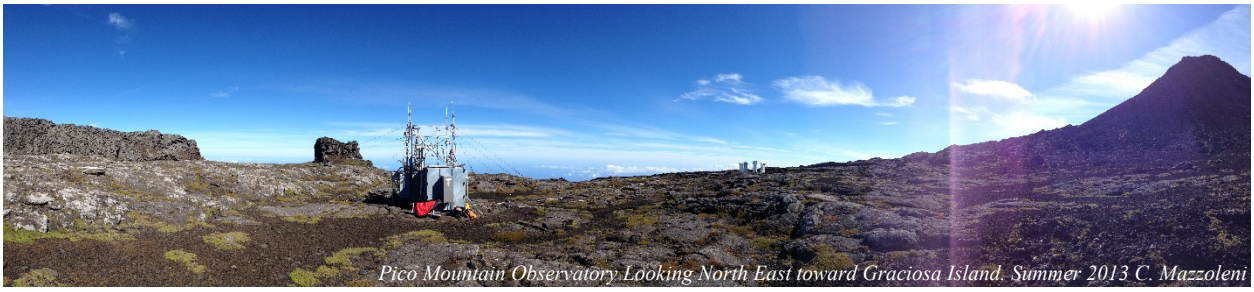
The Radiative Role of Free Tropospheric Aerosols and Marine Clouds over the Central North Atlantic



Pico Mountain Observatory Looking North East toward Graciosa Island. Summer 2013 C. Mazzoleni

Final Report

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Abstract

The scientific scope of the project was to exploit the unique location of the Pico Mountain Observatory (PMO) located in the summit caldera of the Pico Volcano in Pico Island in the Azores, for atmospheric studies. The observatory, located at 2225m a.s.l., typically samples free tropospheric aerosols laying above the marine low-level clouds and long-range transported from North America. The broad purpose of this research was to provide the scientific community with a better understanding of fundamental physical processes governing the effects of aerosols on radiative forcing and climate; with the ultimate goal of improving our abilities to understand past climate and to predict future changes through numerical models. The project was 'exploratory' in nature, with the plan to demonstrate the feasibility of deploying for the first time, an extensive aerosol research package at PMO. One of the primary activities was to test the deployment of these instruments at the site, to collect data during the 2012 summer season, and to further develop the infrastructure and the knowledge for performing novel research at PMO in follow-up longer-term aerosol-cloud studies. In the future, PMO could provide an elevated research outpost to support the renewed DOE effort in the Azores that was intensified in 2013 with the opening of the new sea-level ARM-DOE Eastern North Atlantic permanent facility at Graciosa Island.

During the project period, extensive new data sets were collected for the planned 2012 season. Thanks to other synergistic activities and opportunities, data collection was then successfully extended to 2013 and 2014. Highlights of the scientific findings during this project include: **a)** biomass burning contribute significantly to the aerosol loading in the North Atlantic free troposphere; however, long-range transported black carbon concentrations decreased substantially in the last decade. **b)** Single black carbon particles – analyzed off-line at the electron microscope – were often very compacted, suggesting cloud processing and exhibiting different optical properties from fresh emissions. In addition, black carbon was found to be sometimes mixed with mineral dust, affecting its optical properties and potential forcing. **c)** Some aerosols collected at PMO acted as ice nuclei, potentially contributing to cirrus cloud formation during their transport in the upper free troposphere. Identified good ice nuclei were often mineral dust particles. **d)** The free tropospheric aerosols studied at PMO have relevance to low level marine clouds due, for example, to synoptic subsidence entraining free tropospheric aerosols into the marine boundary layer. This has potentially large consequences on cloud condensation nuclei concentrations and compositions in the marine boundary layer; therefore, having an effect on the marine stratus clouds, with potentially important repercussions on the radiative forcing.

The scientific products of this project currently include contributions to two papers published in the Nature Publishing group (Nature Communications and Scientific Reports), one paper under revision for Atmospheric Chemistry and Physics, one in review in Geophysical Research Letters and one recently submitted to Atmospheric Chemistry and Physics Discussion. In addition, four manuscripts are in advanced state of preparation. Finally, twenty-eight presentations were given at international conferences, workshops and seminars.

Introduction

Objectives

The scientific scope of the project was to exploit the unique location of the Pico Mountain Observatory (PMO) in the Azores (2225m a.s.l.), to improve the scientific understanding of aerosol lifecycles and aerosol-cloud interactions and the role that these processes have on radiative balance and climate. The scientific questions that motivated the project are:

1) What are the optical properties of long-range transported aerosols over the Atlantic?
2) How do these properties change/evolve during transport and aging?
3) How do the aerosol radiative properties depend upon source region and emission types?
4) What is the direct radiative effect of free-tropospheric aerosols in clear sky and above marine clouds in the North Atlantic?

The broad goal of the research was to provide climate models with more accurate parameterizations while enhancing the understanding of fundamental physical processes governing aerosol properties and interactions with marine clouds. The project was 'exploratory' in nature, with the plan to demonstrate the feasibility of deploying for the first time an extensive aerosol research package at the PMO and collecting data aimed at gaining some preliminary insights on the scientific questions posed above. The primary objective was to test the deployment of these instruments at the site, and to further develop the infrastructure and the knowledge for performing novel research at PMO in follow-up longer-term aerosol-cloud studies. The aerosol instrumentation installed at PMO included an optical particle counter, a seven-wavelength aethalometer, an aerosol sampler for electron microscopy analysis and a three-wavelength nephelometer. The nephelometer and the sampler have been installed at the station in summer of 2012, as a major activity of this project. These instruments collected data on particle concentration, and optical properties of free tropospheric aerosol and allowed collecting hundreds of samples for morphological and chemical analysis of aerosols. The instrumentation has been operating during most of the summer season of 2012, 2013 and 2014.

This pilot project lays the foundation for future synergistic aerosol and radiation research activities with the observations that take place at the new permanent ARM site at the nearby Graciosa Island, the Eastern North Atlantic (ENA) facility in operation since fall of 2013.

Project Period

The project activities started in September of 2011 and ended in September of 2012, with a no-cost extension continuing the project until September of 2014.

Originally Proposed Specific Objectives were to:

G1) Purchase and install at the Pico Mountain Observatory a 3-wavelength nephelometer to measure aerosol total and backward scattering coefficients and install a filter sampler for aerosol collection for electron microscope analysis.

G2) Measure aerosol scattering and continue past measurements of gaseous species, black carbon, and aerosol size distribution in summer of 2012.

G3) Analyze data available and compare to previous seasons to study trends and variability.

G4) Mine satellite measurements and data from the Graciosa AMF 2009-2010 deployment to explore the statistical characteristics of local marine clouds and aerosols.

G5) Use retroplume analysis, in combination with CO, O_3 and NMHC measurements, to study the origin and age of the sampled air-masses.

G6) Use the SBDART atmospheric radiative transfer model to investigate the direct radiative effect of aerosols above clouds and in clear sky by utilizing the 2012 dataset.

A succinct summary of the outcomes of the project with respect to the original objectives is next:
G1 and G2) A three-wavelength nephelometer (American Ecotech Aurora3000) was purchased in winter of 2011 and shipped to the Azores. A new dedicated inlet was installed at PMO in spring of 2012 and the instrument was deployed at the site starting in mid-June of 2012. The station was closed at the end of October of 2012 for the winter. The station was reopened in April of 2013 and the nephelometer continued normal operation until mid-June, when the instrument developed an issue with the backscattering arm. Scattering data are therefore sparse between mid-June of 2013 and the beginning of September of 2013 due to several attempts to troubleshoot the problem with the backscattering measurements and the difficulty to perform the repair on-site without the possibility for direct technical support. In August of 2013 it was decided to remove the backscattering arm and to continue collecting only scattering data until the station winter closure in October of 2013. The nephelometer was removed from the station and brought back to the US. During winter of 2014 the instrument remained at Ecotech for repair. After the instrument came back from the manufacturer, the instrument was brought back to PMO for the summer season of 2014 and started operation in April of 2014 until the end of the project in fall. It was later discovered that the backscattering arm was still not operating correctly, so only scattering data are available for 2014[2]. To summarize, despite the unfortunate issues with the backscattering arm in 2013 and 2014, we have a full nephelometer dataset (including backscattering data) for the initially proposed 2012 season, and we obtained good total scattering data for long periods during the two additional 2013 and 2014 seasons. Some example of the analysis of these data and the outcomes will be presented later in this report.

The original optical particle sizer installed at the site in 2011 (not part of this project) was damaged in the harsh winter conditions in 2012. Therefore, in summer of 2012 a 2 channel optical particle counter was installed in its place and operated in 2012, 2013 and part of 2014.

Nephelometer and particle count data collected in 2012 are an integral part of a recent paper that was published on the Atmospheric Chemistry and Physics Discussion and that we are currently revising, following favorable reviews for final publication (Dzepina et al. 2014).

A custom made sequential particle sampler was installed in 2012 for the collection of membranes for scanning electron microscopy analysis. During winter of 2013 a new improved sampler was developed at Michigan Tech. The new sampler allows to collect a membrane for scanning electron microscopy and a grid for transmission electron microscopy simultaneously and can run for about 5 days autonomously to collect 5 samples (typically one-day long each). From 2012 to 2014 we collected more than 200 membranes and 160 grids.

Analysis of a selected number of samples collected in 2012 for electron microscopy is the subject of a recent paper submitted to Geophysical Research Letters and currently under review (China et al. 2014b). Also ***polluted mineral dust samples from PMO analyzed at the electron microscope have been used in a paper submitted very recently (Scarnato et al. 2014).***

[2] We are having an on-going discussion with the company on the reasons for the backscattering arm failures and potential solutions for future possible deployments at the station.

G3) The aethalometer is the instrument that has the longest data record at PMO. It provides black carbon mass and iron-containing dust concentrations. Together with the nephlometer, the aethalometer is used to calculate the aerosol absorption and the single scattering albedo. ***The Black carbon data trends since 2001 to 2014 have been analyzed and are being summarized in a paper under preparation (Kumar et al. 2015).*** Some selected results will be presented below. CO and O_3 data have also been collected; however CO data for the 2014 season are sparse due to a computer failure. Archived ***gaseous and BC data are also being analyzed for a climatology paper that is under preparation (Zhang et al. 2015)***. Finally ***non-methane hydrocarbons data have also been analyzed and a manuscript is in preparation discussing the results (Helmig et al. 2015)***.

G4) Several satellite data (e.g.; from CALIPSO and MODIS) have been collected and plotted for quick reference for data interpretation. The satellite plots are available on our password-protected project wiki for use by PIs, students and collaborators.

Since the beginning of the project, a new DOE-ARM permanent facility was installed at sea level in Graciosa Island (Azores), the Eastern North Atlantic (ENA) station. The station begun data collection in fall of 2013. As we were able to collect data also in summer of 2014, we have now a full season for comparison of simultaneous aerosol measurements from ENA and PMO. As the AFM deployment during the period of the CAP-MBL study did not overlap with the PMO deployment during this project, we found the ENA data to be more relevant to this project and an example of ENA and PMO data comparison is reported later in this report and will be the subject of further analysis and publication.

G5) A full set of retroplumes using the Lagrangian FLEXPART numerical model was developed for 2012 and 2013 and is currently under processing for 2014. In addition, retroplumes were generated for the past years (since 2001) to allow for further mining of archived data. Several simulation products (e.g.; plots of residence time vs. latitude and longitude, residence time vs. altitude, residence time count by source region and CO age spectra) have also been developed and uploaded on the team wiki. The products are available on our project wiki for consultation during data interpretation and for publications. Some of these products have been used in most of our manuscripts submitted or in preparation.

G6) Direct radiative forcing calculations have been performed in a recent manuscript that is currently under review (China et al. 2014b); although not using the SBDART model. We have in plan to use the SBDART or similar models in the near future exploiting the data recently collected.

Following is a description of Pico Mountain Observatory and field and data analysis activities during the project. We then discuss some science highlights and preliminary results, and conclude with lists of products (outcomes) from this project.

Pico Mountain Observatory

Pico Mountain Observatory (PMO)[3] is located in the North Atlantic (Fig. 1), far from persistent local sources, at an elevation that allows sampling free tropospheric air masses (Kleissl et al. 2007, Remillard et al. 2012). Pico is a small island (447 km^2) with a prominent steep inactive volcanic cone. The volcano top is by far the highest elevation point in a radius of several

[3] http://instaar.colorado.edu/pico/

hundreds of miles and is the tallest mountain in Portugal and part of Pico's Natural Park, the largest Natural Park in the Azores. Total island population is rather low (~15,000) and is concentrated near sea level. Figure 1 is a composite of images showing the location of the Azores (panel a), situated in the Central North Atlantic, the location of Pico Island with respect to Graciosa Island (panel b) where the permanent ENA ARM facility is located, and PMO (inset of panel c). PMO was established by the late Dr. Richard Honrath[4] in 2001 (Honrath et al. 2004), and Michigan Tech, in close collaboration with the University of Colorado and the University of the Azores, has lead the activities since.

The Observatory

PMO is located near the northern cliff of the summit caldera at an altitude of 2225 m (Fig. 1). The altitude is well into the lower free troposphere during summertime, average marine boundary layer height was found ~ 1200 m by (Kleissl et al. 2007), while (Remillard et al. 2012) found somewhat higher values during CAP-MBL (~1500m), but still much lower than the mountain top. The nearest road ends at an altitude of ~ 1200 m. Most instruments presently running at PMO are automated and remotely controlled. Electrical power is provided via a cable reaching the station from the Casa da Montanha, a local visitor center at the end of the road, 1000 m below PMO.

The value of PMO stems from the fact that this is the only permanent mountaintop monitoring station in the mid-latitude Eastern North Atlantic that is typically above the marine boundary layer and often receives air characteristic of the lower free troposphere (Fig. 2). Airmasses are often transported from North America, the Arctic and the Ocean and less frequently from Europe and North Africa, due to the prevailing synoptic winds. Due to the location of PMO in the Atlantic, the marginal influence of local sources and the elevation of the station, the measurements performed at the station have relevance to larger spatial scales than typical point-measurement locations and can be used for satellite comparison, models input and/or validation and comparison with ENA data. Initial focus at PMO was on gaseous species (*e.g.*; non-methane hydrocarbons, O_3, CO, NO_{xy},). Measurements have continued since 2001 mostly during the summer seasons. The only aerosol measurement carried out at PMO since 2001, was black carbon mass equivalent concentrations (BC_{eq}) using a 7-wavelength (AE31 Magee) Aethalometer. In the summer of 2010 an ARM-DOE pilot study was conducted to measure radiation and aerosol size distribution. In 2012, new aerosol instrumentation and samplers were installed at PMO as part of this project; data collection started in May 2012 and ended in October of 2014. The set-up included a 3-wavelength nephelometer to measure aerosol scattering and backscattering coefficients, four high volume samplers for the collection of aerosol for off-line chemical analysis (installed as part of an NSF funded effort), a sequential sampler to collect aerosols for electron microscopy, and a 2-channel optical particle counter, an economical pyranometer was also added in 2013 to monitor the solar radiation and screen for cloudy vs. clear-sky periods.

[4] Deceased, spring 2009

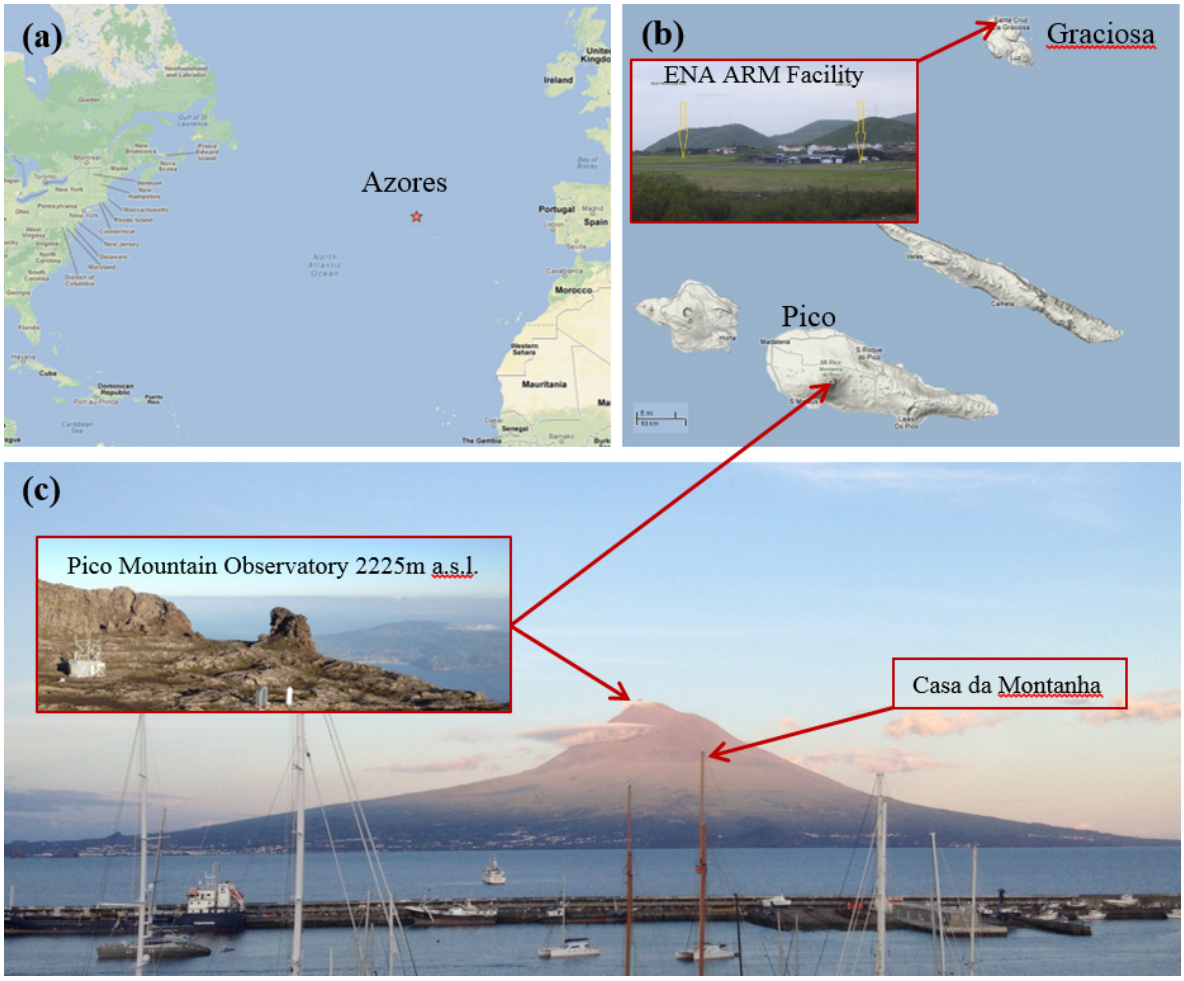

Figure 1. Panel (a): Azores location in the North Atlantic. **Panel (b):** Map showing Pico and Graciosa Islands. In the scale the upward ticks represent 5 miles, the downward ticks represent 10 km; the inset is a picture of the ENA ARM Facility (https://www.arm.gov/sites/ena). **Panel (c):** Picture of Pico Mountain from Horta. The inset is a picture of Pico Mountain Observatory, located in the summit caldera of the Pico Volcano at 2225 m a.s.l. Evident is the boundary layer well below the station elevation. Indicated is also the location of the Casa da Montanha (1225 m a.s.l.) where the paved road ends, and the hiking trail to the Observatory begins.

Figure 2. Left, an aerial view of Pico Mountain showing the stratification of the atmosphere. **Right,** a picture of the station also showing the evident decoupling between the local atmosphere and the atmosphere below.

Activities

New instrumentation acquisition, development and deployment

A new three-wavelength nepehlometer (Ecotech Aurora 3000) was ordered in the fall of 2011 and was delivered to MTU in February of 2012. The instrument was calibrated and tested in our Environmental Optics Laboratory (EOL)[5] at MTU, where preliminary comparisons have been performed with a multi-wavelength integrated photoacousitc and nephelometer instrument (built at MTU in collaboration with the University of Nevada, Reno) and other ancillary measurements such as aerosol size distributions from an SMPS, particle counts from condensation particle counters, BC mass from a seven-wavelength aethalometer, and aerosol optical size distribution with an intracavity laser optical sizer (Figure 3). An LabView code was developed to collect the data from the nephelometer, calculate averages and standard deviations and plot several parameters; the code has been used to remotely control the instrument and to collect data and store them on a local HD synced via internet, to a cloud storage volume, remotely accessible to the project PIs for download, archival, further processing and analysis.

The nephelometer was shipped via air-cargo to the Azores in spring of 2012 and installed at the station in late spring. A calibration set-up was also installed, but the CO_2 cylinder needed for the calibration was brought up at the station only later in the season due to the unavailability of the helicopter from the local air force (see later). A smaller cylinder (~80 lb) was ordered and brought up to the station by MTU technician Mike Dziobak, using a cargo backpack. A calibration was performed immediately; the instrument was found to be very stable as no significant change in the calibration slope was detected since the initial calibration.

A sequential sampler was developed at MTU in 2010 for the Carbonaceous Aerosols and Radiative Effects Study (CARES), CA. The sequential sampler was also shipped via air-cargo to the Azores in April of 2012 and reached the Terceira Island at the beginning of May of 2012. The sampler was installed in summer of 2012 and was used for the collections of filters and/or grids for scanning electron microscopy (SEM) and/or transmission electron microscopy (TEM) analysis. In spring 2013 a new sampler was developed to minimize particle losses and allow for better remote control (Figure 4). The new sampler was installed at PMO in summer of 2013.

Figure 3. The set-up for the Aurora 3000 nephelometer in the Environmental Optics Laboratory at MTU during the calibration/test sessions in March of 2012 (left panel). The nephelometer installed inside the PMO in summer of 2012 (middle panel). Right panel: custom-made Lab-View code developed for acquiring the scattering, backscattering, temperatures, RH and pressure data from the Aurora 3000. The software collects data every 10 seconds and calculates 10-second averages and standard deviations for plotting and data archival. The solid lines represent 10-second averages, while the dashed lines represent the standard deviations. The blue line represents data (in inverse megameters) collected at 450 nm, the green at 525 nm and the red at 635 nm.

[5] https://sites.google.com/a/mtu.edu/eol/

Figure 4. Left: old aerosol sampler operated at PMO in summer of 2012. **Center:** new sampler installed at PMO in summer of 2013 and operating at PMO since then. **Right:** picture of the inside of the new sampler and custom-made stainless steel manifold of the new sampler designed to minimize aerosol losses and to accommodate up to 12 sample lines. The new sampler allows simultaneous collection of membranes for scanning electron microscopy and grids for transmission electron microscopy.

In Figure 5, we show some pictures of the aerosol inlets installed in spring of 2012. The inlets are heated to reduce the possibility of water making it through the lines to the instruments and to reduce ice formation early in the season.

Figure 5. Optical particle counter, aerosol sampler and nephelometer inlets (left) and a zoomed in picture of the heated sampler and nephlometer inlets installed at the station during year 1 of this project (summer of 2012).

Field deployments

In Table 1 we summarize the personnel presence in Pico during the 2012, 2013 and 2014 season as supported by this and a concurrent NSF project (the table reports only the personnel directly related to this DOE project).

Table 1: Field deployments at the Pico Mountain Observatory in 2012, 2013 and 2014.

Personnel	2012	2013	2014
M. Dziobak (MTU)	27 April - 1 June 18 September - 26 October	3 April - June 6 25 September - 17 October	19 April - 1 June 10 September - 21 October
C. Mazzoleni (MTU)	5 May - 14 June 15 July - 2 August	1 July - 28 July	23 April - 7 May 8 June - 13 July
J. Hueber (CU)	11 June - 21 July	10 April - 22 April 28 July - 11 August	18 April - 30 April
S. Kumar (MTU)	24 July - 6 September	-	-
H. Helmig (CU)	-	16 June - 29 June	21 September - 28 September
K. Wright (MTU)	-	15 July - 24 August	9 July - 17 September

Team meetings

Two 3-day-long team meetings took place during the project, one in 2012 and a second in 2014 at Michigan Technological University. In 2013 a virtual team meeting was carried out using conference call applications. Participants included all the MTU personnel, D. Helmig from CU and P. Fialho from the University of the Azores, among other interested parties.

Challenges and actions taken to overcome them

Instrument transportation to the site

At the time of the proposal submission it was understood that the Portuguese air-force would have provided, free of charge, helicopter lifts for the heavier material up to the top of Pico Mountain. This has been the case each previous year since the station was established in 2001. The air-force was performing trainings on the volcano and helped with the material lift as part of the training operation, at no cost until 2011. Unfortunately, by the time the project was funded, due to the economic downturn, the Portuguese authorities stopped any regular training activities on the volcano; therefore not being able to provide any help for the lifting of the new instrumentation and material to the top. PI's, technicians, students and collaborators worked together to overcome this challenge by carrying most of the instrumentation and components at the station using cargo backpacks. For the heavier material, such as the 4 high volume samplers (~40 kg each), we hired local mountain guides for the task (Figure 6).

Figure 6. Left: Mountain guide Nilton Nunes carrying one of the high volume samplers at the station (summer of 2012). **Center:** Collaborator Lynn Mazzoleni carrying material (including stainless steel tubing) for the new nepehlometer inlet. **Right:** PI Claudio mazzoleni carrying the 3-wavelength nephelometer.

Weather conditions

Weather conditions are often harsh in late winter due to the relatively mild temperatures (meaning temperatures close to, but not much below, the freezing point) and the saturated conditions that result in severe riming, often damaging the station structure that requires small repairs at the beginning of each season. Figure 7 (left panel) shows an example of the modest but still challenging riming conditions found after the station had already been opened in April of 2012 (winter riming is typically much more severe, often engulfing the entire station as seen in the right panel of Figure 7). In addition to the difficulties to operate the station in early season, the ice-covered rocks make the hike to the station more difficult.

Figure 7: Pico Mountain Observatory in late spring and winter riming conditions.

The weather conditions have been very wet and windy during a large fraction of the summer season of 2012 and the second part of the summer season of 2014, while it has been quite favorable in summer of 2013. For most of the early summer of 2012 the weather was wet, windy and cold making the new instrument installation more challenging than expected. In late summer of 2012 the Azores were tangentially touched by hurricane Nadine that produced tropical storm winds on the islands for several days. The high winds imparted some damage to the station and made aerosol sampling quite challenging for most of the late season. In mid-late summer of 2014 a severe lightning thunderstorm affected the station operations as discussed in the next sub-section.

Station Power

The power to station is provided by a high-voltage cable that lays on the flank of the mountain starting from the Casa da Montanha and reaching the station 1000 m above it by means of two transformers and 10 junction boxes. The power inside the PMO is conditioned using a line conditioner and a UPS. In summer of 2012 the line conditioner was damaged by bad weather and had to be changed. The power line is protected from lightning strikes by means of two lightning arrestors (one for each conductor) at each junction box and transformers. Seasons 2012 and 2013 were relatively calm from the point of view of the lightning activities; however during July-August of 2014 several lightning hits damaged the power line, requiring the replacement of more than 7 lightning arrestors and some significant cable repair. In addition, during winter of 2014 the cable was damaged at the last section due to strong winds that caused the cable to rub against the rocks severing the cable and requiring the installation of an additional junction box.

Despite, these challenges we were able to operate the station for substantially more time than initially planned for this project.

Internet connection

Internet connection at the station is provided through a wireless link to the village of Madalena. The antenna for the wireless link and a router are mounted on the edge of the summit caldera cliff (Figure 8). The antenna needs to be removed during winter and reinstalled each season in spring. Overall the connection has been reliable in 2012 and 2013 and the first part of the 2014 season. To cover some of the periods when the connection might not be available, in summer of 2014 we installed a backup system that allows a 3G connection through cellular network (Figure 9). The connection has been tested this season and although slower than the wireless connection, it allows a redundant communication avenue that has been critical during some of the 2014 harsh weather conditions and damages that followed the lightning strikes.

Figure 8: Internet link to the village of Madalena, at the cliff edge of the summit caldera of the Pico volcano. The antenna is hanging below the cliff edge.

Figure 9: New redundant 3G cellular network Internet link pointing toward Horta. The antenna (red circle) is installed at the northern corner of the station top structure.

Instrumentation

The main challenge at the station related to instrument maintenance, is the remoteness from maintenance facilities and the difficulty of transporting the instrument to and from the station. Following is a brief summary of some of the major difficulties encountered with instrumentation and the actions taken.

- At the beginning of the 2012 season, the optical particle sizer that has been in operation at the station in 2010 and 2011 was found to be damaged by the cold winter conditions and was beyond reparable. Therefore, we brought to the station an economical 2 channels particle counter and developed a software for data download and storage on a cloud folder for remote analysis.
- In early summer of 2013 the nephelometer backscattering arm broke. This not only invalidated the backscattering data but also initially affected the collection of total scattering data. Several attempts were made at the station to address the issue, including the installation of a new light source and new firmware, but continued performance issues did not allow for the collection of backscattering data. We therefore reverted to the pervious configuration, but with a new firmware that allowed for total scattering data collection until the end of the season. During winter the instrument was brought back to the US for maintenance and recalibration. The instrument was then brought back to Pico and reinstalled at the station in

April of 2014. Despite the repair, the backscattering arm did not operate correctly in 2014; however, total scattering data were collected without being affected.

- The PC that controls the CO and meteo data acquisition had a fatal HD crash in summer of 2014. Tests and actions to attempt to repair the computer were unsuccessful until later in the season (September 2014). In the meantime, a new independent meteostation (Davis Pro Vantage 2) was installed at the station and collected data since August.
- The original sampler for electron microscopy was not performing as desired toward the end of summer of 2012 and was therefore developed a new sampler, as discussed earlier in this document. The new sampler was installed in 2013 and has been operational since.

Despite the several difficulties described above, the actions taken to overcome the problems and the hard work of the entire team allowed to collect an extremely reach and long dataset that can be used to further our understanding of free tropospheric aerosols. A few preliminary results demonstrating the significance and the value of the data and samples collected at PMO will be discussed later in this report.

Personnel involved

C. Mazzoleni managed the project and participated in field activities (see table 1) and directed the data analysis activities.

L. Mazzoleni (not funded by this project) also participated in the field activities as part of an NSF funded project.

Louisa Kramer provided satellite data re-analysis and synthesis plots.

Robert C. Owen provided FLEXPART simulations and student training for new model runs and analysis interpretation.

Sumit Kumar (post doc) was hired as an integral member of this project team and began his research activity at MTU on April 2nd 2012. Dr. Kumar has experience with atmospheric radiative modeling and aerosol measurements, field deployment and data analysis. His role was to participate in the field deployment of the new instrumentation, sample collection, contribution to data analysis, and to perform radiative modeling simulations for the estimation of the radiative forcing of North Atlantic aerosols. Dr. Kumar left the group earlier than planned to move back to India (for family related reasons) in 2013, but he is still working with us on a collaborative basis to complete some of the data analysis and publication.

An MTU PhD student, Bo Zhang, was involved in the research (only partially funded by this project) and performed extensive FLEXPART retroplumes for Pico.

Katja Dzepina, another post doc working with L. Mazzoleni (although not funded by this project) also participated in the field deployment, data and sample collection and analysis.

Two MTU graduate students, funded with NASA fellowships also participated in the project: a) Kendra Wright, PhD student in Physics participated extensively in field work in 2013 and 2014 and is currently working on analyzing some of the data collected during this project. b) Swarup China, PhD student in Atmospheric Sciences analyzed several aerosol samples at the electron microscopes for single particle analysis. He also analyzed samples at Stony Brook University in collaboration with Dr. Daniel Knopf, to study the ice nuclei activities of the free tropospheric aerosols collected at PMO. S. China submitted recently a manuscript to GRL that is currently under review (China et al. 2014b) and is preparing another manuscript on the ice nucleation activities of PMO samples (some of the results are briefly discussed later in this report). S. China graduated in August 2014, but is currently still working with us.

Technician Mike Dziobak was critical to the project success. He participated in field work at Pico since the very first installation of the station back in 2001 and has been opening and closing the station in all three years of this project.

Co-PI Detlev Helmig and technician Jacques Hueber also have a long-term experience at the station and were also critical to the field deployment. They especially maintained the non-methane hydrocarbon instrument during the project and analyzed the data.

Paulo Fialho is a collaborator at the University of the Azores. He also was involved with the station development and operation since its conception in collaboration with the late Richard Honrath. P. Fialho has a key role in the station operation, he maintains (remotely) the internet connection and networking system at the station, he also assure smooth communication with the local authorities to maintain electrical power at the station. P. Fialho is responsible for the aethalometer data, including data processing and analysis.

Scientific collaborations developed during the project

Thanks to connections developed during the 2014 spring DOE ASR meeting, we begun a fruitful collaboration with Dr. Daniel Knopf at Stony Brook University. He kindly accepted to have our student S. China visiting his labs in spring of 2014, to train him and to assist him during the analysis of samples collected in 2013 at PMO for ice nucleation and water activity measurements. S. China is now working on a manuscript discussing the results of this collaborative effort.

We recently begun a collaboration (also sparked during ASR meetings) with Dr. Ryan Moffet from the University of the Pacific to analyze some of the PMO samples collected in 2013 using Scanning Transmission X-ray Microscopy (STXM) at the Lawrence Livermore National Laboratory.

Since 2013 we developed a strong and very effective collaboration with Dr. Barabra Scarnato, Professor at the Naval Postgraduate School in California and currently Visiting Scientist at the University of Oslo. B. Scarnato is an expert in numerical simulation of aerosol optical properties using the Dipole Discrete Approximation (DDA). Samples collected at PMO provided input parameters to the single particle optical calculations for two manuscripts, one currently in review in GRL (China et al. 2014b) and one submitted to ACPD. Some highlights of this research will be presented next.

Highlights of selected scientific results

Following is a succinct summary of some of the more relevant scientific outcomes of this project and includes a discussion of some concrete future plans and collaborations.

Analysis of archived black carbon data

Black carbon concentration data have been collected at PMO using a 7-wavelength aethalometer since 2001 (typically during the summer, but longer period records exist for some years), providing a medium-term database for black carbon equivalent mass concentrations (BC) in the North Atlantic. Summit Kumar (former post-doc under Dr. Mazzoleni's supervision in 2012-2013), Claudio Mazzoleni and Paulo Fialho (University of the Azores and person in charge for the aethalomter data retrieval and processing) are leading an analysis of the archived data and to synthesize them in a manuscripts that is currently in advanced stage of preparation and should be submitted to Atmospheric Chemistry and Physics within a few months.

Examples of the data analysis of the BC decadal dataset available for Pico are shown in Figure 10 and 11. Monthly averages of BC are reported for the twelve years of operation since 2001. A seasonal cycle with a clear peak in BC in mid-summer is evident. The peak is likely related to biomass-burning occurrences in North America and the general eastward and free tropospheric-dominated airmasses sampled at PMO during summer. Figure 11 shows BC mass concentration monthly anomalies, evidencing a strong decreasing trend of BC in the last decade. This is a very substantial decrease in black carbon that can have consequences on the radiative forcing in the Atlantic. The cause for the decrease is uncertain at this time, but it might be related to emission reductions in the US and Canada, or in changes in air patterns in the North Atlantic.

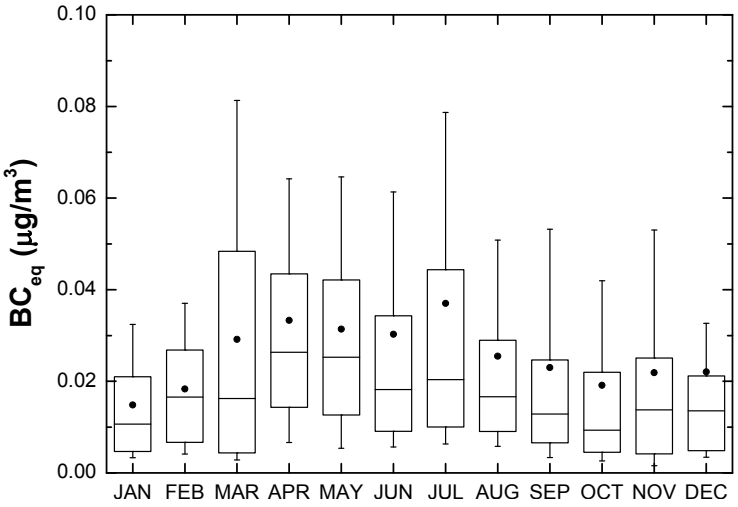

Figure 10: Seasonal variability of black carbon mass concentrations as measured by a seven-wavelength aethalometer at the Pico Mountain Observatory in the Azores. The archive contains data since 2001. The solid circles represent means, the divisor segments are medians (50th percentile), the lower and upper lines of the boxes are the 25th and 75th percentiles and the whiskers indicate the 10th and 90th percentiles. (Kumar et al. 2015)

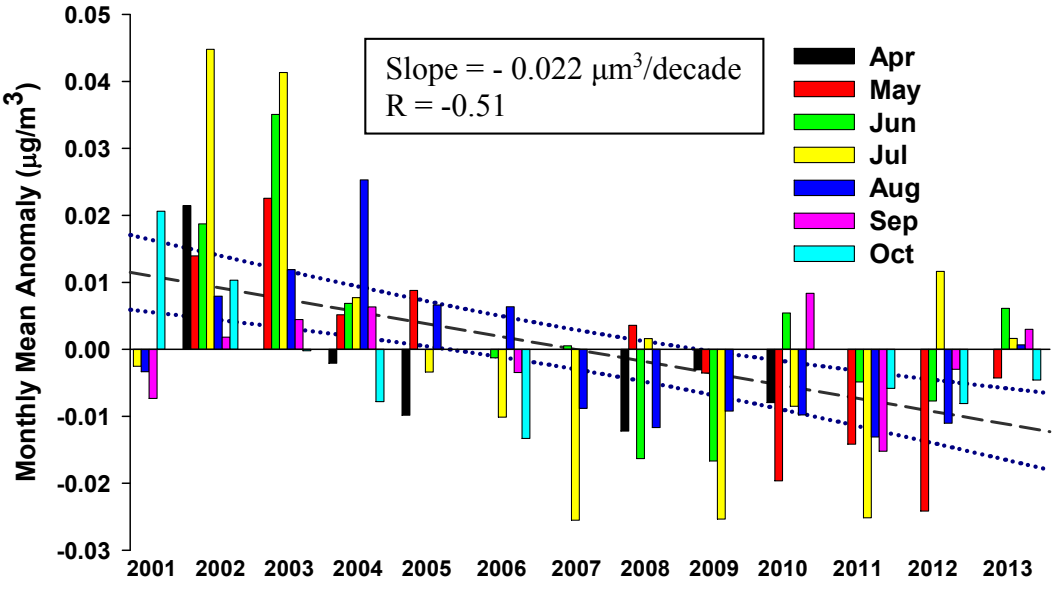

Figure 11: Black carbon monthly mean anomaly trend at PMO, including data from 2001 to 2013 (Kumar et al. 2015).

Aerosol optical and morphological properties

Light scattering and absorption of aerosol particles

Daily averages of scattering coefficients and BC mass concentration are shown in Figure 12. The data show large day to day variations; this is a clear indication of the variable transport that is seen at PMO and the different air mass origins and histories. However, overall BC and aerosol scattering coefficients trend well together, indicating often well mixed air. This also suggests that BC could potentially be used as an approximate proxy of the aerosol loading for the past years, when the only aerosol species measured at PMO was BC. A similar pattern has been measured in 2013. 2014 data are currently being analyzed, but suggest a similar trend.

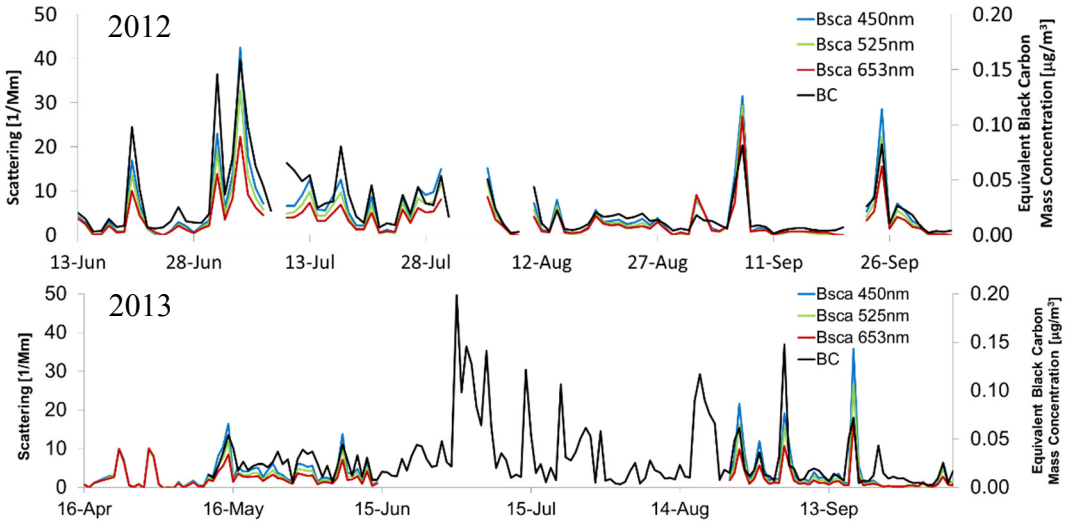

Figure 12: Time series of daily averaged scattering coefficients at three wavelengths and BC_{eq} mass concentration at PMO in 2012 and 2013. Notice the missing data for part of the 2013 summer season due to the backscattering arm failure (some scattering data are available in this period, but will require further QAing that is currently on-going).

In figure 13 we show the single scattering albedo estimated for the 2012 season and the backscattering signal. Both these quantities are critical for radiative transfer calculations. The single scattering albedo is typically larger than 0.95, typical of very aged aerosols. The backscattering fraction is typically between 0.1 and 0.2 as often measured in the atmosphere.

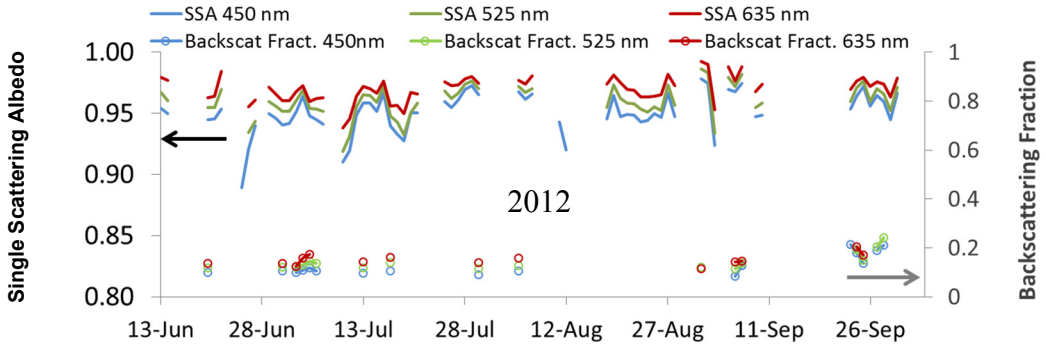

Figure 13: Time series of daily averaged single scattering albedo and backscattering fraction at three wavelengths at PMO in 2012. The missing data are due to threshold filters applied to the raw data to calculate meaningful values. Interesting is the slight raising trend of the single scattering albedo from June to the end of August, possibly indicating different source contribution, source conditions or aging processes.

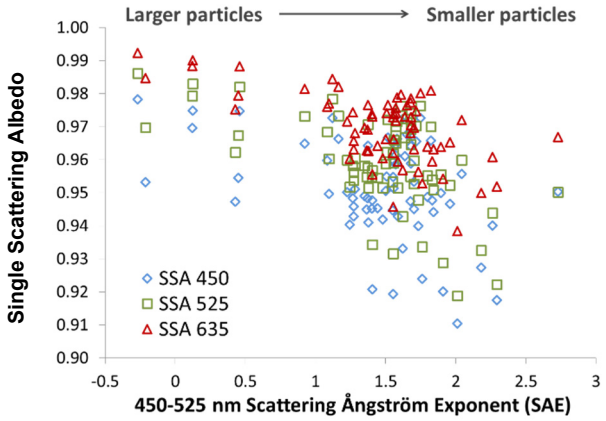

Figure 14: Single scattering albedo vs. scattering Ångström exponent for the 2012 dataset. The trend suggests that darker particles (typically from combustion sources) are also smaller in size.

In Figure 14 we show the daily averaged single scattering albedo vs. the scattering Ångström exponent for the 2012 dataset. The single scattering albedo is the ratio of light scattering to the total extinction (scattering plus absorption). Therefore, a lower single scattering albedo corresponds to particles that are more absorbing. The scattering Ångström exponent (SAE) is a measure of the wavelength dependence of scattering and – in this analysis – is calculated from the $\lambda_1 = 450$ and $\lambda_2 = 525$ nm wavelength as:

$$SAE = -ln\left(\frac{B_{sca}(\lambda_1)}{B_{sca}(\lambda_2)}\right)/ln(\lambda_1/\lambda_2)$$

Where $B_{sca}(\lambda)$ is the scattering coefficient at the respective wavelength. *SAE* depends on the particle size, being larger for smaller particles. Figure 14 provides evidences that smaller particles are statistically "darker" (or more absorbing) than larger particles, implying that the smaller particles are those affected more by combustion sources.

Aerosol Morphology

A selected set of substrates (nucleopore membranes and grids) collected at PMO in 2012, 2013 and 2014 has been analyzed with electron microscopy to study the single particle morphology including mixing and shape (e.g.; China et al. 2014b and Dzepina et al. 2014). One of the most interesting results of this analysis is that the morphology of BC particles that reached PMO is often very compacted, much more so than freshly emitted BC. To quantify the compaction we calculated several morphological parameters, including the convexity (China et al. 2013). Convexity (also known as solidity) is a measure of the topology of the particle, and is calculated as the ratio of the projected area of the particle to the area of the smallest convex polygon inscribing the particle (convex hull polygon). Higher convexity corresponds to higher compaction, while lower convexity corresponds to lacy BC particles (China et al. 2014a, China et al. 2014b); examples are depicted in Figure 15, where PMO samples are compared with samples from Mexico City, Sacramento and Ann Arbor. The convexity shifts from lower values close to the source (Ann Arbor samples were collected on a freeway on-ramp) to higher values for very aged BC particles (PMO samples). At PMO 70% of the soot particles had convexity higher than 0.8 on samples analyzed for two episodes in 2012, reflecting the highly aged aerosols transported over long paths across the Atlantic (China et al. 2014b). The apparent lack of thick coating on these compacted BC particles suggests

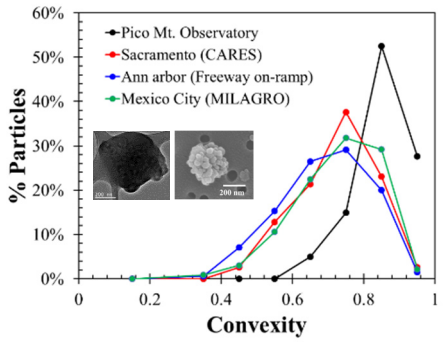

Figure 15: Convexity (a measure of compactness) distribution for soot particles. Soot particles collected at PMO are very compact.

intense cloud processing during the transport. We performed discrete dipole approximation simulations and showed that aggregate compaction could result in increase of soot single scattering albedo up to 54%. We also calculated the top of the atmosphere direct radiative forcing and found it typically smaller for compacted than mass-equivalent fresh soot. The radiative forcing calculated using Mie theory was found to be within 12% of that calculated from the discrete dipole approximation for compacted particles and high surface albedo (China et al. 2014b). This suggests that Mie theory might be a valuable approximation for aged particles and numerical models that use Mie theory, such as climate models, might capture the behavior of BC in remote regions of the Atlantic with reasonable accuracy, when considering BC particles as spheres of mass equivalent diameter (mass provided for example by single particle soot photometers, or the commonly used filter based instruments such as the aethalometer). More research is needed to understand how frequent these geometries are in the North Atlantic and to determine the range of variability of the convexity and packing density of the BC aggregates.

Aerosol ice nucleation

The onset conditions for heterogeneous ice nucleation and water uptake of particles were determined from four samples collected at PMO in 2013 exhibiting different aging times and stemming from different origins. Samples were deposited on silicon nitride coated discs installed in the second stage of a four-stage cascade impactor (MPS-4G1) with a 50% cut off diameter of 0.50 µm. The analysis was performed using an ice nucleation cell coupled to an optical microscope allowing discrimination of the ice nucleation mode (Knopf et al. 2010, Wang et al. 2011). The onset conditions for heterogeneous ice nucleation (immersion and deposition mode) and water uptake were investigated as a function of particle temperature (T_p) and relative humidity with respect to ice (RH_{ice}). Single particle analysis was carried out using the MTU field emission SEM (FE-SEM) (Hitachi S-4700) on the same silicon nitride substrates, but only after concluding the ice nucleation experiments. This sequence was chosen to remove ice nucleation artifacts by potential modifications of the particles in the microscope vacuum or by the electron beam energy. The mean onset conditions of immersion freezing and water uptake by particles on the four samples are presented in Figure 16. The dotted lines show water saturation, 90%, 80%, 70%, 60%, and 50% RH. The solid blue line indicates the RH_{ice} thresholds for homogeneous ice nucleation. Water uptake was observed at 258 K but no ice formation was observed before reaching water saturation for all four samples. Ice nucleation occurred via immersion freezing at 248 K close to saturation and at 238 K also at subsaturated conditions. Results showed no significant differences in RH_{ice} between the samples in the immersion freezing mode. At 223 K, ice nucleation occurred well below conditions necessary for homogeneous ice nucleation (Koop et al. 2000). These findings suggest that PMO aged particles can act as ice nuclei under mixed-phase and cirrus cloud conditions. Water uptake by the four samples occurred between 42% and 66% RH for temperatures between 238 K and 267

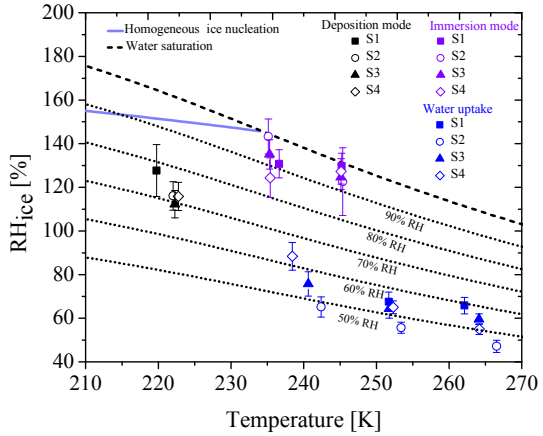

Figure 16: Mean onset conditions for ice nucleation via deposition (25 events) and immersion modes (29 events) and water uptake. Error bars are the standard deviation of the RH_{ice}. S1, S2, S3 and S4 denotes the four different samples collected at PMO (China et al. 2015).

K. Furthermore, we used the optical microscopy setup and electron microscopy to identify and characterize the ice nuclei. Identified ice nuclei were mostly mineral dust, often internally mixed with other material.

Vertical profiles

Vertical profiles of temperature, pressure, relative humidity, particle concentrations at two size ranges (> 0.3 µm and > 0.5 µm) and aerosol scattering were collected by K. Wright and C. Mazzoleni using portable instrumentation for some of the ascents to PMO, when good weather was present on the mountain, during the field seasons of 2013 and 2014. Data were collected using a 2 channels MetOne (227B) optical particle counter, an Extech (RHT50) RH, T and P USB battery-powered logger, and a Radiance Research (M903) nephelometer powered with a moped-size 12V lead-acid battery. The instruments were carried out using a cargo backpack, and inlets were mounted as high as possible on the backpack rack (Figure 17). The data were downloaded on a computer at the end of the day. The profiles were collected to study the vertical structure of the atmosphere from the altitude of the Casa da Montanha (1225 m a.s.l.), where the hiking trail starts, to the volcano caldera, where PMO is located (2225 m a.s.l.). As an example, in figure 18 we show particle concentrations for July 1st 2014. Evident is a sharp drop in particle concentrations (for both size ranges) above about 880 hPa. Also interesting is the fact that particles in the layer below 880 hPa exhibited more uniform and smaller sizes. The relative humidity and temperature profiles in figure 19 show that a thermal inversion was present starting at 880 hPa with drier air underneath. Finally the scattering coefficient also shows a strong stratification with a sudden reduction at 880 hPa.

Figure 17: Graduate student Kendra Wright hiking to PMO and carrying the instrumented cargo backpack. The white cylinder protruding from the top of the backpack is part of the cell of the nephelometer.

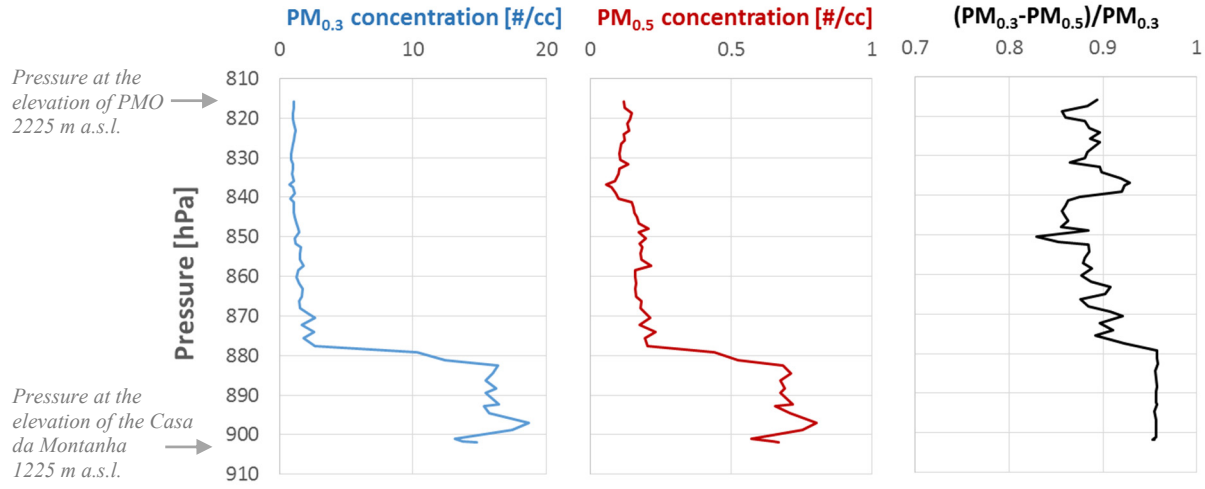

Figure 18: Vertical profile of concentrations of particles larger than 0.3 µm (blue) and larger than 0.5 µm (red). Evident is the dramatic drop in concentrations above the marine boundary layer around 880 kPa. The black line in the right plot is the normalized difference between total and larger size concentrations, showing a smaller fraction of fine particles above the marine boundary layer. This profile was collected with a portable particle counter while ascending at PMO on July 1st, 2014.

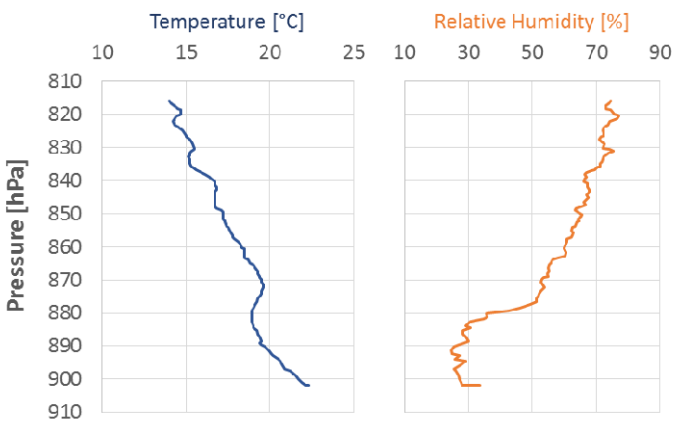

Figure 19: Vertical profile of temperature and relative humidity for the ascent to PMO on July 1st 2014. Evident is the inversion starting at ~880 hPa.

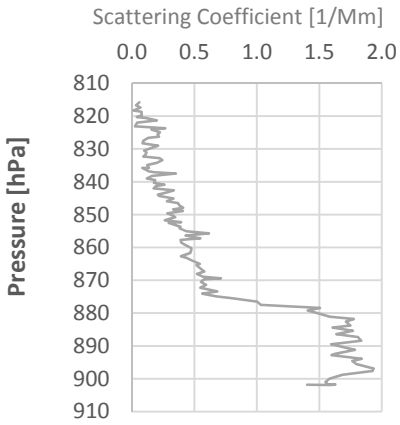

Figure 20: Vertical profile of the aerosol scattering measured during the ascent to PMO on July 1st 2014 (data not standardized).

The vertical profiles measured at Pico almost always show a clear stratification of the atmosphere, in agreement with past evidences that PMO lays almost always above the marine boundary layer. This finding underlines again the uniqueness of the station and the information that can provide, especially in comparison to data that can be obtained at sea level such as at the ARM ENA facility. Future analyses of data obtained at the two stations can therefore provide new insights on the vertical structure of the atmosphere (in the marine boundary layer at ENA and in the lower free troposphere at PMO). The instantaneous decupling between the marine boundary layer and the free troposphere as seen in figures 18 to 20 and as it is often the case at PMO, does not imply however a complete absence of interactions between the marine boundary layer and the free troposphere. For example, in presence of subsidence, air first sampled in the free troposphere could potentially entrain and mix into the marine boundary layer with some lag time depending on the subsidence and the mixing time scales. To study this possibility we investigated an episode in July of 2014 for which we have data available from PMO and from ENA simultaneously, and the findings are discussed next.

Comparison between PMO and ENA: a case study on 21-24 July 2014

During the summer season of 2014 there was considerable overlap in the data collected at PMO and at the ARM eastern North Atlantic (ENA) permanent facility in Graciosa Island. In the top panel in Figure 21 we show data from the 450 nm scattering signals measured at PMO and ENA for a specific period during July 22nd to 24th (we choose 450 nm as it is a common wavelength between the two instruments, the data have been smoothed with a running average of ~30 min). In the afternoon of July 22nd, a large plume reached PMO resulting in a large enhancement in the scattering signal. A few hours later a similar signal (but smaller in amplitude and broader in time) was measured at ENA as well. The bottom panel in Figure 22 shows that the Aerosol Chemical Speciation Monitor (ACSM) located at ENA observed the same plume, with preliminary data indicating that the plume was composed of particles with a much higher organic content than before or after the plume. A FLEXPART residence time map shows a transport from the Arctic regions (Figure 22 top panel) with continuous subsidence from the upper free troposphere to PMO in the lower free troposphere (Figure 22 bottom panel). An analysis of MODIS AOD data also confirms a large plume extending over the North Atlantic to

the Azores during the period of July 21st to 23rd (Figure 23 left panel). By combining FLEXPART with biomass burning emission data (GFASv1.0) (Kaiser et al. 2009), we show in Figure 23 (right panel) that this plume had a strong contribution from a large biomass burning episode taking place in the Canadian Northwest Territories between Great Slave Lake and Great Bear Lake, as visible also in fire counts satellite images (not shown here). This suggests that biomass burning aerosols that are typically rich in organic matter, were transported in the free troposphere over the Azores while subsiding, reaching PMO first and then mixing into the marine boundary layer. The bottom panel of Figure 21 shows how this probable intrusion enhanced the aerosol organic matter measured by the ACSM at ENA, while diluting the sulfate, possibly of marine origin.

This episode provides a compelling evidence of intrusion of long range transported aerosol from the free troposphere to the marine boundary layer identified thanks to the simultaneous measurements at PMO and ENA. This types of events pose several interesting questions for future studies: How often are these episodes occurring in the Azores? What is the effect on the marine boundary layer aerosol concentrations, composition, optical properties and CCN activity? How does this mixing of free troposphere and marine boundary layer contribute to low level cloud properties in the Northeastern Atlantic Ocean? How do the aerosol properties change due to aging and cloud processing during their journey to the Azores?

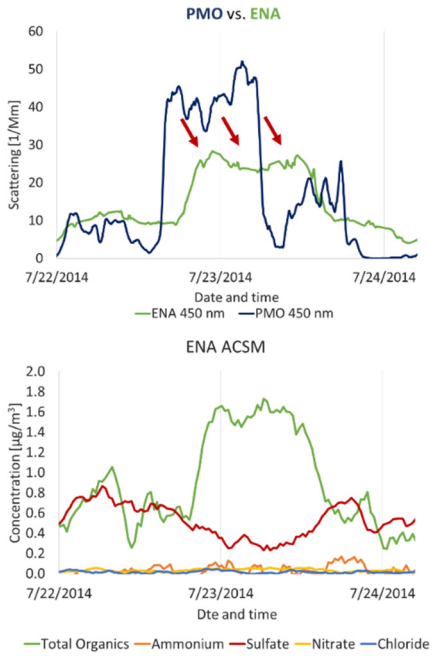

Figure 21: Top, scattering coefficients at ENA and PMO. Bottom, aerosol composition from the aerosol chemical speciation (ACSM) at ENA. ENA data are uncorrected for collection efficiency and sensitivity calibration factors.

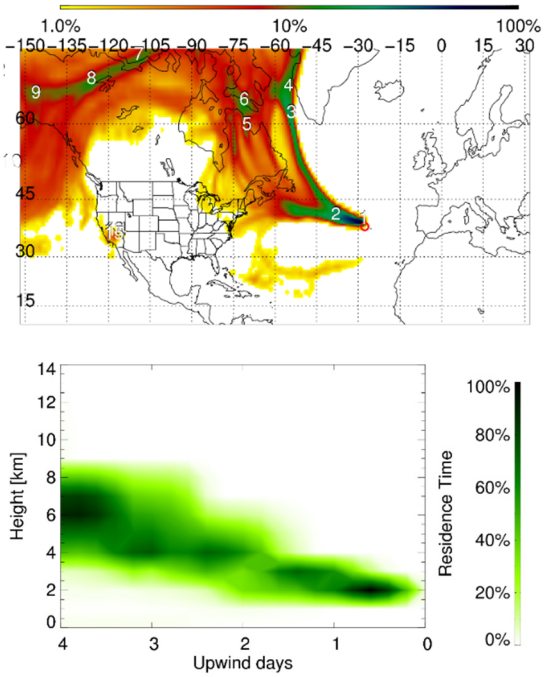

Figure 22: Top, FLEXPART simulated residence time distribution for July, 22nd. The white numbers indicate the upwind transport time in days. Bottom, residence time distribution on a height vs. upwind time view. The color intensity indicates the residence time fraction.

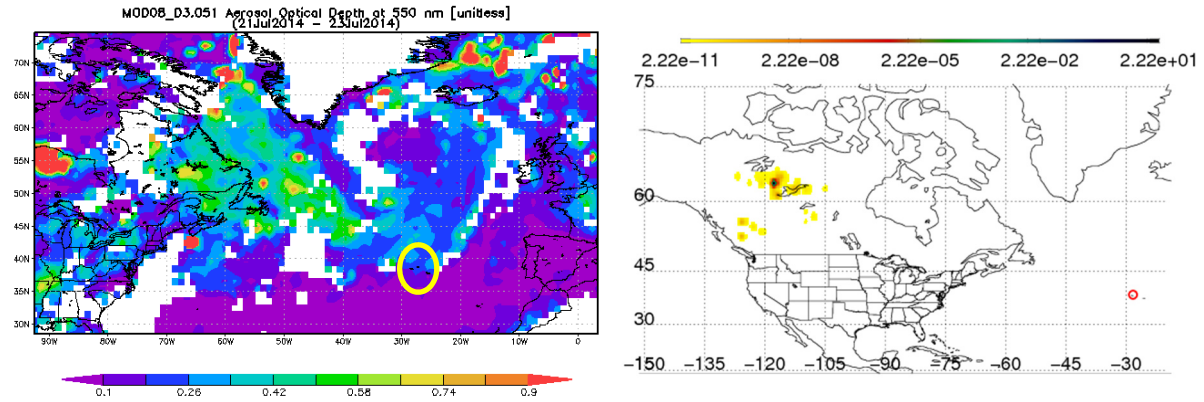

Figure 23: Left, MODIS AOD showing a plume with high AOD crossing the Atlantic and reaching the Azores on 21-23 of July. Right, distribution of FLEXPART simulated biomass burning CO (in unit of ppbv/(1° latitude × 1° longitude grid cell)) transported to PMO (circles) at 21:00 (UTC), July 22.

Climatology of Non-Methane Hydrocarbon Emissions

A record spanning ten years of non-methane hydrocarbon (NMHC) data from PMO was analyzed for the seasonal NMHC behavior, atmospheric processing and NMHC trends. The location of PMO allows these data to be used to investigate the background conditions and pollution transport events in the lower free North Atlantic troposphere. The *ln([propane]/[ethane])* was calculated from the data and used as an indicator to investigate the degree of photochemical processing and the occurrence of pollution transport events in air samples collected at the station. The PMO data were compared with three other continuous NMHC data sets from sites bordering the North Atlantic regions, i.e. Summit, Greenland, Hohenpeisssenberg, Germany, and Cape Verde. Comparisons of these three data sets showed some remarkable differences in the seasonal background *ln([propane]/[ethane])* values and the frequency and dynamical range of *ln([propane]/[ethane])* values.

The statistical distribution of binned monthly *ln([propane]/[ethane])* data was determined and individual sample events were then scaled to the monthly median observed value. HYSPLIT backtrajectory analyses were applied to these data to investigate the source region of air as a function of the degree of photochemical processing.

Results show that PMO is subjected to highly diverse air transport and aging, receiving highly processed air as well as air with recent pollution influence throughout the year, and in particular during summer months. The predominant air transport is from North America, with only occasional influence from continental areas east and southeast (Europe and Africa). The available record was found too variable and still too short to allow a trend analysis of the data. Ethane and propane in the PMO observations were compared with outputs from the atmospheric chemistry and transport model MOZART-4. The model was found to yield good agreement in the description of atmospheric mole fraction, the seasonal cycle, and the regional oxidation chemistry. However, ethane and propone enhancements in transport events were underestimated, indicating that the spatial extend of transport events is smaller than the 2.8°x2.8° model grid resolution. These results are discussed in a manuscript in preparation that should be submitted in the next couple of months (Helmig et al. 2015).

Summary of the research highlights

1. Biomass burning contribute significantly to the BC loading at the site that peaks in summer; however, BC average concentrations decreased substantially at PMO over the last decade.
2. A large fraction of BC particles collected at PMO are slightly coated and very compacted, suggesting cloud processing and exhibiting different optical properties from freshly emitted BC. The compaction (changing shape but conserving mass) has a significant impact on the BC single scattering albedo and therefore on its radiative forcing. In addition to BC, sulfate and organic matter, mineral dust is also present during some episodes.
3. The aerosols collected at PMO act as ice nuclei potentially contributing to cirrus cloud formation during their transport in the upper free troposphere. Good ice nuclei are often mineral dust particles.
4. PMO is typically well above the marine boundary layer, as evident for example in the vertical profile collected during the ascent to PMO on July 1st 2014. The air above show very different characteristics from the air below, in terms of particle concentration, size and optical properties, and thermodynamic parameters.
5. The free tropospheric aerosols studied at PMO have relevance to the marine boundary layer as well. This is because for example, synoptic subsidence – often common in the region – allows for entrainment of free tropospheric long-range transported aerosols in the marine boundary layer. This has potentially large consequences, as the aerosol entrained in the marine boundary layer will affect the CCN concentrations and compositions, therefore having an effect on the marine stratus clouds, with potentially important repercussions on the radiative forcing of low level marine clouds.
6. Non methane hydrocarbon measurements show that PMO is subjected to highly diverse air transport and aging, receiving highly processed air as well as air with recent pollution influence throughout the year, and in particular during summer months. MOZART-4 model simulations were found to yield good agreement in the description of atmospheric mole fraction, the seasonal cycle, and the regional oxidation chemistry.

To conclude this section, in table 2 we summarize the most important measurements performed at PMO since its establishment in 2001. In red are underlined the last three years of sampling, most relevant to this project.

Table 2: Measurements/sampling performed at the Pico Mountain Observatory since 2001[6]

	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014
Black carbon mass equivalent concentration	■	■	■	■	■	■	■	■	■	■	■	■	■	■
CO and O_3, meteorological parameters (T, RH, P, wind)	■	■	■	■	■	■		■	■	■	■	■	■	■
NO_{xy}		■	■	■	■			■	■	■				
Non-methane hydrocarbons (NMHC)				■	■	■			■	■	■	■	■	■
Peroxyacetyl nitrate (PAN)								■	■					
Radiation and aerosol optical size and count > 0.1µm										■	■			
Aerosol optical count >0.3µm												■	■	■
Aerosol scattering and backscattering												■	■	■
Aerosol substrates for chemistry, morphology, IN												■	■	■

[6] Most measurements have been performed during summer months only.

Future scientific opportunities and collaborations

Several potential opportunities and collaborations are currently developing for future measurements (and analysis of archived samples) at PMO as an integral part of atmospheric studies in the Azores including – with a central role – ENA. Specific DOE funded groups, NASA PIs, NOAA PIs and scientists from the Leibniz-Institute for Tropospheric Research (Germany) all demonstrated a strong interest in performing research in the Azores in the next few years, and actively sought our collaboration in case PMO will remain open during these studies. PMO long-term, in-situ measurements will be particularly useful for cross-validation during airborne deployments such as the one proposed by the Leibniz-Institute for Tropospheric Research using their ACTOS helicopter platform, and to allow for an extension to longer time-scale processes. With the additional aim to provide data for such campaigns, we submitted an ARM field campaign and an ASR science proposal in 2014. If awarded, these efforts will allow to extend the scientific activities at PMO such that the observatory could become a strategic counterpart to the sea-level ENA facility as an elevated outpost for measurements in the free troposphere. This will fit within the DOE goal of elucidating cloud and aerosol properties in the North Atlantic.

In addition, we plan to continue the analysis of archived samples also in collaboration with R. Moffet, L. Mazzoleni and D. Knopf and to continue the simulation of optical properties using the discrete dipole approximation in collaboration with B. Scarnato.

Products and Dissemination

Publications

1. China, S., Mazzoleni, C., Gorkowski, K., Aiken, A. C. and Dubey M. K. (2013) *Morphology and mixing state of individual freshly emitted wildfire carbonaceous particles.* **Nature Communications** 4.
   http://www.nature.com/ncomms/2013/130704/ncomms3122/pdf/ncomms3122.pdf

2. Chakrabarty, R., Beres, N.D., Moosmüller, H., China, S., Mazzoleni, C., Dubey, M.K., Liu, L., and Mishchenko, M.I. (2014) *Soot superaggregates from flaming wildfires and their direct radiative forcing.* **Scientific Reports**, 4: 5508.
   http://www.nature.com/srep/2014/140701/srep05508/pdf/srep05508.pdf

3. Dzepina K., Mazzoleni C., Fialho P., China S., Zhang B., Owen R.C., Helmig D., Hueber J., Kumar S., Perlinger J.A., Kramer L., Dziobak M.P., Ampadu M.T., Olsen S., Wuebbles D.J., and Mazzoleni L.R. (2014) *Molecular characterization of free tropospheric aerosol collected at the Pico Mountain Observatory: A case study with long range transported biomass burning plumes.* **Atmos. Chem. Phys. Diss.** 14, 24753-24810. **Currently under revision** for publication in **Atmos. Chem. Phys.**
   http://www.atmos-chem-phys-discuss.net/14/24753/2014/acpd-14-24753-2014.pdf

4. China, S., Scarnato, B., Mazzoleni, L., Owen, R., Zhang, B., Ampadu, M., Kumar, S., Dzepina, K., Dziobak, M. P., Fialho, P., Perlinger, J. A., Hueber, J., Helmig, D., Mazzoleni, C. (2014), *Morphology and Mixing State of Aged Soot Particles at a Remote Marine Free-tropospheric Site: Implications to Optical Properties*. **In review for publication in Geophys. Res. Lett**.

5. Scarnato B., China S. and Mazzoleni C. (2014) *Perturbations of the optical properties of mineral dust particles by mixing with black carbon: A numerical simulation study*. **Submitted to Atmos. Chem. Phys. Diss.**

6. China S., Alpert P., Zhang B., Owen R., Dzepina K., Wright K., Perlinger J., Mazzoleni L., Mazzoleni C., Knopf D. *Heterogeneous ice nucleation and water uptake by free tropospheric particles at a remote marine site*. **In preparation** for **J. of Geophys. Res.** (scheduled submission in winter of 2015)

7. Kumar A., Fialho P., Mazzoleni L, Owen R., Helmig D., Dzioback M., Hueber J., Dzepina K., and Mazzoleni C. *Analysis of eleven years of measurements of North Atlantic black carbon equivalent concentrations at the Pico Mountain Observatory, Azores.* **In preparation** for **Atmos. Chem. Phys. Diss.** (scheduled submission in early 2015)

8. Zhang B., Owen R., Perlinger J., Helmig D., Val Martin M., Kramer L., Mazzoleni C. and Mazzoleni L. *Transport and chemical climatology of pollution tracers observed in the free troposphere over central North Atlantic*. **In preparation** for **Atmospheric Environment** (scheduled submission in spring of 2015)

9. Helmig D., Munoz M., Hueber J., Mazzoleni C., Mazzoleni L., Owen R.C., Val Martin M., Fialho P., Plass-Duelmer C., Palmer P., Lewis A., and Pfister G. *Climatology and atmospheric chemistry of non-methane hydrocarbon emissions over the North Atlantic*. **In preparation** for **Atmos. Chem. Phys. Diss.** (scheduled submission in winter of 2015)

Presentations

Results obtained from the analysis of the decadal BC dataset as well as the three years of aerosol size distributions, and the future plans for the station have been reported in the following presentations:

<u>To be presented at the 2014 AGU fall meeting</u>

1. Dzepina, K., Mazzoleni, C., Fialho, P., China, S., Zhang, B., Owen, R., Helmig, D., Jacques, H., Kumar, S., Perlinger, J., Kramer, L., Dziobak, M., Ampadu, M., Olsen, S., Wuebbles, D., Mazzoleni, L., "Molecular Characterization of Free Tropospheric Aerosol Collected at the Pico Mountain Observatory", American Geophysical Union Annual Meeting, San Francisco, CA (December 15-19, 2014).
2. Zhang, B., Urban, N., Perlinger, J., Owen, R., China, S., Mazzoleni, C., Mazzoleni, L., "Radionuclides reveal age and source of aerosols collected over central North Atlantic", American Geophysical Union Annual Meeting, San Francisco, CA (December 15-19, 2014).
3. Wright, K., Mazzoleni, L., Fialho, P., Dzepina, K., Helmig, D., Jacques, H., Dziobak, M., Kumar, S., China, S., Sharma, N., Mazzoleni, C., "Optical Properties of Aged Free Tropospheric Aerosol Over the Northern Atlantic: Analysis of 2012-2014 Data", American Geophysical Union Annual Meeting, San Francisco, CA (December 15-19, 2014).
4. Mazzoleni, L., Mazzoleni, C., Dzepina, K., Kumar, S., Fialho, P., Zhang, B., Owen, R., China, S., Ampadu, M., Perlinger, J., Schum, S., "Black Carbon and Molecular Characterization of Free Tropospheric Aerosol in the North Atlantic at the Pico Mountain

Observatory **(Invited)**", American Geophysical Union Annual Meeting, San Francisco, CA (December 15-19, 2014).

5. Mazzoleni, C., China, S., Scarnato, B., Moffet, R., Obrien, R., Gilles. M., Fialho, P., Ampadu, M., Kumar, S., Dzepina, K., Wright, K., Sharma, N., Zhang, B., Owen, R., Perlinger, J., Jacques, H., Helmig, D., Dziobak, M., Kramer, L., Mazzoleni, L., "Single Particle Characterization of Free Tropospheric Aerosols at the Pico Mountain Observatory over the North Atlantic", American Geophysical Union Annual Meeting, San Francisco, CA (December 15-19, 2014).

2014

1. Mazzoleni, C., China, S., Scarnato, B., Dubey, M., Aiken, A., Gorkowski, K., Amapadu, M., Sharma, N., Mazzoleni, L., "Absorbing Aerosol Morphology and Optical properties", Atmospheric System Research working group meeting, DOE, Bethesda, MD (November 17-20, 2014).
2. Mazzoleni, C., Mazzoleni, L., Knopf, D., Onasch, T., Helmig, D., Cantrell, W., Dubey, M., Fialho, P., Owen, R., Kramer, L., China, S., Alpert, P., Scarnato, B., Wright. K., Shaw, R., Moffet, R., Subramanian, R., Dzepina, K., Kumar, S., Perlinger, J., Zhang, B., "Morphology and Optical Properties of Free-tropospheric Aerosol – Pico Mountain Observatory (Azores)", Atmospheric System Research working group meeting, DOE, Bethesda, MD (November 17-20, 2014).
3. Mazzoleni, C., Mazzoleni, L., China, S., Sharma, N., Ampadu, M., Gebreeyesus, S., Fialho, P., Kumar, S., Schum, S., Dzepina, K., Dziobak, M., Zhang, B., Perlinger, J., Urban, N., Wright, K., Hueber, J., Helmig, D., Owen, R., Olsen, S., Wuebbles, D., Scarnato, B., "Optical and Morphological Properties of Free-Tropospheric Aerosol at the Pico Mountain Observatory, Azores", 2014 Symposium on Atmospheric Chemistry and Physics at Mountain Sites, Steamboat Spring, CO (August 11-15, 2014).
4. Scarnato, B., China, S., Mazzoleni, C., "Modelling the optical properties of Black carbon mixed with dust and other components with observational constraints", Goldschmidt, Sacramento, CA. (June 8, 2014 - June 13, 2014).
5. Mazzoleni, L. R., Mazzoleni, C., "Properties of Free Tropospheric Aerosol at the Pico Mountain Observatory, Azores", Department Seminar, National Research Council (CNR), Bologna, Italy. (May 27, 2014).
6. Mazzoleni, C., China, S., Amapadu, M., Sharma, N., Schum, S., Gebreeyesus, S., Dzepina, K., Kumar, S., Wright, K., Dziobak, M., Fianlho, P., Hueber, J., Helmig, D., Kramer, L. J., Owen, R. C., Zhang, B., Mazzoleni, L. R., "Free Tropospheric North Atlantic Aerosols Observed at the Pico Mountain Observatory.", Atmospheric System Research Science Team Meeting, DOE, Potomac, MD. (March 10, 2014 - March 13, 2014).

2013

1. Mazzoleni, C., Mazzoleni, L, Fialho, P., Kumar, S., Dzepina, K., Dziobak, M., Kramer, L. J., Olsen, S., Owen, R., Helmig, D., Hueber, J., Wright, K., Zhang, B., China, S., "Properties of Aerosol in the North Atlantic Free Troposphere at the Pico Mountain Observatory, Azores", ASR Science Team Meeting, DOE, Potomac, MD. (March 2013).
2. Helmig, D., Hueber, J., Munoz, M., Mazzoleni, C., Mazzoleni, L., Owen, R., Val-Martin, M., Fialho, P., "Climatology and Atmospheric Chemistry of Non-Methane Hydrocarbon

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3. Dzepina, K., Kumar, S., China, S., Mazzoleni, C., Dziobak, M., Fialho, P., Hueber, J., Helmig, D., Kramer, L., Olsen, S., Mazzoleni, L., "Chemical Characterization of Free Tropospheric Aerosols in the North Atlantic Measured at the Pico Mountain Observatory during Summer of 2012.", American Geophysical Union Annual Meeting, American Geophysical Union, San Francisco. (December 9, 2001 - December 13, 2013).
4. Wright, K., Mazzoleni, C., Mazzoleni, L. R., Dzepina, K., Hueber, J., China, S., Sharma, N., "Vertical Profile of Aerosol Properties at Pico Mountain, Azores", American Geophysical Union Annual Meeting, American Geophysical Union, San Francisco. (December 9, 2013 - December 13, 2013).
5. Harkness, L. , Mazzoleni, L. R. , Dzepina, K. , Mazzoleni, C., China, S. , "Developing Atmospheric Science Tools for Teachers Based on Research at the Pico Mountain Observatory, Pico Island, Azores.", American Geophysical Union Annual Meeting, American Geophysical Union, San Francisco. (December 9, 2013 - December 13, 2013).
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10. Louisa K., Claudio Mazzoleni, Lynn Mazzoleni, Paulo Fialho, Detlev Helmig, Seth Olsen, Robert Owen, Mike Dziobak, Jacques Hueber, Katja Dzepina and Sumit Kumar, "Measurement of Aerosols and Trace Gases in the Free Troposphere at the Pico Mountain Observatory in the Azores", European Geosciences Union General Assembly, Vienna Austria, Poster (April, 8-12, 2013).
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Bo Zhang, Swarup China, "Properties of Aerosol in the North Atlantic Free Troposphere at the Pico Mountain Observatory, Azores", ASR science team meeting 2013, Potomac, MA, Poster. (March 18 - 21, 2013).

2012

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5. Mazzoleni, C., Mazzoleni, L., Helmig, D., Fialho, P., Owen, R., Kramer, L., Olsen, S., Gorkowski, K., Dziobak, M., Hueber, J., Dzepina, K., Kumar, S., "Planned Aerosol Measurements at the Elevated Site of the Pico Mountain Observatory in the Azores", ASR Atmospheric System Research Science Meeting, DOE, Arlington, VA, Oral. (March 12 - 16, 2012).

Data sharing

Data and updates have been regularly shared between PIs and collaborators using a password protected project wiki. The wiki is especially useful during the field deployment to keep track of activities, findings, interesting observations, and problems and for data archival. During the off-season period the wiki is especially useful for quick look at plots of previous season data and for planning future activities. Some examples of wiki pages are shown next.

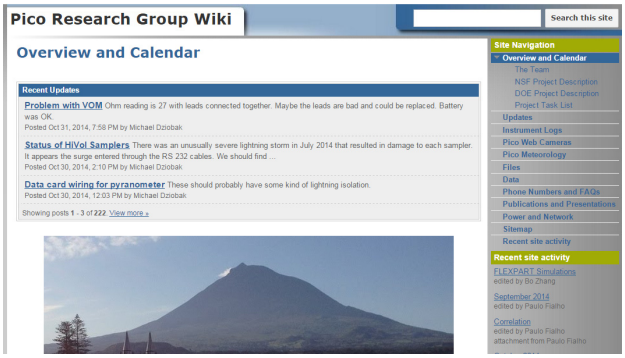
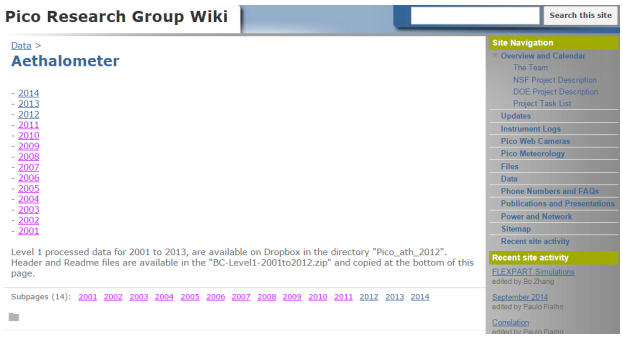


Figure 24: Home page of the Pico Mountain Observatory collaboration team wiki: https://sites.google.com/a/mtu.edu/pico-wiki/

Figure 25: Data page of the Pico Mountain Observatory collaboration team wiki.



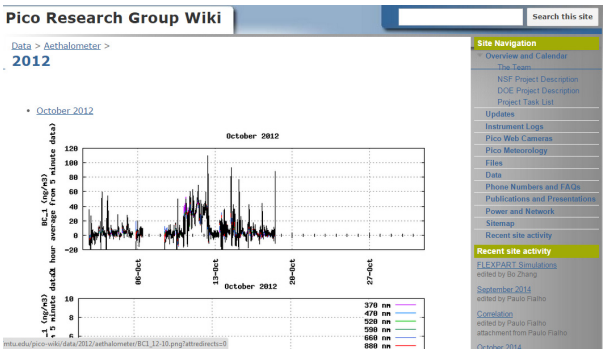


Figure 26: Examples of Aethalometer data pages.

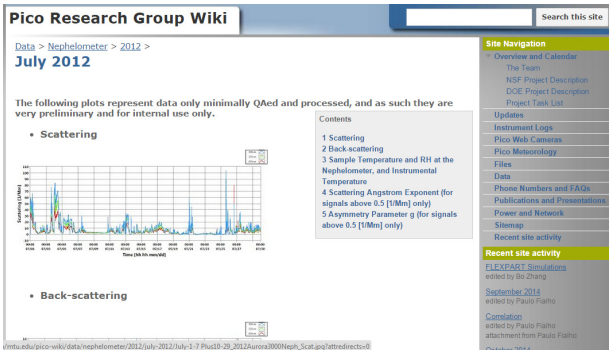
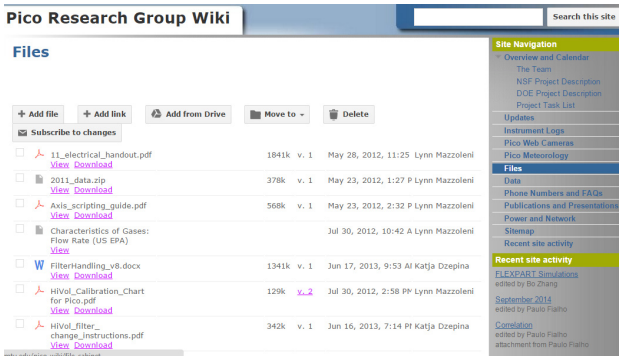


Figure 26: Examples of Nephelometer data pages.



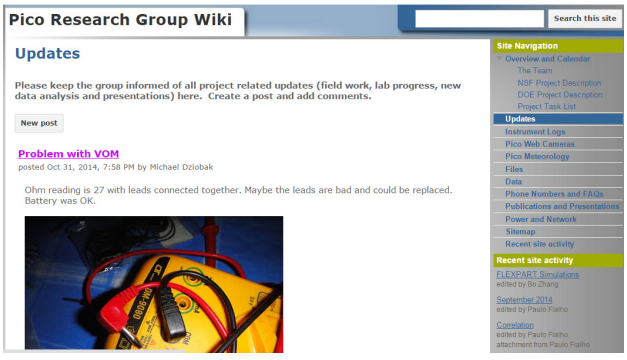


Figure 27: Examples of file exchange and updates pages.

A Pico Mountain Observatory open website was also developed and hosted on an INSTAAR portal (http://instaar.colorado.edu/pico/). On the website are also provided a few basic plots of some of the historic datasets open to the public, in addition images of the station from two webcams are also regularly updated on the website during the field deployment season. Another public website was developed in the last two years to share the meteorological data available from the station in quasi real time (typically within 15-60 minutes). The website shows several running charts including temperature, pressure, relative humidity, wind, solar irradiance (https://sites.google.com/a/mtu.edu/pico-mountain-atmospheric-observatory/). Both these pages are used by the public, especially hikers who plan to climb the volcano and wants to know the weather conditions and visibility at the top.

Future plans include sharing several of the data streams within the ARM framework.

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