Decadal trends in atmospheric organic aerosol: Analysis of network data and method development

by

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ABSTRACT

Organic aerosol (OA) makes up a substantial fraction of atmospheric particulate matter, yet its sources and controlling factors – and thus its impacts on climate and human health – are not well understood. Recently-developed analytical techniques have provided new insight into OA chemistry, but major uncertainty remains in how OA has changed over the past few decades. Characterizing long-term trends in OA would allow for better calibration of models that currently struggle to replicate ambient organic measurements as well as answer questions of how changes in OA relate to changes in emissions sources, anthropogenic-biogenic emissions interactions, altered chemistry, and more. This work represents a two-fold effort to better constrain our understanding of OA trends spatially, temporally, and chemically. First, trends in aerosol species concentrations over the past two decades are examined using existing data from the U.S. Interagency Monitoring of Protected Visual Environments (IMPROVE) network to provide insight into the long-term OA evolution across the rural U.S. Along with large decreases in total aerosol amounts (30-50%), OA is found to decrease at a fractional rate nearly equivalent to the decreases in three other major aerosol species: nitrate, sulfate, and elemental carbon. This suggests a link between the controlling factors of the different species, but explaining these observations is made challenging by the lack of chemical characterization of historic OA measurements that would help point to changing sources and chemistry. Thus, the second part of this work introduces a technique that enhances our ability to obtain important chemical information from small-volume environmental aerosol samples, such as filter extracts from remote regions like those monitored by the IMPROVE network, that were previously excluded from Aerodyne aerosol mass spectrometer (AMS) analysis due to the prohibitive volumes required for standard atomization. The Small Volume Nebulizer (SVN) nebulizes microliter-sized liquid samples, allowing for highly time- and mass-resolved chemical analysis of dissolved organic species on the AMS and providing valuable insight into the factors that control observed OA trends. By examining historic trends in particulate matter loading and composition, and expanding AMS coverage to include small-volume environmental samples, we can begin to answer the question of how and why OA has changed over the past few decades – and what that means for OA chemistry, the climate, and regional and global air quality.

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1. Introduction

Atmospheric particulate matter ("aerosol") can have a profound influence on human health, global climate, and air quality. Aerosols affect cloud formation and light scattering in the atmosphere, which in turn can influence the radiative balance of the atmosphere and have important impacts on climate (Yu et al., 2006; IPCC, 2013). Ambient aerosol exposure has been linked to daily mortality, and respiratory and cardiovascular system damage (Schwartz et al., 1996; Harrison and Yin, 2000; Davidson et al., 2005; Arden Pope III and Dockery, 2006). Particle reactions can produce more toxic compounds with potentially mutagenic and carcinogenic effects (Finlayson-Pitts and Pitts, 1997). We need to understand aerosol formation, composition, and aging processes in order to address their health and environmental impacts, but our knowledge of these aerosol characteristics is currently limited. One research avenue that will help us address some of these unknowns is developing an understanding of historical aerosol trends. This will allow us to better identify aerosol sources, characterize aerosol responses to regulations and other changing factors, and calibrate models for investigating the factors that control aerosol. There are two main strategies for characterizing historical trends: analyzing existing data for trends, and expanding the dataset by measuring the chemical composition of existing samples. The first strategy is addressed in Chapter 2 with the analysis of aerosol data from rural parts of the United States, and the second strategy requires method development that is characterized in Chapter 3. The rest of this introduction will provide the background and motivation for this two-fold approach to characterizing historical trends in aerosol.

As awareness of the dangers of poor air quality spread in the first half of the twentieth century, the United States began introducing important air quality legislation to combat the effects of air pollution. The original Air Pollution Control Act of 1955 provided support for research on air pollution but contained no regulatory actions; a series of acts followed that strengthened the fight against air pollution by providing more funding, setting emissions standards, and establishing regulatory bodies to enforce the changes (US EPA, 2015). The Clean Air Act of 1963 was the first act to allocate funding for research into methods for monitoring and controlling air pollution. The Motor Vehicle Air Pollution Control Act (1965) set up reductions for hydrocarbons and carbon monoxide, which was followed by major amendments in 1970 that expanded regulations to include both mobile and stationary sources. These amendments also established the U.S. Environmental Protection Agency (EPA) and required it to enact National Ambient Air Quality Standards (NAAQS) for states to meet via individualized implementation plans. The NAAQS dealt with the six criteria air pollutants, including sulfur dioxide, nitrogen dioxide, and particulate matter. Efforts were expanded further with the 1990 amendments, which addressed a range of pertinent and emerging issues including smog, motor vehicle emissions, acid rain, ozone depletion, and toxic air pollution. New emissions standards were implemented for motor vehicles built after 1995. In 1997, the EPA tightened ozone and particulate matter NAAQS. Each of these acts and amendments, which represent only a small selection of those implemented during this period, helped establish stricter guidelines and controls on emissions and subsequently led to the reduction of many different air pollutants.

As a response to the various legislative acts, many national and state agencies were established to monitor the atmospheric concentrations of pollutants. The Clean Air Act required each state to develop its own network of air monitoring stations, collectively titled the State and Local Air Monitoring Stations (SLAMS). Within this network is the National Air Monitoring Stations (NAMS), a subset of sites with more stringent requirements for equipment, quality assurance, and reporting. These locations cover a range of locations, but are typically located in urban regions where air quality monitoring is important for understanding health impacts on daily life. Other urban sites are monitored by the Photochemical Assessment Monitoring Station (PAMS), which measures ozone precursors, and the Speciation Trends Network (STN), which monitors particulate matter at urban sites and was established by regulation in 1999 to support attainment of the NAAAQS (CSU, 2010; IMPROVE, 2012). Conversely, where other agencies monitor urban regions, the Interagency Monitoring of Protected Visual Environments (IMPROVE) provides a picture of how air quality is changing at rural locations across the U.S. IMPROVE was introduced in 1987 to help implement the Clean Air Act legislation by identifying pollutants and sources causing impaired visibility in Class I areas (Joseph et al., 1987; IMPROVE, 2012). Together, the large collection of monitoring networks run by both state and government agencies provides a wealth of information about long-term changes in air quality.

We can use the network data to look at how certain aerosol components that are better understood have changed across the United States over the past few decades. Combining data from a range of networks, the US EPA (2014) has found that particulate matter (PM) has decreased nationally over the past few decades; these results are consistent with other studies on fine PM (Blanchard et al., 2013; Murphy et al., 2011). Urban concentrations of sulfur dioxide (SO_2) and nitrogen dioxide (NO_2) (precursors to sulfate and nitrate particulate matter) are well characterized and have been steadily decreasing: the national average concentration of SO_2 decreased by 75% and NO_2 decreased by 45% over the past twenty years (US EPA, 2014). IMPROVE data is particularly valuable for trend analysis because data has been collected for over twenty years at spatially distributed sites with fairly consistent sampling methods. At most

IMPROVE sites, sulfate concentrations were shown to have decreased over the past twenty years of sampling (Malm et al., 2002; Hand et al., 2012). Decreases have also been observed in light absorbing (EC) carbon concentrations (Murphy et al., 2011; Chen et al., 2012; Blanchard et al., 2013) and total carbon (OC + EC) concentrations (Hand et al. 2013). Most of the decreases have been linked to regulations controlling anthropogenic emissions (Murphy et al., 2011; Hand et al., 2012; Blanchard et al., 2013; Blanchard et al., 2015).

While these networks have provided valuable information on the trends in some aerosol components, many uncertainties persist in our characterization of aerosol due to historic and current limitations in instrumentation, source tracking, and chemical speciation of aerosol. One particularly influential source of uncertainty is the organic aerosol (OA) component of particulate matter, which accounts for approximately 50% of total aerosol mass but remains poorly constrained in terms of chemical composition and knowledge of sources (Malm et al, 1994; Zhang et al., 2007; Jimenez et al., 2009). OA is characterized as either primary, having been emitted in the particulate form directly from a source, or secondary, which forms from the oxidation of gas phase species and the subsequent condensation of lower volatility products (Chung & Seinfeld, 2002; Tsigaridis & Kanakidou, 2007). In both forms, but especially secondary OA (SOA), OA presents a challenging task for characterization: identified organic species number in the thousands (Goldstein and Galbally, 2007), there are many complex reaction pathways and products often with non-linear behavior (Tsigaridis & Kanakidou, 2007), efforts to replicate environmental oxidation levels often fall short in the laboratory (Qi et al., 2010; Donahue et al., 2012), and models struggle to represent significant sources of OA that are likely secondary processes (Heald et al., 2005). Similarly, OA sources are not well understood because there are a wide variety and number of sources, volatile organic compounds (VOCs) can be difficult to measure, SOA yields are not always well known for different VOCs, and reporting of emissions inventories is subject to many uncertainties in measurement techniques, emission rates, chemical speciation, and more (Kanakidou et al., 2005). Although monitoring networks provide valuable bulk speciation information, they are unable to distinguish the degree of oxidation in their organic carbon measurements, which has been shown to be a good metric for characterizing OA (Kroll et al., 2011).

Fortunately, recently developed analytical techniques have provided new insight into OA composition where previously our understanding was extremely limited. One such instrument that is critical for the work in this thesis is the Aerodyne aerosol mass spectrometer (AMS), which measures non-refractory sub-micron aerosol loading and chemical composition via flash vaporization of the particles with subsequent electron impact ionization of the vapor (Jayne et al., 2000; Allan et al., 2003; Jimenez et al., 2003; Drewnick et al., 2005). The AMS has been used in laboratories and field campaigns since its introduction in 2000 and has helped answer many questions about the chemical composition and loading of aerosol around the globe (e.g. Canagaratna et al., 2007; Zhang et al., 2007; Jimenez et al., 2009). Analytical instruments like the AMS have greatly expanded our ability to measure and chemically characterize OA both in laboratory studies and in-situ field campaigns.

However, there still remains a lack of historical information of OA due to the relatively recent introduction of these analytical techniques. The uncertainty in historical OA measurements has been particularly challenging for constraining model predictions. Global chemical transport models struggle to accurately represent total OA concentrations in the atmosphere (Bey et al., 2001; Kanakidou et al., 2005), and under-predict OA concentrations by factors up to 10-100 in the free troposphere, likely missing a source of secondary organic aerosol

(Heald et al., 2005). We do not have a good understanding of how OA has changed over the past few decades. If we are to better predict OA effects on important environmental issues, we need to develop a historic OA record to provide insight into OA changes in the US, and how these changes relate to emissions regulations, changing vehicle fleets, large biomass burning events, and other activities that affect organic concentrations so we can better model the processes that control OA (Kanakidou et al., 2005). One way to develop this historic record is by examining existing data from the national networks and comparing the aerosol trends with other changing variables like the emissions changes due to the previously mentioned policies. Correlating OA with anthropogenic activities will help us identify how much OA can be attributed to these activities, and therefore how much particulate OA we can control with regulation. With better insight into the controlling OA factors, we can better predict what future changes will improve air quality further as well as help constrain projections of future air quality and climate conditions.

A second way to develop this historic record is by analyzing stored historic samples using modern measurement techniques. Many of the monitoring networks have collected aerosol samples on filters or in liquid samples to be analyzed at a later date or separate location, including the STN and IMPROVE (Coutant & Stetzer, 2001; IMPROVE, 2012). These networks provide valuable spatial and temporal coverage of aerosol information, as well as an opportunity for further analysis of archived samples and more extensive analysis of modern samples using instruments that are too costly or unwieldy to transport for in-situ analysis. However, in order for these archived samples to be analyzed using modern techniques, they must be converted into useable forms like liquid filter extracts. For the AMS, atomizers are frequently used to convert liquid samples into aerosol for analysis. This technique limits our ability to analyze small-volume samples because standard atomization requires tens of milliliters of liquid. To expand the dataset to include AMS characterization of archived samples, it is necessary to develop a method that will allow for the extraction and analysis of microliter-sized liquid solutions on the AMS.

These two approaches for developing an understanding of historic trends in aerosol – analyzing existing data for trends and developing a technique for modern analysis of historic samples – are addressed in this thesis. The main research objectives that guided our analysis with respect to these two approaches are to:

(1) Analyze how aerosol amount and composition has changed in the rural United States over the past twenty years; and
(2) Develop a technique that will allow us to analyze small-volume liquid samples on the AMS and gain valuable insight into their chemical composition.

In Chapter 2, we tackle the first objective by analyzing historical trends in aerosol at rural sites across the United States using data from the Interagency Monitoring of Protected Visual Environments (IMPROVE) network. We present evidence of large decreases in total aerosol concentrations with simultaneously small changes in aerosol composition over this time period, and discuss potential explanations for these trends. The work in Chapter 2 provides motivation for the work in the following chapter, where we develop a nebulization technique that will allow us to analyze more extensive data both spatially and temporally using the AMS. Chapter 3 introduces the Small Volume Nebulizer (SVN), including a description and characterization of the technique as well as preliminary results from field and laboratory SOA studies. The future of the technique is discussed in terms of both suggested improvements as well as a range of applications for which it could be useful. Finally, Chapter 4 provides a brief summary of the implications and questions raised by the observed trends in rural aerosol, and how the SVN can provide valuable new information to the discussion of organic aerosol.

2. Evidence for Decreasing Organic Aerosol Concentrations in the Rural United States Over the Last Quarter-Century

2.1 Rationale

As discussed in Chapter 1, our understanding of organic aerosol (OA) sources and controlling factors, and thus its impacts on climate forcing and human health, is hindered by uncertainties in how OA has changed over the past few decades. The analysis presented in this chapter seeks to resolve some of that uncertainty by using existing aerosol data from the U.S. Interagency Monitoring of Protected Visual Environments (IMPROVE) Network to examine recent trends in aerosol species concentrations. One of the many monitoring networks in the U.S., IMPROVE offers the opportunity to examine rural locations where biogenic emissions contribute significantly to the makeup and where we can consider how changes in anthropogenic emissions of sulfate, nitrate, and elemental carbon are related to changes in both anthropogenic and biogenic sources of organics. While the accuracy and specificity of the US networks' previous OA measurements are limited by the technology used to obtain them, we can still develop a general understanding of how organics have evolved in the atmosphere over the past twenty years from this data.

IMPROVE data is particularly valuable for trend analysis because data has been collected for over twenty years at spatially distributed sites with consistent sampling methods. An analysis of the existing data on OA in the US, combined with a comparison to the better-constrained measurements of sulfates and nitrates, will provide an introductory understanding of the ratio of organics to sulfates and nitrates as well as organic trends in the rural US. Additionally, this initial characterization of atmospheric organics motivates and informs the subsequent development of a nebulization technique (Chapter 3) for obtaining measurements of archived filter samples using modern aerosol analytical techniques, which ultimately will provide us with a new understanding of the global temporal evolution of organic aerosols.

This chapter focuses on IMPROVE data available on the Visibility Information Exchange Web System (VIEWS) website. Using IGOR Pro, raw data is analyzed for twenty-five different locations from 1990 to 2010. Changes in OA are characterized both on an absolute scale and relative to other key atmospheric constituents, including sulfate, nitrate, and ammonium. The observations are used to discuss potential controlling factors for OA trends and are interpreted in terms of historic changes to a number of factors that may affect relative and absolute loadings: emissions of primary organic aerosol (POA), changes in emissions of precursors to both secondary organic aerosol (SOA) and secondary inorganic aerosol, and other factors that may affect aerosol formation (e.g., NO_x levels and aerosol acidity). By examining trends in particulate matter loading and composition, we can begin to answer the question of how OA has changed over the past few decades and what that says about the factors controlling OA concentrations.

2.2 Method

2.2.1 IMPROVE Network

This project uses data from the US rural-based IMPROVE network. The network was started in 1985 to support the 1977 Clean Air Act, and was intended to monitor visibility impairment in Class I areas (mainly, national parks > 6000 acres, wilderness areas and national memorial parks > 5000 acres). It is run by a steering committee of representatives from eight agencies, including the EPA, the National Park Service (NPS), and the USDA Forest Service (USFS). Figure 1 shows the locations of the more than 200 IMPROVE measurement sites; the 25 sites used in this study are marked with stars and colored by their grouping into western (blue), mid-US (yellow), and eastern (orange) regions.

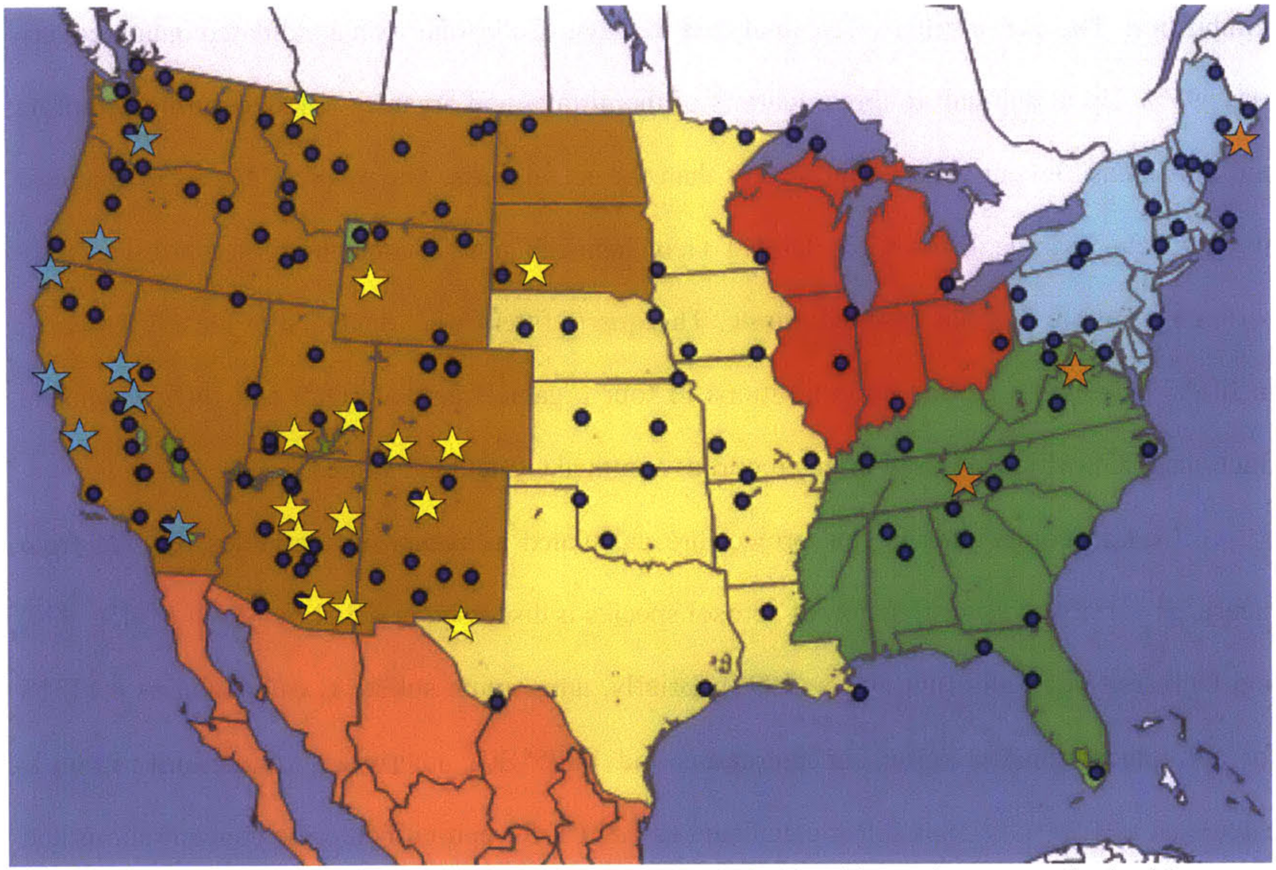

Figure 1: All IMPROVE Network locations. Sites included in this study are marked with a star, where the color of the star represents the division made in this work to represent the Western states (blue), mid-US states (yellow), and Eastern states (orange). Figure adapted from the IMPROVE website.

IMPROVE samples were collected bi-weekly every Wednesday and Saturday in 24-hour increments (local time midnight to midnight). The sampling process is presented in detail by the University of California Davis (1995); we will discuss the protocol briefly here. As shown in

Figure 2, samplers consist of four modules: a primary Teflon filter for fine particulates and PM10 analyzed using gravimetric Particle Induced X-Ray Emission/Proton Elastic Scattering Analysis (PIXE/PESA) X-Ray Fluorescence (XRF) absorption, a nylon filter with preceding denuder for nitrates and sulfates analyzed using ion chromatography (IC), and tandem quartz filters for carbon fraction measurements analyzed using Thermal Optical Reflectance (TOR) combustion. The Teflon filters were analyzed in Davis, California with a validated data recovery rate >95%. Up to one-half to three-quarters of the nitrates and organics volatize during sampling and thus measurement values may be less than the actual mass. The nylon filters were analyzed at Research Triangle Institute or Global GeoChemical; nitrate concentration represents only particulate nitrate and not gaseous nitrate. The quartz filters were analyzed at Desert Research Institute, calculating carbon concentrations in four organic fractions (OC) and three elemental fractions (EC), which are used in this report as summed OC and EC values.

Certain compounds in this project are calculated as composite variables derived from measured variables. Determination of aerosol species is discussed in detail by Malm et al. (1994) and University of California Davis (1995). Briefly, ammonium sulfate is calculated as 4.125*S for non-null particulate sulfur concentrations and $1.375*SO_4$ otherwise. Ammonium nitrate is calculated as $1.29*NO_3$. Sea salt is calculated as $1.8*Cl^-$ for non-null chloride concentrations and 1.8*Cl otherwise. Total organic carbon is the sum of the organic carbon fractions and total elemental carbon is the sum of the carbon leftover after all the organic carbon is burned off.

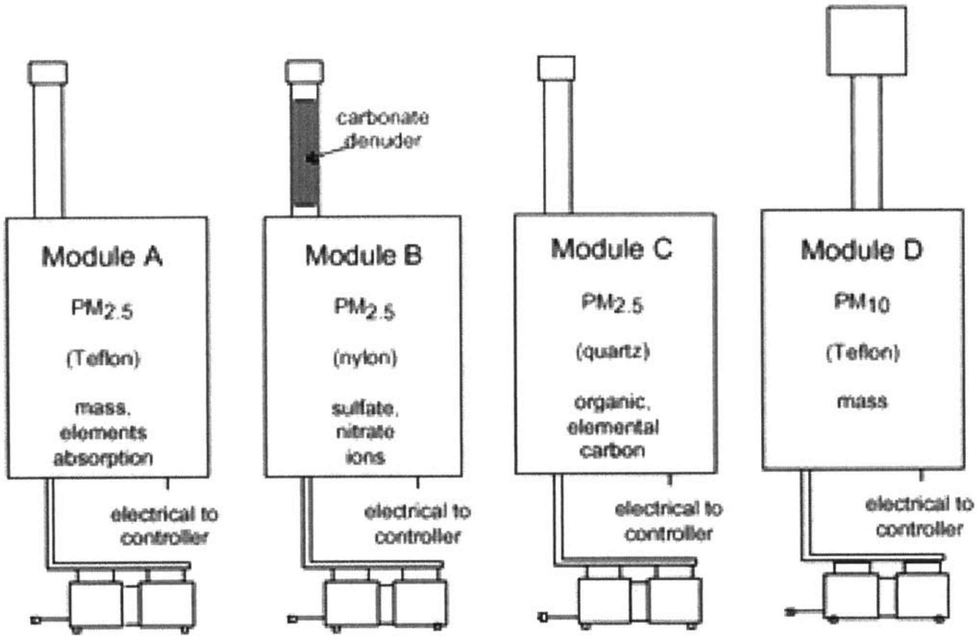

Figure 2: Schematic of the IMPROVE sampler showing the four modules with separate inlets and pumps. (From http://vista.cira.colostate.edu/improve/Overview/IMPROVEProgram_files/v3_document.html)

2.2.2 Data Acquisition

IMPROVE data was downloaded from the VIEWS Data Wizard public archive (http://views.cira.colostate.edu/fed/DataWizard/Default.aspx), an online integrated database compiling data from over a dozen monitoring networks and campaigns. This project uses a subset of data from the IMPROVE network. Download setting selections made on the Data Wizard are provided in Table 1.

The twenty-five sites included in this study were selected because they have the oldest and longest-running data sets in the IMPROVE aerosol network, monitored bi-weekly from 1988 to 2011. A few additional sites were sampled during this time period but were not included because their location was not part of the contiguous United States (Hawaii and Alaska), they had inconsistent monitoring years (Everglades, FL), or they were from an urban area (Washington D.C.).

Table 1: Data Wizard selections for IMPROVE data used in this study.

PULL DOWN TAB	SELECTION
Reports	Raw Data
Datasets	IMPROVE Aerosol
Sites	Acadia National Park, ME; Badlands National Park, SD; Bandelier National Monument, NM; Bliss State Park, CA; Bridger Wilderness, WY; Bryce Canyon National Park, UT; Canyonlands National Park, UT; Chiricahua National Monument, AZ; Crater Lake National Park, OR; Glacier National Park, MT; Great Sand Dunes National Monument, CO; Great Smoky Mountains National Park, TN; Guadalupe Mountains National Park, TX; Indian Gardens, AZ; Mount Rainier National Park, WA; Petrified Forest National Park, AZ; Pinnacles National Monument, CA; Point Reyes National Seashore, CA; Redwood National Park, CA; Saguaro National Monument, AZ; San Gorgonio Wilderness, CA; Shenandoah National Park, VA; Tonto National Monument, AZ; Weminuche Wilderness, CO; Yosemite National Park, CA
Parameters	Ammonium Nitrate (Fine), Ammonium Sulfate (Fine), Elemental Total Carbon (Fine), Organic Total Carbon (Fine), PM10 Mass (Total), Nitrate (Fine), Sulfate (Fine)
Dates	"By Date Range" from 3/2/1988 to 10/30/2011
Fields	Select: Dataset, Site, Date, Parameter, Data Value, Unit, Latitude, Longitude
Filters	Select Aggregations: Non-Aggregated; Select Flags: (none)
Options	Output Medium: Excel; Row Format: Standard; Content Options: Data & Metadata; String Quotes: None; Missing Values: -999; Date Format: MM/DD/YYYY

2.2.3 Data Analysis

All the data was imported into and analyzed with IGOR Pro, scientific data analysis software developed by WaveMetrics. Data from the downloaded text files was input into IGOR, and divided into folders based on location names. This allowed for easier data handling, as all compound waves had the same name under the different folders (ex: "OCf_Value" contained organic carbon measurements under each location folder). Organic carbon (OC) values were multiplied by a factor of 1.8 to convert to organic mass (OM); this factor was chosen as a reasonable approximation based on urban and rural values suggested by Turpin and Lim (2001) and IMPROVE-specific values suggested by Malm and Hand (2007), but the selection of this factor does not affect the resulting trends in OA.

Functions were created to run each of these tasks: reformatting the date, filtering the concentration, removing major fire influence, averaging yearly values, averaging monthly values, and making ratios of average values. Date waves were reformatted to facilitate easy identification of month and year information for each measurement point. The months were taken from the original waves via string identification, but the years were pulled from the original wave and turned into a new wave of only year values to address the software's issues handling the transition from "99" to "00." Concentration waves were filtered to replace all negative concentrations, representing missing values, with NaNs (Not a Number). Excluding data from dates where fine mass was greater than 50 μg m^{-3} minimized the impact of fires on measurements, and particularly organic carbon values. Average values for each compound were calculated monthly, seasonally and yearly/temporally. The month-averaged values combine measurements for each month across all years, averaged to the number of days with real (concentration ≥ 0) measurements (i.e. days with missing concentrations were not included in the averaging). Seasonal measurements were divided according to the following cutoffs: Dec/Jan/Feb for winter, Mar/Apr/May for spring, June/July/Aug for summer, and Sept/Oct/Nov for autumn. The year-averaged values combine measurements for each separate year, averaged to the number of days with real measurements. Ratios of organic carbon to other species were calculated by dividing the average monthly or yearly values. Additional waves were created

(Months and Years) for use in plotting the average values. To compare aerosol loading in 1990 with loading in 2010, data was averaged over 1989-1991 and 2009-2011 respectively when data for those years was available. For a few sites with limited data, the averages were calculated from 1990-1991 and 2009-2010 data only. Finally, sites were grouped according to location for regional comparisons: Western, Mid-United States, and Eastern (general grouping provided in Figure 1; specific site names provided in Appendix 2, 4, and 6). We selected broad groupings based on their similar trends and out of necessity due to the limited number of sites with data for the entire period; Malm et al. (2004) suggest much more detailed regional classifications, which should be considered for shorter-term studies with a greater number of sites in the dataset.

2.3 Results and Discussion

Total aerosol loading has dropped significantly (up to 60%) from 1990-2010 across the rural United States (Figure 3; Appendix 3, 5, and 7). The decrease is observed across all species considered here: sulfate, nitrate, elemental carbon (EC), and organic carbon (OC). The largest changes occur in the Western and Eastern regions, where respective average decreases are 49% and 51%. In the Midwest, the average decrease is only 31%. Despite the significant drop in total aerosol loading, the fractional composition has remained relatively unchanged: the pie charts in Figure 3 show how the total amount of each aerosol species has decreased much more strongly than any of the slight compositional changes. Notably, the organic fraction has stayed relatively constant, meaning total organic aerosol (OA) is decreasing despite no direct regulations on OA emissions other than potential reductions in primary OA (POA) that arise from controls on total particulate matter (PM) concentrations.

Figure 4 show the changes in average concentrations of each aerosol species relative to their 1990 values and divided into the three major US regions. The Western sites have the closest tracking of all four species, with the largest changes in EC and nitrate. This is likely due to the Western sites being the closest to anthropogenic emissions and therefore reflecting the strong emissions controls on EC and nitrate. Additionally, the Western sites start out with the largest fraction of nitrate emissions relative to the other sites, and thus have the highest opportunity for emissions controls to significantly impact nitrate concentrations. Conversely, the Eastern sites see strong decreases in sulfate, OM, and EC with less change is nitrate. The strong decrease in sulfate in the Eastern US is expected due to historically high sulfate concentrations and thus high responses to anthropogenic sulfate emissions controls that have affected both stationary and mobile sources, especially with regards to coal combustion. The Mid-US sites exhibit the smallest decreases in aerosol species, which could perhaps be attributed to their initial total aerosol loadings being smaller than the coastal sites (4.3 $\mu g\ m^{-3}$ in West, 8.1 in East, and 2.7 in Mid-US; Figure 3) and therefore less responsive to emissions controls.

These results are consistent with other studies looking at aerosol composition and loading during similar time periods. Over the period of 2000 to 2013, which is equivalent to the second half of the period of data considered in our analysis, the US EPA (2014) measured an average decrease of 39% in total particulate matter (PM) in the regions we have classified as Eastern, 20% in the Western region, and 14% in the mid-US region. Murphy et al. (2011) found 25% decreases in rural EC and fine PM from 1990 to 2004 using IMPROVE data, and connected these changes to emissions reductions. Hand et al. (2012) used rural IMPROVE data, urban Chemical Speciation Network (CSN) data, and emissions reports from power plants to investigate sulfate ion and sulfur dioxide (SO_2) trends. They found that both sulfate concentrations and SO_2 emissions have been steadily decreasing from the early 1990s to 2010. This suggests a linear relationship between anthropogenic SO_2 emissions and measured sulfate concentrations, although some seasonal and regional trends were unexplainable with emissions data and therefore indicate other contributing influences (Hand et al., 2012). Hand et al. (2013) looked at total carbon (TC = EC + OC) and found that over the same period considered here (1990 to 2010), there have been widespread decreases in rural TC with more seasonal variability in the West as compared to the East. Other groups have also reported declines in EC in a variety of national networks (Chen et al., 2012; Blanchard et al., 2013). Blanchard et al. (2013) also report decreases in other important PM and gaseous species, including EC, organic matter, sulfate, nitrate, SO_2, oxidized nitrogen species (NO_y), carbon monoxide, and ozone, and link these decreases primarily to emissions reductions; for fine PM, they suggest the decreases are a result of reductions in primary PM, including EC and some OM, as well as reductions of gas precursors known to form particles. Blanchard et al. (2015) looked at urban data in the Southern region of the U.S. and attributed about half of the measured declines in OA to emissions reductions for combustion processes, including motor vehicle fossil-fuel use and biomass burning, based on similar declines in EC and related gaseous species. Nguyen et al. (2015) find similar decreases in aerosol liquid water content and particulate OC, and link this to the hypothesis of water facilitating biogenic SOA formation.

There are a number of potential mechanisms that could explain the observed decrease in total OA. For those we were able to investigate, an explanation follows this list. Many of the mechanisms will need to be considered from a modeling perspective or through greater data collection in order to determine their impact on the observed trends. Changes in any of the following factors could be responsible for the OA observations:

- **Biomass burning**: Fires release OC into the atmosphere, so a decrease in fire activity would result in lowered emissions of OC and thus lower OA concentrations.
- **Meteorology**: Biogenic emissions increase with temperature; a decline in temperatures could lead to a decrease in OA precursor emissions. Rainfall represents a significant aerosol deposition process, so increases in frequency and amount of rain could drive the decreased concentration of OA. Another meteorological phenomenon that could contribute to the observed OA decreases is relative humidity (RH): declines in RH would lower the water content of inorganic aerosol, which could lead to lowered partitioning of water-soluble gas-phase species into the particle phase.
- **Land use**: Biogenic emissions depend on vegetation type and amount, so changes in land use such as deforestation or reforestation could alter total VOC emissions and the composition of those emissions. Decreased VOCs concentrations, especially of species with high SOA yields, could be responsible for the observed decrease in OA.
- **Oxidant concentrations**: Decreases in oxidants such as ozone and hydroxyl radicals would decrease the oxidation of OC and therefore be expected to result in lower total OA.
- **Primary OA emissions**: If regulations that control particulate matter, like black carbon, have also led to decreasing emissions of primary OA, this could contribute to the observed decline in measured OA.
- **Secondary OA formation**: Secondary OA (SOA) is formed from both anthropogenic and biogenic emissions of VOCs. Decreases in SOA could be due to reduced VOC emissions (lowered precursor concentrations would lead to reduced SOA formation), changes in aqueous aerosol content (it has been proposed that sulfate oxidation of VOCs can occur via aqueous phase chemistry; Xu et al., 2014), or other effects on

anthropogenic-biogenic chemistry. Reductions in anthropogenic emissions of species like NO_x, SO_x could potentially alter the oxidation and formation of SOA, or indirect reduction of anthropogenic VOCs in tandem with emissions regulations on other species could decrease the precursors available for SOA formation.

Characterizing the extent to which any of these factors contribute to the observed trends is beyond the scope of this work and would likely require extensive modeling. However, we can begin to address the likelihood that some of these factors contributed to the trends by analyzing the existing data for trends in biomass burning markers, weekday/weekend effects, and sulfate and organic measurements.

Changes in biomass burning could alter OA formation, but this is unlikely to explain our observations due to the removal of large fire events from the data set. Additionally, Figure 5 shows that while potassium, a marker for biomass burning, and OA mass have similar trends, the total fire acreage burned in the US has increased over this period and thus would be expected to cause an increase in OA, not a decrease as observed. Spracklen et al. (2007) also found an increase in wildfire area burned between 1989 and 2004 with large inter-annual variability and a corresponding increased summer OC concentrations. Thus, although we cannot use our data to definitively rule out a change in biomass burning as a contributing factor to the observed changes in OA, it seems unlikely to be the reason OA has declined over this period.

To consider the influence of anthropogenic emissions, we separated changes in organic mass (OM) and elemental carbon (EC) by their weekday and weekend effects. The weekday was defined as Thursday + Friday and weekend was defined as Sunday + Monday based on work by Murphy et al. (2008). This division helps adjust for transport time for anthropogenic influences to reach these remote regions and accommodates the shifted anthropogenic activity in national parks relative to the normal urban classification of weekday-weekend. Because of a sampling frequency shift in 2000 that provided more data for the weekday/weekend split, the trend is shown for post-2000 only. As Figure 6 shows, the fractional decrease is stronger for both EC and OM on the weekdays than it is on the weekends. There is a larger weekly cycle for EC as demonstrated by the larger gap in trend lines; the stronger weekly cycle in EC as compared with OM is consistent with Murphy et al. (2008), who also found a pronounced weekly cycle in nitrate similar to EC but no weekly cycle in sulfate. The similar behavior in EC and OM, as well as nitrate, could indicate an anthropogenic mechanism controlling the observed decrease in OA. Perhaps emissions reductions that controlled black carbon could have resulted in a similar, unintentional reduction of organic particulates. Or perhaps there was a reduction in SOA due to reductions in more chemically active particulate species like sulfate and nitrate, which have similar trends as the EC due to shared anthropogenic sources. For example, it has been shown that NO_x can drive SOA production from isoprene in urban regions; this mechanism could be particularly influential in the Western region where NO_x concentrations are the highest in the U.S. and many sites are in close proximity to urban influences (Lin et al., 2013). Other groups have suggested alternate mechanisms by which anthropogenic emissions can influence biogenic SOA formation (Carlton et al., 2010; Hoyle et al., 2011; Schindelka et al., 2013). Regardless of the mechanism, the presence of a weekday/weekend cycle in OA suggests that a significant portion of the OA is either anthropogenically emitted directly or else influenced by anthropogenic emissions via secondary pathways.

One potential secondary pathway is the sulfate-particulate water-organic mechanism. Modeling results suggest that sulfate increases the particulate water content and thus the partitioning of organics into aerosol (Carlton and Turpin, 2013); therefore, recent reductions in sulfate emissions might have driven the similar reduction in OA formation. Figure 7 shows how decreases in the total amount of sulfate and OM are correlated non-uniformly across the country. The correlations might be explainable by the Carlton et al. modeled mechanism, but the non-uniformity in this dataset could indicate a non-linear feedback of sulfate concentrations on OA. The recent reductions in sulfate emissions could be contributing to the reduction in OA formation either indirectly, through chemistry such as water partitioning, or directly, via simultaneous emissions reductions of organics along with directly regulated species. If emissions controls, which have reduced anthropogenic contributions to aerosol, have decreased OA loading as well, this would be a highly noteworthy unintended consequence of the regulations.

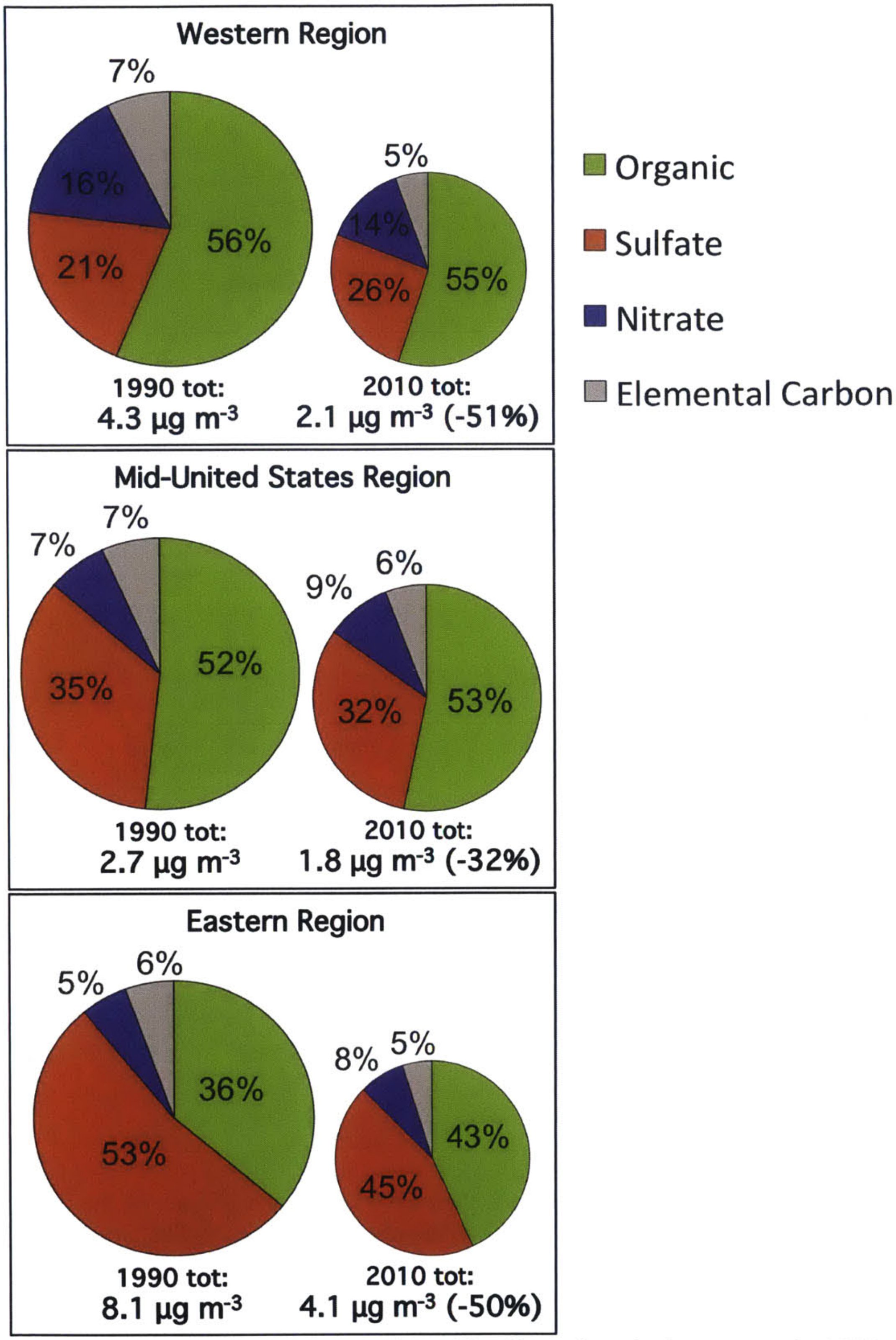

Figure 3: Average composition and total loading of particulate matter in 1990 and 2010 across the rural United States.

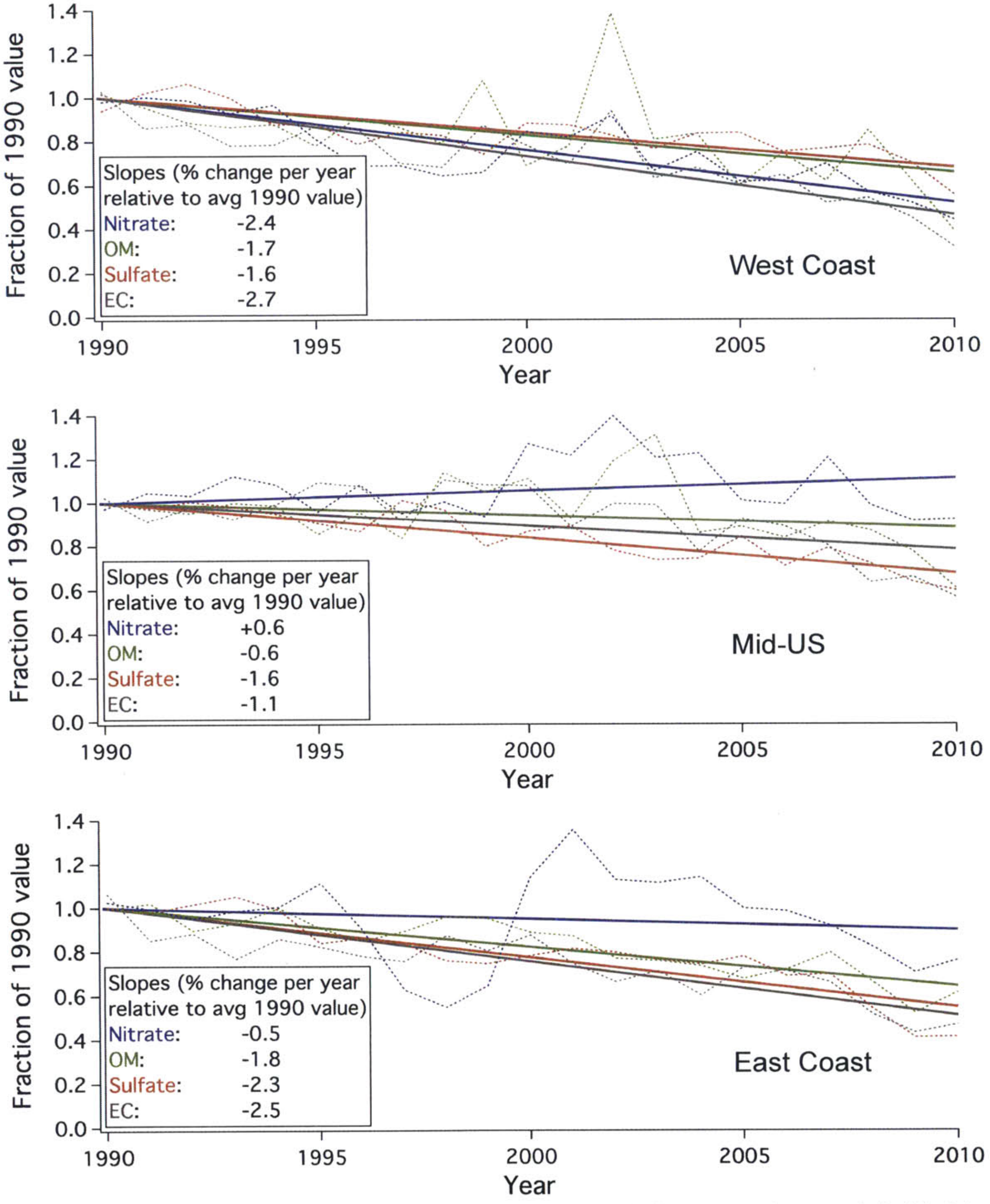

Figure 4: Average trends in aerosol species relative to their 1990 values and divided by the three US regions. The West and East coast regions had a 50% decrease in total aerosol between 1990 and 2010, whereas the Mid-US had a smaller average decrease at 30%. Organic aerosol mass decreased at an average of nearly 2% per year on the coasts and 0.6% per year in the mid-US.

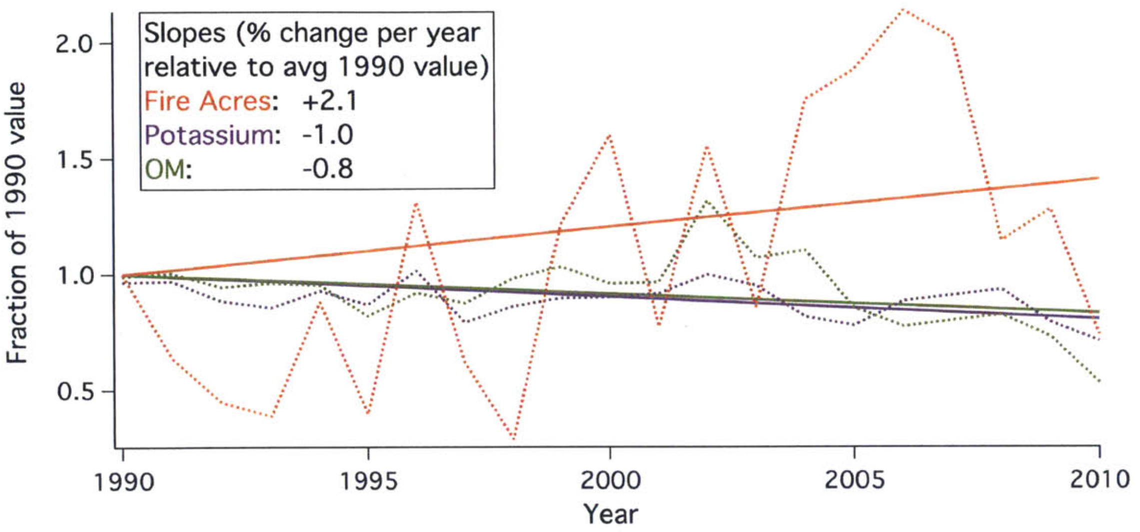

Figure 5: A comparison of organic mass and potassium with fire acres burned across the US to investigate a potential biomass burning influence on OM trends. The similar percentage decrease in potassium and OA mass indicates a possible connection, but the increase in total fire acreage burned in US suggests biomass burning may not be responsible for organic decrease. (Fire data: National Interagency Coordination Center).

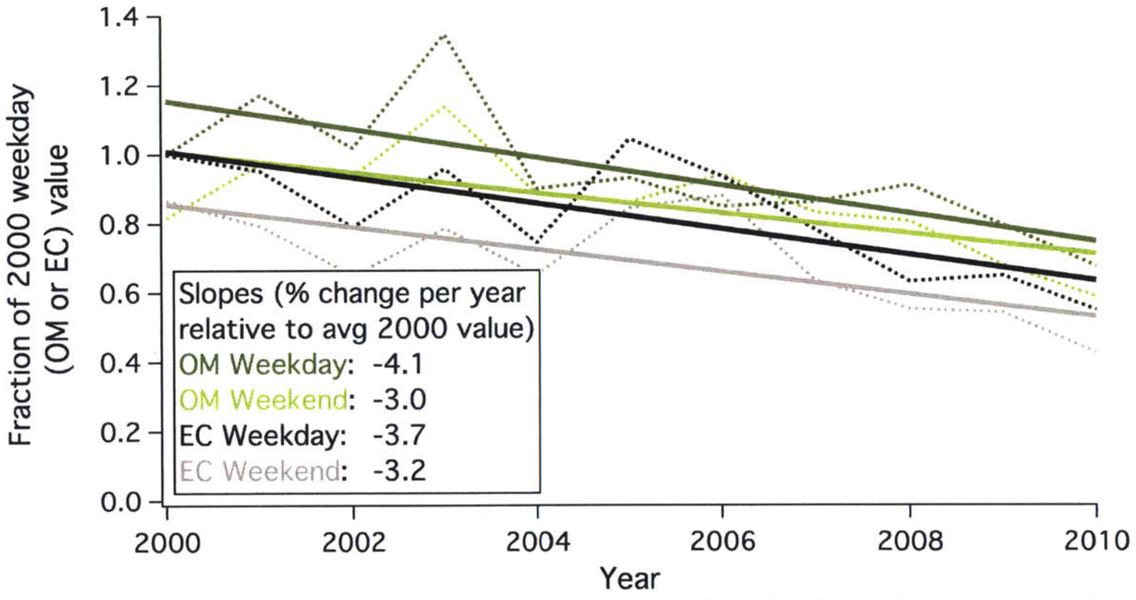

Figure 6: Average weekday (Th+F) and weekend (Su+M) effects for all sites with data from post-2000 due to the sampling frequency shift in 2000.

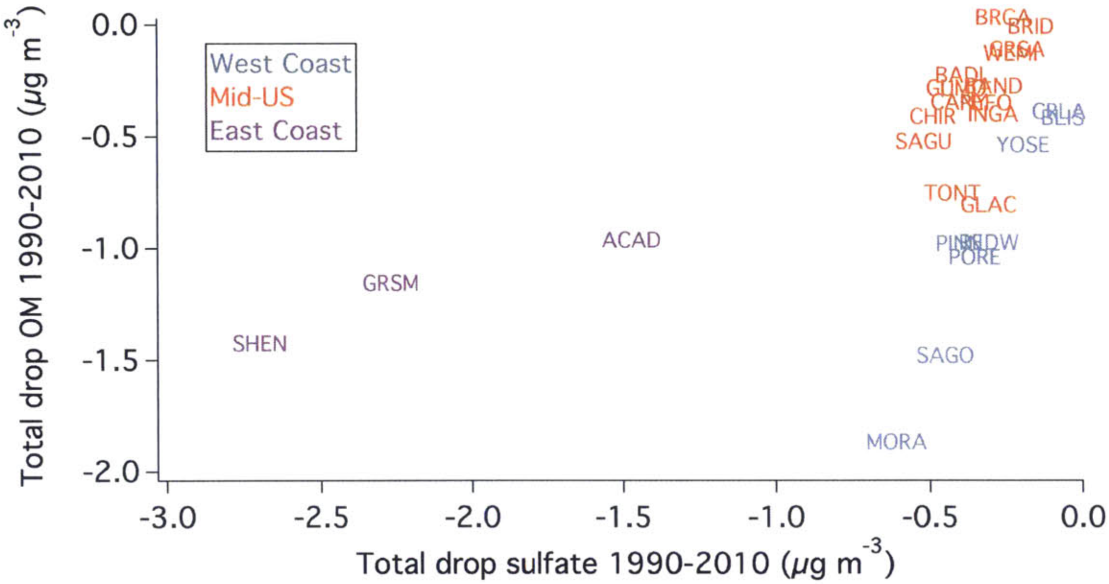

Figure 6: A comparison between the total drop in organic mass with the total drop in sulfate over the 1990-2010 period. Regions are color-coded. Each of the regions has a unique slope associated with the correlated drop in species, suggesting non-uniform behavior across the country. Each point is identified by its site abbreviation (Appendix 1).

2.4 Conclusions

Examining existing data from the IMPROVE network allowed us to characterize the historic trends in aerosol. Over the period 1990 to 2010, total aerosol loadings decreased by an average of 30-50% across the rural United States. While the total loading decreased, the fractional composition remained relatively constant. Notably, the organic aerosol (OA) contribution decreased along with sulfate, nitrate, and elemental carbon (EC) species despite emissions regulations that control only total particulate matter, not OA directly, and certainly not secondary OA.

Potential factors controlling the observed decrease in OA are changes in biomass burning, meteorology, land use, oxidant concentrations, primary OA (POA) emissions, and secondary OA (SOA) formation. Using the existing data, we were able to show that biomass burning is unlikely to be a controlling factor, and that anthropogenic emissions are probably related to the OA decrease due to the similar weekday-weekend trends in EC and OA as well as the similar relationship between sulfate and OA declines. Modeling results have suggested that biogenic SOA can be controlled up to 50% by anthropogenic emissions (Carlton et al. 2010); therefore, it is possible that recent decreases in anthropogenic emissions could have resulted in a decrease in measured SOA from both anthropogenic and biogenic emissions. Additionally, most rural OA has been shown to be predominantly secondary (Brown et al., 2002; Zhang et al., 2007), which suggests that the factors controlling OA trends are likely not associated with POA emissions and instead related to factors that control SOA. If changes in anthropogenic emissions were indeed one of the contributing factors, this would indicate that emissions controls have been responsible for greater air pollution control than intended. However, better characterization and explanation of the factors controlling OA trends will require extensive modeling that is outside the scope of this study.

The work in this chapter provides motivation for the next chapter, where we develop an instrument to analyze small filter extractions. IMPROVE data is constrained to basic, aggregate measures of aerosol components. Analyzing this data allowed us to consider trends in total OA, but makes it difficult to understand precisely what is going on with the organic component: what types of organic aerosols are decreasing? What is the cause of this decrease? Can we describe the chemical composition changes due to changes in emissions or chemistry? These questions led us to develop the Small Volume Nebulizer (SVN), which will allow for the future expansion of the existing historical aerosol dataset by making it possible to collect detailed chemical composition data from archived filter samples.

3. Development of a nebulization technique for obtaining AMS spectra from small volume liquid samples

3.1 Motivation

Atmospheric particulate matter (aerosol) is well understood to degrade air quality and alter the radiative balance of the atmosphere, but direct characterization of aerosol effects is difficult due to variances in aerosol reactions, composition, and spatial distribution. In particular, organic aerosol (OA) contributes significantly to this uncertainty. OA averages between 20 and 60% of aerosol mass worldwide (Zhang et al., 2007) and consists of thousands of different organic compounds (Goldstein and Galbally, 2007). Despite its prevalence and importance, OA remains difficult to capture in models. Model predictions of OA can be off by a factor of up to 100, significantly under-predicting the contribution due to secondary OA (Heald et al., 2005) and hindered by our limited understanding of the complex OA chemistry and historical aerosol trends with which we could calibrate the models.

Addressing the uncertainty in OA chemistry and composition, online aerosol mass spectrometry (AMS) measurements provide important insights into the chemical composition of particles. AMS deployment, however, is costly and restricted to a single location or field campaign. Conversely, filter samples are routinely collected across the country and often around the world, but analyses generally do not provide the same information (e.g., elemental ratios) given by the AMS. Bridging the gap between techniques, and taking advantage of the valuable insight provided by the AMS and the ease of filter collection, filter extracts offer an opportunity to expand the spatial and temporal coverage of the AMS.

In order to analyze filter extracts on the AMS, we need a technique that produces aerosol particles from small liquid samples. Traditional AMS measurements require atomization of sample volumes on the order of milliliters, but filter extracts typically produce volumes on the order of microliters, especially if they must be concentrated. Here, we introduce the Small Volume Nebulizer (SVN): a nebulization technique that requires only a few microliters to characterize a sample. This technique allows us to gain valuable AMS information from small environmental samples and thus lends itself to a variety of useful and novel applications.

3.2 Methods

3.2.1 Small Volume Nebulizer

The Small Volume Nebulizer (SVN) coverts microliter-sized liquid samples into aerosol droplets, which allows for their introduction into the Aerodyne aerosol mass spectrometer (AMS) for chemical analysis. The technique expands analysis of liquid samples to encompass volumes too small for standard atomization. The SVN is cased in PVC and is cylindrically shaped at 8cm tall with an outer diameter of 4.5cm and an inner diameter of 1.75cm where the tube connects at the top; Figure 8 shows a schematic of its structure. The primary nebulization mechanism works via a vibrating gold plate (Sonaer 2.4MHz nebulizer module with 24Au crystal) whose ultrasonic vibrations transmit through a reservoir of water and a 0.001" thick film of Kapton Polyimide, which is stretched over the reservoir of water, to nebulize liquid droplets placed in the center of the film. The vibrations are controlled via an on-off depressor switch. Clean house air input at 160 sccm through two side ports directs nebulized particles up the glass tube and into the HR-ToF-AMS. The glass tube was wrapped with Teflon tape around the bottom to seal the airflow. The Kapton Polyimide film was wiped with a Kim Wipe as necessary and rinsed clean with methanol before each series of runs. The glass tube was rinsed with hexanes, dichloromethane, and methanol between uses.

Other films were tested, including 0.0005" polyester film and 0.002" thick Teflon RPTFE film, but these were found unsuitable for the following respective reasons: too much organic contamination and too thick to transmit enough ultrasonic vibrations to nebulize the droplet. An additional film, 0.001" thick FEP film, was found to be suitable for use but was not selected because the clear film color diminished droplet visibility and made it difficult to detect when nebulization was complete. Results from the testing of these additional films are provided in Appendix 9 through 12.

A sample droplet size of 8μL was experimentally determined to maximize signal, and the minimum observable sample concentration was determined to be ~0.15 g L^{-1} (Figure 10 in Results). Droplets are placed on the film by lifting the glass tube and using a 10 μl syringe to inject the sample onto the center of the film. The glass tube is fitted back into place, we wait ten seconds to allow any room air to flush out of the system, and then AMS collection is started. In the original collection timing, droplets were nebulized once the "open" runs began and the entire signal was measured in "open." In the subsequent collection timing, droplets were nebulized once the "open" runs began but the signal was measured in both the "open" and "closed" settings. MilliPore water droplets are used as the initial runs and between each sample as a blank to verify that no particles remain on the film between samples. Each sample is run at least three times to account for variability in total signal between runs and to check sample consistency.

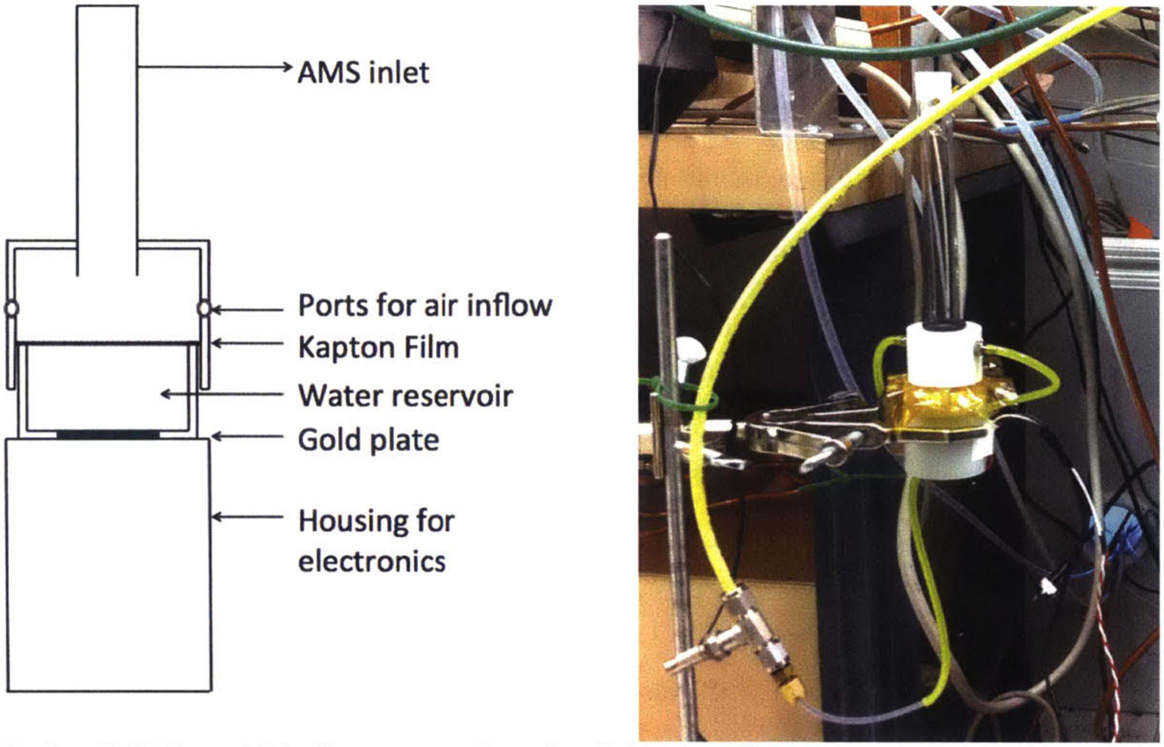

Figure 7: Small Volume Nebulizer set up. For simplicity, the illustration does not show the air lines connected to the ports, nor the depressor switch connected to the electronics that control gold plate vibrations.

3.2.2 Standards and Sample Generation and Storage

Both organic and inorganic standards were mixed in lab with MilliPore water (MilliQ) to characterize the Small Volume Nebulizer (SVN). Solutions of the following standards were mixed to 1 g/L: ammonium sulfate, ammonium nitrate, sucrose, citric acid, and a mixture of the organic and inorganic compounds. Some additional concentrations of these solutions were also tested to characterize signal-response behavior. All equipment was cleaned with a hexane mixture, dichloromethane, and methanol solvents. When possible, equipment was also combusted at 500°C for eight hours.

Online AMS measurements were taken from a 7.5 m^3 experimental UV-chamber with simultaneous filter collection of particles for comparison using our offline technique. Hunter

(2015) has described the chamber in detail; briefly, it is made of 0.005 inch thick perfluoroalkoxy (PFA) Teflon film and maintained at a constant temperature of 20°C during experiments. Particles were collected on PTFE Zefluor Membrane filters with pore size 0.5 μm using a filter sampler with a vacuum pump pulling 1 lpm for approximately 3 to 8 hours depending on experimental duration. The filter extraction method is shown in Figure 9. Filters were extracted in either MilliPore water or ultra pure methanol, and then sonicated in room temperature water for 45 minutes. Sonicated samples were blown dry under a gentle stream of dry nitrogen and reconstituted with 50-200 μL of either MilliPore water or 50:50 (v:v) water and methanol to reach an estimated concentration greater than 0.15 g L^{-1}, the experimentally determined minimum concentration for detection (Figure 10). Filters were stored in combusted aluminum foil and extractions were stored in combusted glass vials; these were placed in either a 4°C refrigerator or −20°C freezer for storage.

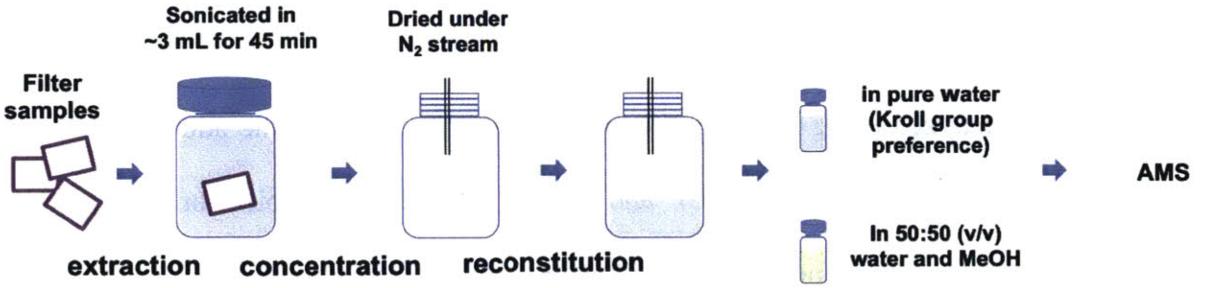

Figure 8: Extraction method for filter samples during solvent reconstitution tests. The top pathway, where samples are reconstituted in pure water, was selected as the ideal pathway for SVN measurements. (Figure modified from Surratt group.)

3.2.3 Data Collection and Processing

Detailed particle information, including the identity of individual ion peaks, was measured using an Aerodyne high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) that works via electron impact ionization at 70 eV (Drewnick et al., 2005). The HR-ToF-

AMS provides valuable information about the mass concentration and elemental composition of non-refractory particulate matter; notably, this includes organic, sulfate, nitrate, and ammonium chemical families. Using HR-ToF-AMS data, we are able to calculate important elemental ratios such as oxygen-to-carbon (O/C) and hydrogen-to-carbon (H/C) for the characterization of samples.

For this technique, the HR-ToF-AMS samples in Fast MS mode. Whereas normal MS collects both open and closed signal during a single run and averages these signals to produce a difference mass spectra for that run, Fast MS collects only open or closed in a given run, and must subtract an integrated closed signal across the open runs to get a difference spectra. The original procedure consisted of 1 second run saves (cycle of 6s closed, 40s open, 6s closed). Nebulization occurs for ~10-15s during first few open runs. A modified procedure was later developed with 0.5 second run saves (cycle of 3s closed, 10 open, 3 closed) to allow the HR-ToF-AMS to collected both open and closed data for each nebulized sample, enabling better background signal subtraction.

Data was analyzed using WaveMetrics IGOR Pro software with the add-ons ToF-AMS Analysis Toolkit v1.56D (SQUIRREL) and v1.16 (PIKA), available for download at <http://cires1.colorado.edu/jimenez-group/ToFAMSResources/ToFSoftware/>.

3.3 Results and Discussion

3.3.1 Technique Characterization

The optimal sample volume to be placed on the Small Volume Nebulizer (SVN) film was determined to be 8 μL after a range of droplet sizes (4 to 16 μL) were tested at constant concentration (Figure 10). This test used a filter extract from a decyl-2-nitrite + NO chamber experiment. The filter extract had a total concentration of 0.29 g L^{-1} and an organic-to-sulfate ratio of 1:6, as calculated based on the online chamber AMS data. Additional data for the 10 μL droplet size, where the concentration was 1 g L^{-1} for two separate standards of ammonium sulfate and sucrose, is plotted with a black border. The duration of the signal from a nebulized droplet remained consistent for all droplet sizes. The 8 μL droplet size was selected because it produced the highest peak concentration in the AMS and also kept the volume sufficiently small to allow for multiple runs of limited-volume environmental samples.

The minimum concentration for AMS detection of a nebulized 8 μL drop was determined to be approximately 0.66 μg. A 1:1 (m:m) solution of ammonium sulfate and sucrose was run on the SVN at a range of concentrations to characterize the minimum concentration and ideal droplet size for running samples on the SVN. Figure 10 shows the results from these tests, where the concentration and droplet size are multiplied to calculate the nebulized mass and compared to the mass observed in the AMS, which is found by integrating under the signal curve. The minimum nebulized mass for detection of an 8 μL drop in the AMS was determined to be approximately 0.66 μg for sulfate and 1 μg for organic species. This corresponds to a minimum concentration of ~0.08 g L^{-1} for sulfate and ~0.125 g L^{-1} for organic. Thus, reconstituted samples should target concentrations above 0.125 g L^{-1}, preferably by at least a factor of two for optimal detection, and especially when the sample is expected to be mainly organic in composition.

This technique currently has a 10^3 mass loss factor from the mass in the nebulized drop to the mass observed by the AMS. The AMS detects signal that is 1000 times lower than the signal that would be expected from the total dissolved mass in the drop (Figure 10). This large mass loss factor limits our detection ability and greatly increases the necessary minimum concentration in a given sample. Additionally, for a given concentration or droplet size, signal varies by a factor of up to 10. This presents a challenge for quantification when the concentration of the solution is unknown, and suggests a need for the addition of a standard at known concentration if quantification is desired when running environmental samples on the SVN. Despite the large mass loss and the variability in absolute signal, however, composition measurements are quite constant: organic/sulfate is 1.91+/-0.05 for all experiments above minimum signal (>0.66 μg entering AMS at an organic-to-sulfate ratio of 1:1 in the solution). Therefore, although total signal on the SVN can vary by an order of magnitude, the technique produces consistent composition measurements for the same nebulized solution.

Both the total mass loss and the signal variability are likely dominated by droplet splatter to walls. When a droplet is nebulized, it forms both fine particles and smaller droplets. Most of these droplets adhere to the walls of the glass tube, significantly reducing the amount of mass entering the AMS. This loss of liquid mass to the walls is highly visible in the glass tube and is believed to be the major contributor to the 10^3 mass loss factor. Similarly, the signal variability is likely controlled in large part due to inconsistencies in nebulized droplet formation and therefore differences in adherence to the walls. Both of these effects suggest the need for droplet splatter reduction to improve quantification and the sensitivity of the technique. Design modifications to reduce droplet splatter are discussed in the conclusion section.

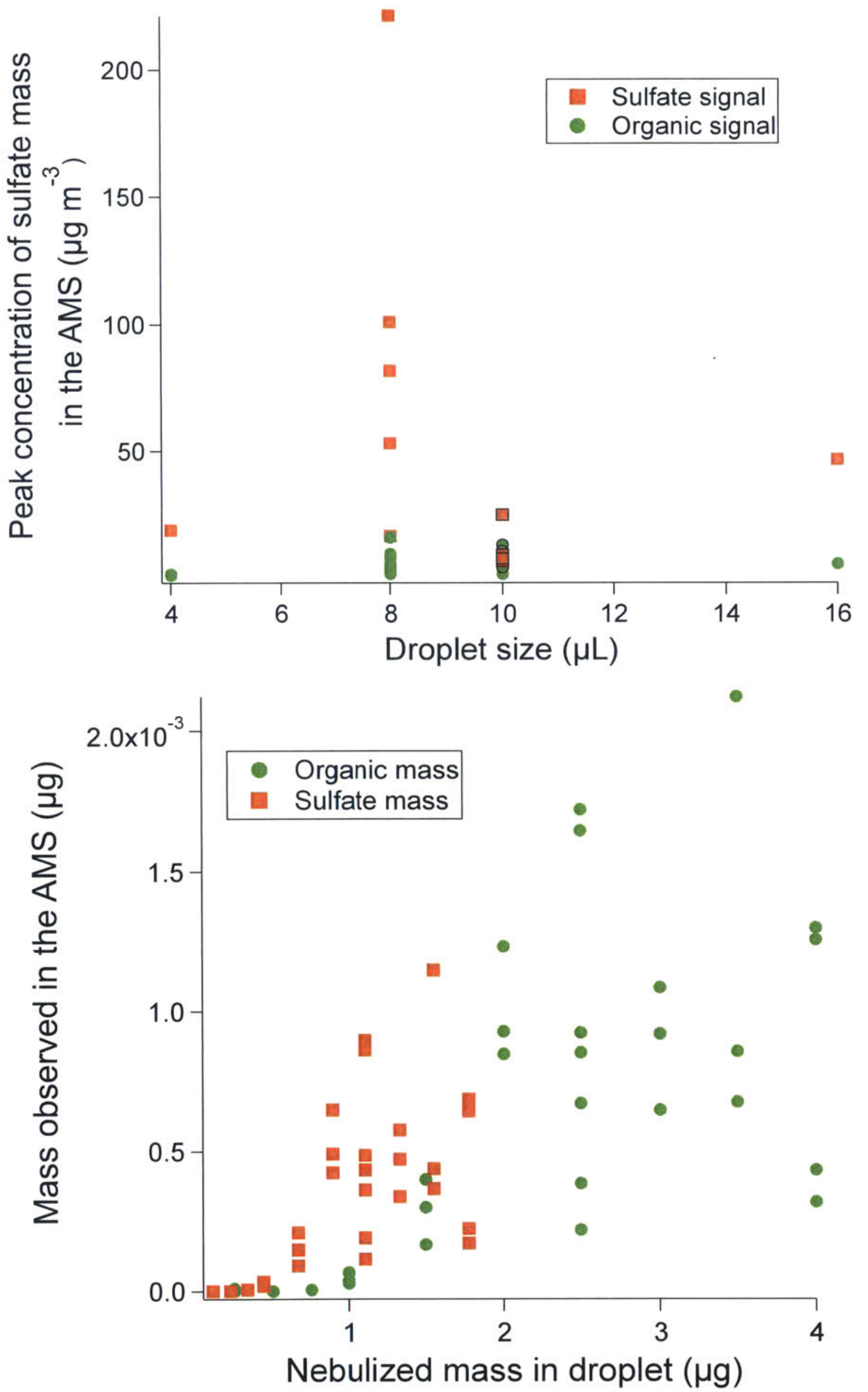

Figure 9: In (a), the peak concentration observed in the AMS is plotted against the droplet size nebulized on the SVN for a sample with total concentration 0.21 g L^{-1} and an organic-to-sulfate ratio of 1:6. The black-lined points at 10uL are from two standards, ammonium sulfate and sucrose, each with a concentration of 1 g L^{-1}. The droplet size of 8 µL was chosen to maximize signal. In (b), the total mass observed in the AMS is plotted against the nebulized mass in the droplet, where all droplets were 8 µL in volume. We see that as nebulized mass increases, the observed mass also increases – but with a factor of 10^{-3} mass loss.

3.3.2 Comparison with Standard Atomization

The SVN was compared with a standard atomizer (TSI) to characterize its accuracy in producing expected mass spectra. Three standard solutions, each with a concentration of 1 g L^{-1}, were made of ammonium nitrate, ammonium sulfate, and sucrose. These standards were run on the respective techniques and introduced into the AMS to produce mass spectra for comparison. Results are shown in Figure 11 and Table 2

Comparing the mass spectra for each standard on the SVN and the TSI atomizer suggests that SVN nebulization produces particles of similar composition and elemental ratios to atomization. As shown in Table 2, the two methods agree strongly for the ammonium-to-nitrate ratio (NH_4/NO_3), which is higher than the actual solution ratio for both methods. The agreement between the SVN and the TSI suggests the ratio difference might be an instrument-specific error of the AMS, perhaps caused by an error in the relative ionization efficiencies of the species. The two methods agree within error for the ammonium-to-sulfate ratio (NH_4/SO_4), and the actual solution ratio is lower than that of atomization but falls within range for nebulization. These results suggest that small samples run on the SVN will produce mass spectra that are very similar to the spectra we would expect from running the same samples on the TSI atomizer, and that knowing how they reproduce spectra relative to known original solutions – i.e. how they increase or decrease ratios of species – will help us characterize unknown solutions.

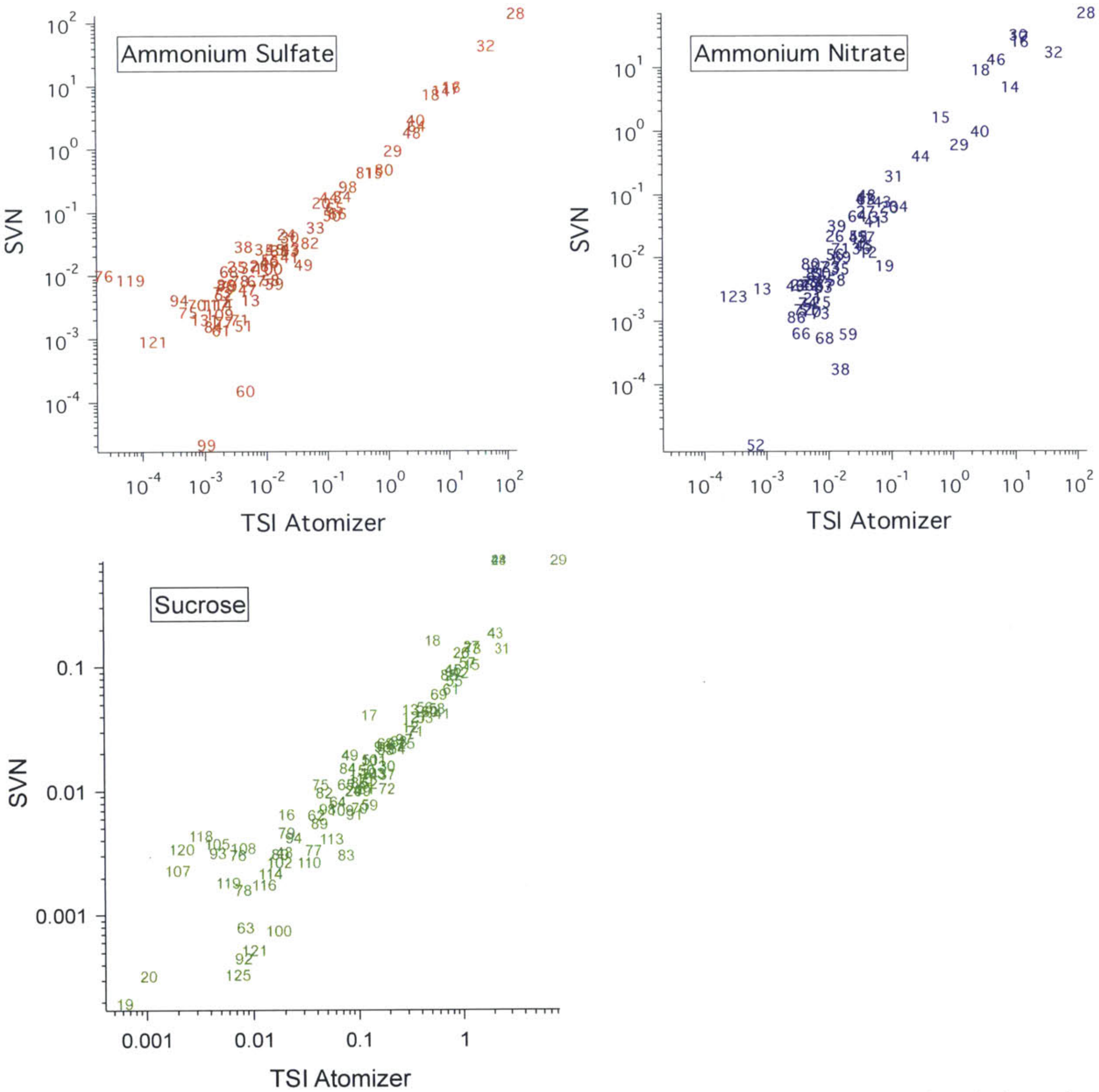

Figure 10: A comparison of the SVN technique to the TSI Atomizer. For each solution, the mass spectra are plotted against each other with the number representing each mass-to-charge (m/z) value.

Table 2: Ammonium-to-nitrate and ammonium-to-sulfate ratios for the solution, the TSI atomizer, and the SVN nebulization technique.

Ratio	Actual	Atomization	Nebulization
NH_4/NO_3	0.28	0.32 ± 0.01	0.31 ± 0.02
NH_4/SO_4	0.38	0.45 ± 0.03	0.38 ± 0.07

3.3.3 Determination of the Optimal Sample Solvent

We tested ultrapure methanol and MilliPore water as potential solvents for solutions and extracts run on the SVN. Three cases were tested: (1) ultrapure methanol, (2) MilliPore water (also known as MilliQ), and (3) a 1:1 (v:v) mixture of the two solvents. For each case, we nebulized a solvent blank and a solution of ammonium sulfate + organic species (sucrose or citric acid). When methanol was used alone both in the blank and as the solution solvent, the drop did not appear to nebulize and no signal was observed in the AMS. Conversely, the other two cases produced an AMS signal but the MilliPore water blank was much lower in contamination relative to the 1:1 solvent blank, which showed significantly elevated methanol peaks at m/z 15, 29, and 31 (Appendix 13). When these solvents were used in the ammonium sulfate + organic solutions, a 2-4 times higher signal was produced with the MilliPore water alone as the solvent as compared to the 1:1 mixture of MilliPore water and methanol, and the 1:1 mixture showed elevated methanol peaks (Appendix 13).

To determine the size range of particles produced, particle time-of-flight (PToF) measurements were taken for the two cases that produced an AMS signal: MilliPore water and the 1:1 mixture of MilliPore water and methanol. Results are shown in Figure 12. In both instances, nebulization of these solvents produces particles whose sizes fall within the range of AMS detectability (diameter between 50 nm and ~1 μm; Canagaratna et al., 2007). For the 1:1 mixture, the particle size distribution shifts to slightly lower diameters and total signal is also lowered.

The analysis performed here indicates that MilliPore water is the best solvent for use on the SVN. Methanol is not suitable due to its inability to produce any AMS signal, which could potentially be due to methanol's lower viscosity that makes particle formation during nebulization less favorable. The other two cases, MilliPore water and the 1:1 mixture of water and methanol, both produce particles in the appropriate size range for AMS detection. However, the elevated methanol peaks in the 1:1 mixture present a complication for analysis because they inaccurately inflate the total organic measurements and organic-to-sulfate ratios. Solutions made with MilliPore water as the sole solvent do not show this contamination and, furthermore, produce a higher signal on the AMS relative to 1:1 mixtures, increasing the technique's sensitivity to low-concentration samples. Thus we determined that MilliPore water is the best solvent for mixing standards and filter extract reconstitutions.

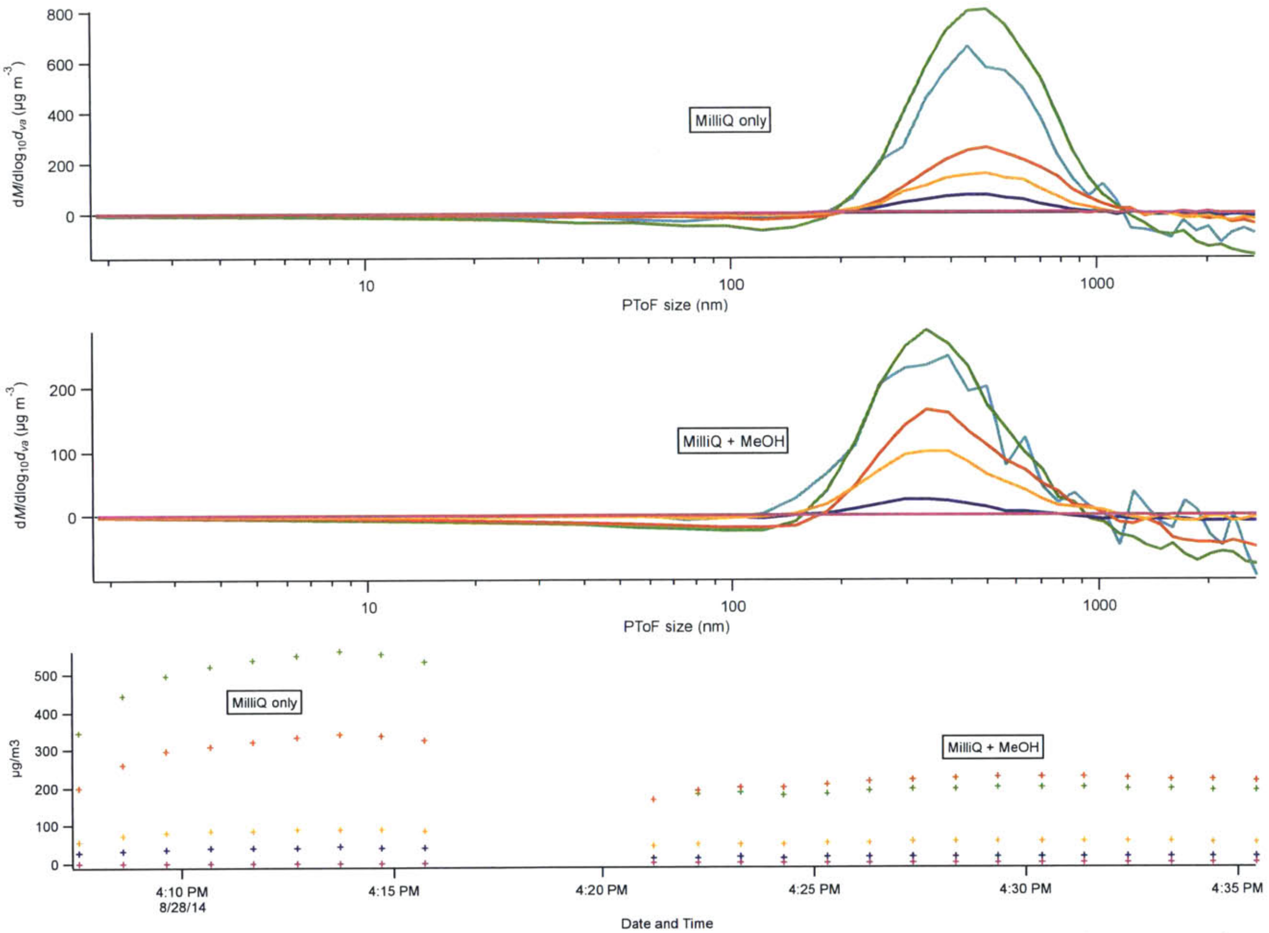

Figure 11: Particle time-of-flight (PToF) data showing particle size produced on the SVN when the solution is (a) MilliQ water only, or (b) a 1:1 mixture of MilliQ water and methanol. In (c), we see a decrease in observed signal when methanol is included in the solution.

3.3.4 Testing Laboratory SOA

Filters collected from laboratory chamber studies allow us to compare online and offline spectra to demonstrate that filter extracts nebulized with the SVN can be used to replicate the sampled air particles. While running a standard alpha-pinene and ozone SOA chamber experiment, we collected chamber air on a Teflon filter. The filter sample was extracted in 4mL of methanol, sonicated for 45 minutes, blown dry under a gentle stream of clean air, and reconstituted in 0.7mL of MilliQ before nebulization. Comparing the mass spectra (Figure 13) suggests that particles generated from the filter extract generally match the original chamber particles, although low signal may be responsible for noise in the organic spectrum and HR analysis reveals an alkane contamination from an unknown source. The sulfate spectra are very similar between the chamber and the extract, showing that the relative concentrations of different mass-to-charge values stay the same.

Although the spectra for organics and sulfate mostly agree between the online and offline measurements when considered separately, the organic-to-sulfate ratio is 9.5 ± 0.5 in the online chamber measurements and 21.3 ± 5.7 in the offline filter extract measurements. The elevated organic-to-sulfate ratio in the extract relative to the online measurement suggests either organic contamination, less efficient sulfate collection, or loss of sulfate during the extraction-nebulization-measurement process. It is possible that during chamber experiments, organic compounds coat the sulfate particles and help them enter and be measured in the AMS, whereas the filter extraction process may separate organics from the sulfate, and thus nebulization may produce particles of different compositions relative to the chamber. Then, if sulfate particles are not coated by organics and therefore more susceptible to "bounce" in the ionization process, they may not be measured at the same rate in the extract as they were in the chamber. Nevertheless, the SVN produces consistent results for every nebulized drop of a given solution, so correcting for differences in species' recovery and measurements may simply require applying an accounting factor.

A second comparison of online and offline techniques was performed for chamber studies of SOA from isoprene epoxydiols (IEPOX). In this case, two separate experiments that had the same IEPOX SOA were run: one with an Aerodyne Aerosol Chemical Speciation Monitor (ACSM) measuring in real time, and one with a filter collecting aerosol for later study on the AMS. A comparison of the normalized mass-to-charge values for the two instruments is shown in Figure 14. Mass-to-charge values at 16, 17, and 18 represent aerosol water and are elevated in the ACSM spectrum relative to the AMS spectrum due to differences in how each instrument calculates the fraction of measured water that can be attributed to aerosol. Mass-to-charge values at 15, 29, and 31 represent methanol peaks and are elevated in the AMS spectrum due to the use of methanol in the filter extraction solvent. Aside from these differences, the two techniques have very similar spectra. The agreement shown in Figure 14 indicates that filter extracts nebulized into the AMS via the SVN can suitably represent online spectra collected online by a similar mass spectrometric instrument.

Using filter extracts to characterize aerosol requires an appreciation for the potential weaknesses of the offline technique. There may be lower volatility organic compounds that would be directly measured in the AMS but that are lost in the offline process. Potential losses of organic compounds could occur during filter collection if the steady airflow and pressure difference on the other side of the filter caused species to re-volatilize. Other losses could occur during transport due to high temperatures or during storage, if the filters are not stored at sufficiently cold temperatures (ideally -20°C). Losses could also occur during the extraction process, whether compounds stayed on the filter and did not dissolve in the solvent or volatilized out of the solvent after extraction. Comparing online AMS measurements of laboratory generated SOA with nebulized filter extracts from the same experiment can help characterize some of these particle losses, but scaling these losses to actual environmental samples where online measurements were not taken will be an important area for consideration when presenting results using this technique.

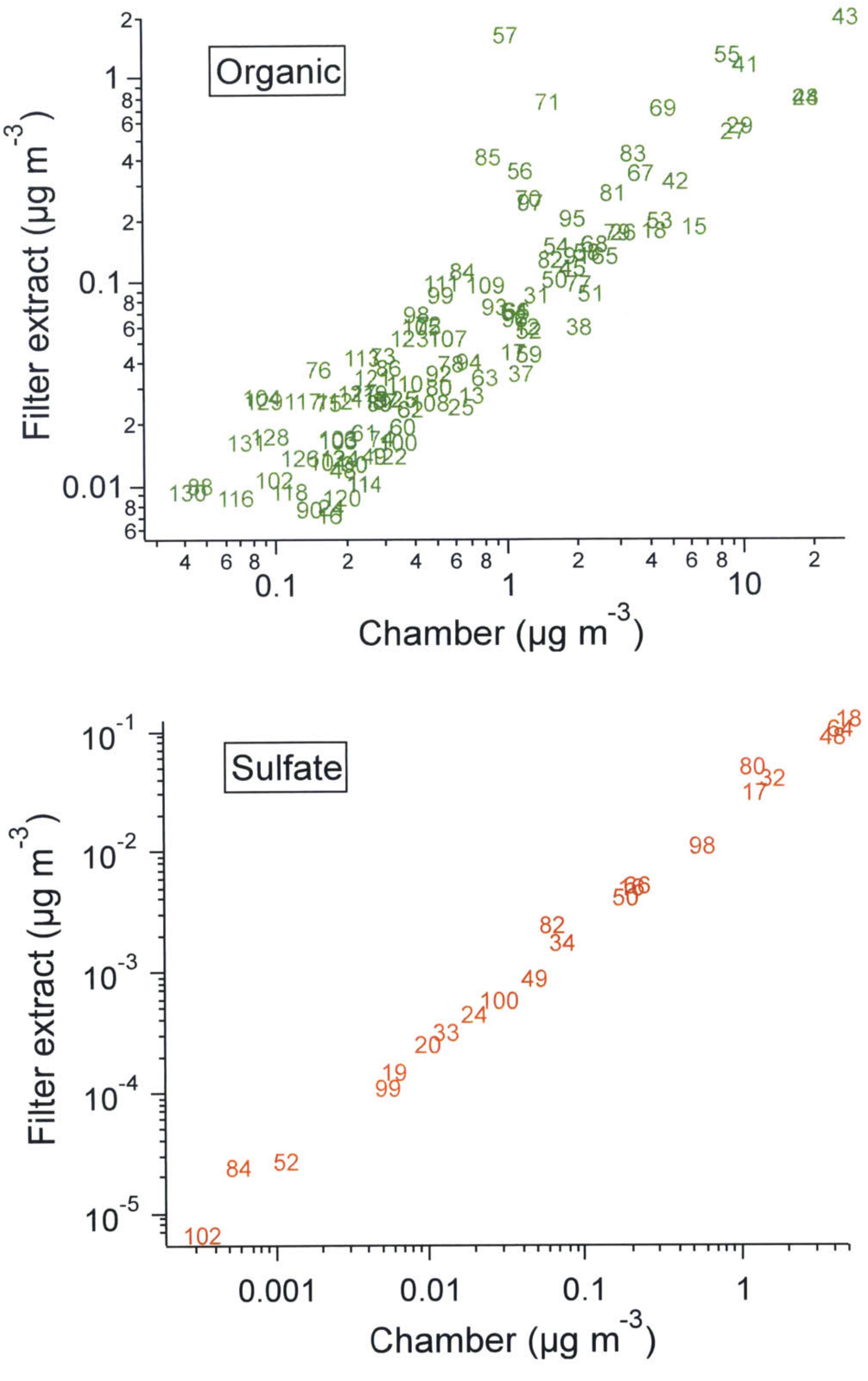

Figure 12: A comparison of offline AMS measurements of filter extracts on the SVN with online AMS measurements directly from the chamber for the same alpha-pinene + ozone SOA experiment. Mass-to-charge values are plotted for both organic and sulfate aerosol species.

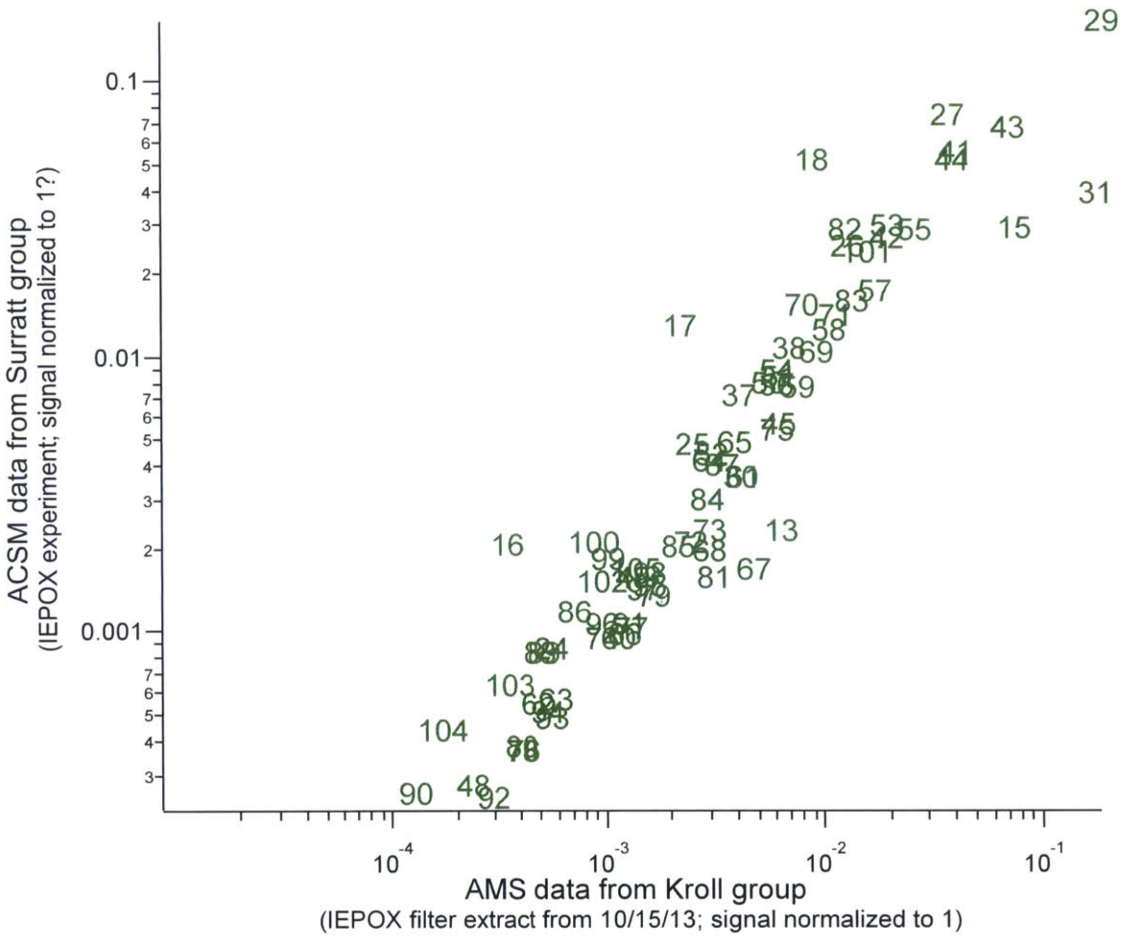

Figure 13: A comparison of ACSM and AMS data for SOA experiments, where the ACSM data was collected online and the AMS data is from filter extracts nebulized on our offline technique. This represents data from two separate but similar IEPOX SOA experiments. The total signal sum is normalized to 1 for easier comparison of mass-to-charge values between the techniques.

3.4 Conclusions

We have demonstrated an ability to produce AMS measurements from liquid sample volumes on the order of microliters. For a given sample, this technique produces consistent mass spectra in terms of species prevalence and aerosol component ratios (e.g. organic/sulfate). There is a factor of ≤10 in variability in absolute signal mass and a 10^3 mass loss factor from nebulized mass to AMS measured mass. The loss factor is likely dominated by droplet splatter to walls, which may also contribute to signal variability.

Potential applications of this method are varied. As demonstrated in this study, the SVN can be used effectively for offline analysis of filters. Similarly, this technique could be used for other small volume or limited sample mass applications, such as concentrated rainwater samples. Additionally, the small volumes required for characterizing a sample as well as the small size of the SVN make this technique useful for testing standards and calibrations. The addition of a standard for quantification would greatly improve this technique.

Future designs will hopefully improve the SVN and improve its robustness and expand its applicability. Designs will target splatter reduction to reduce the large signal loss and variability. Continuous sample delivery via slow injection could also help reduce the loss factor by producing smaller droplets with less splatter, thus increasing instrument sensitivity. In the current design, the glass tube must be lifted to allow a single drop to be placed in the center of the film using a syringe. Once the glass tube has been replaced, we nebulize the drop and observe signal for approximately 15-20 seconds. Adding a side port with a small syringe or tube that hovers above the film and allows us to slowly inject sample at a rate consistent with nebulization, such that sample never pools on the film, would remove the need to lift the glass tube and also lengthen signal time significantly. This will hopefully also reduce droplet splatter, because the sample will nebulize as soon as it contacts the film instead of nebulizing from a single 8 μL drop, which produces large droplets that impact the walls of the glass tube.

Additional improvements should be made to the side air input ports and the overall shape of the SVN to encourage more laminar and less turbulent airflow. Current air input comes from only two side ports and is perpendicular to the direction of aerosol production and flow into the glass tube and AMS. Angling the air input upward and toward the center of the device would help guide nebulized aerosol sample through the system. Additional adjustments to the shape of the nebulization cavity to reduce droplet splatter and encourage re-nebulization of droplets along with adjustments to the shape of the tube above the film could also encourage more smooth, laminar airflow. In the current design, when large droplets are produced during nebulization, they impact the walls of the glass tube. If the cavity and tube were altered, perhaps into a wider and more conical shape, it might cause large droplets to fall back onto the film and be re-nebulized into smaller aerosol droplets instead of sticking to the walls. Improvements to the design of the SVN will expand the applicability and strength of the technique, allowing for better characterization of small-volume liquid environmental samples and widening the coverage of the AMS.

4. Summary

Atmospheric particulate matter (aerosol) significantly degrades air quality, is detrimental to human health, and alters the radiative balance of the atmosphere (Schwartz et al., 1996; Harrison and Yin, 2000; Davidson et al., 2005; Arden Pope III and Dockery, 2006; IPCC, 2013). Our ability to model and understand aerosol, however, is limited by the complexity of the problem: the thousands of compounds (Goldstein and Galbally, 2007), variety of changing sources, complex chemistry, and, in particular, the uncertainty associated with organic aerosol (OA) which makes up approximately 50% of aerosol and yet remains the least characterized of aerosol components (Zhang et al., 2007). In addition to OA's complexity of sources and species, it is poorly represented by models (Heald et al., 2005; Kanakidou et al., 2005); this makes it difficult to predict and understand OA. Characterizing the historic trends in total loading of OA in tandem with other important aerosol species like sulfate, nitrate, and black carbon allows us to begin to probe the potential drivers of OA concentration. Additionally, characterizing the historic changes in OA chemical composition allows us to better investigate these drivers. The work in this thesis provided a historic view of aerosol using rural data from the Interagency Monitoring of Protected Visual Environments (IMPROVE) network and developed a new technique, the Small Volume Nebulizer (SVN), to enable the chemical characterization of existing samples using the Aerodyne aerosol mass spectrometer (AMS).

In Chapter 1, we investigated historic aerosol trends using existing IMPROVE data. We found large changes in total average aerosol loading across the rural United States: 30% decreases in the mid-U.S. and 50% decreases in the Western and Eastern regions. Along with these large decreases in total loading, we found that the fractional contribution of OA to total aerosol stayed relatively constant. This suggests that some factor, or factors, has led to decreased OA concentrations despite there being no direct controls on emissions of secondary OA (SOA), which has been shown to be the largest source of rural OA (Brown et al., 2002; Zhang et al., 2007). We considered a few potential factors using the existing data, and found that changes in biomass burning are unlikely to have caused the decrease in OA, which is consistent with previous results (Spracklen et al., 2007). We found similar weekday-weekend effects on concentrations of OA and elemental carbon (EC), which suggests that anthropogenic emissions may be related to the decline in OA, although the cycle difference was stronger in EC. Finally, we looked at the relationship between sulfate and OA concentrations and found similar regional behaviors with a non-linear relationship at the national level. This could support an SOA hypothesis that sulfate levels can control SOA formation either through aerosol water content or via oxidation (Carlton and Turpin, 2013; Xu et al., 2015), but the non-linearity suggests it may not be the only factor controlling the OA decrease. Or, perhaps there may be another factor driving the decrease in both species, like anthropogenic emissions regulations that have unintentionally controlled emissions of SOA precursors. In fact, this last point – the potential indirect influence of emissions controls on SOA – would mean emissions regulations from the EPA have been even more effective at decreasing $PM_{2.5}$ concentrations than currently believed. Understanding the historic trends in aerosol species helps us identify the potential factors controlling OA and, with additional modeling to better characterize how factors relate to changes in OA, could help constrain our currently limited understanding of OA.

In Chapter 2, we developed a method to augment our understanding of historic OA trends by expanding the dataset to include AMS measurements of extracts from existing archived filter samples. Where standard techniques require milliliter-sized liquid volumes of sample, the Small

Volume Nebulizer (SVN) reduces the requirement to microliter-sized samples and provides an opportunity to obtain chemical characterization of OA from small environmental samples. The nebulization technique produces measurements that are chemically consistent over time and comparable to standard atomization. Additionally, we demonstrated the applicability of this technique to offline filter extract measurements on the AMS and found that the results of the offline analysis are comparable to online measurements taken from a similar instrument, the Aerodyne Aerosol Chemical Speciation Monitor (ACSM). With further characterization and improvements, the SVN will greatly enhance our ability to characterize the chemical composition of OA in small environmental samples, allowing us to expand the existing dataset and better address the question of what factors contribute to historic OA trends.

Additional analyses related to the work performed here would greatly enhance our understanding of aerosol trends. Using a global chemical transport model would allow us to investigate OA sources and trends by running simulations to determine which of the factors proposed in this work contribute to the observed OA trends. Additionally, it would allow us to consider both the effect of an individual factor working in isolation as well as the effects of multiple factors working together. In terms of improvement to the SVN and thus expansion of the historic aerosol dataset, future work should address its large 10^3 mass loss factor from nebulized mass to AMS-observed mass and its factor of 10 in total signal variability between different nebulization runs of the same sample and drop size. One major design improvement would be a switch from single drop to continuous nebulization, which would require the addition of a continuous injection line. Additional improvements could include altering the shape of the SVN to be more conical, which would encourage re-nebulization of large droplets that otherwise adhere to the walls, and angling air input ports upward, thereby encouraging less turbulent and more directed airflow for nebulized particle transport into the AMS. Future applications of the SVN should include analysis of archived filter samples, including those from the IMPROVE network, to expand the historic dataset for OA. Producing chemical characterization of historic aerosol samples would significantly improve our understanding of the factors controlling OA trends and help validate model results. The SVN should also be used to characterize other small-volume environmental samples that are currently excluded from AMS analysis. Such samples could include collected rainwater or modern filter extracts from remote regions that are inaccessible or cost-prohibitive for online measurements. Expanding our understanding via modeling of OA sources and trends, improvements to the SVN to increase its sensitivity, and applications of the SVN to obtain chemical speciation of small-volume environmental samples will allow for even further characterization of OA relative to the work performed here.

An understanding of OA, and particularly its sources and historical trends, would represent a significant step toward characterizing the aerosol of which OA makes up the majority contribution. Because of the impact of aerosol on air quality, human health, and climate, an ability to accurately represent its largest contributor in models would improve our ability to understand and predict OA responses to changing factors and its effects on these major environmental and social issues. By developing a historical perspective on rural aerosol using existing data from the IMPROVE network and introducing a nebulization technique that will allow for the further expansion of the historical dataset, we have began to address these gaps in our OA understanding. Further improvement and application of our nebulization technique, along with significant modeling efforts to investigate the proposed factors controlling OA, will augment the work performed here and continue the process of understanding and characterizing OA and its impacts on human health and the environment.

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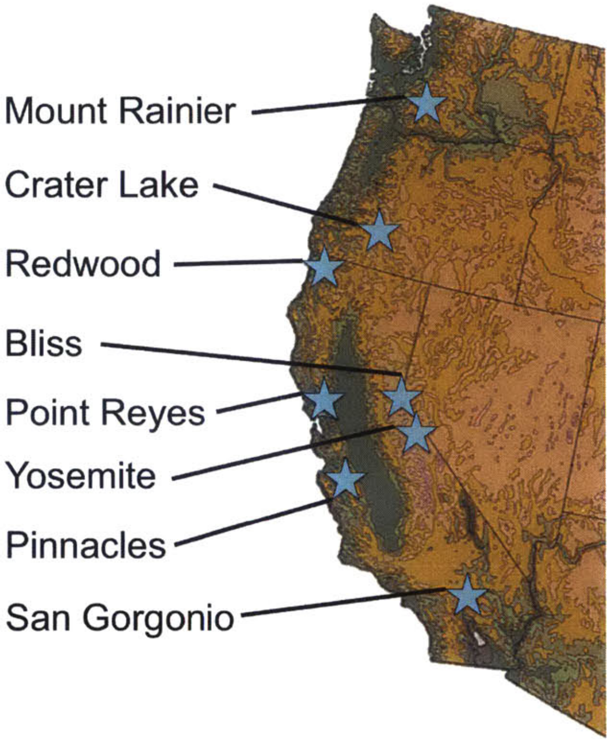
6. Appendix

6.1 Average Aerosol Pie Charts for Individual IMPROVE Sites

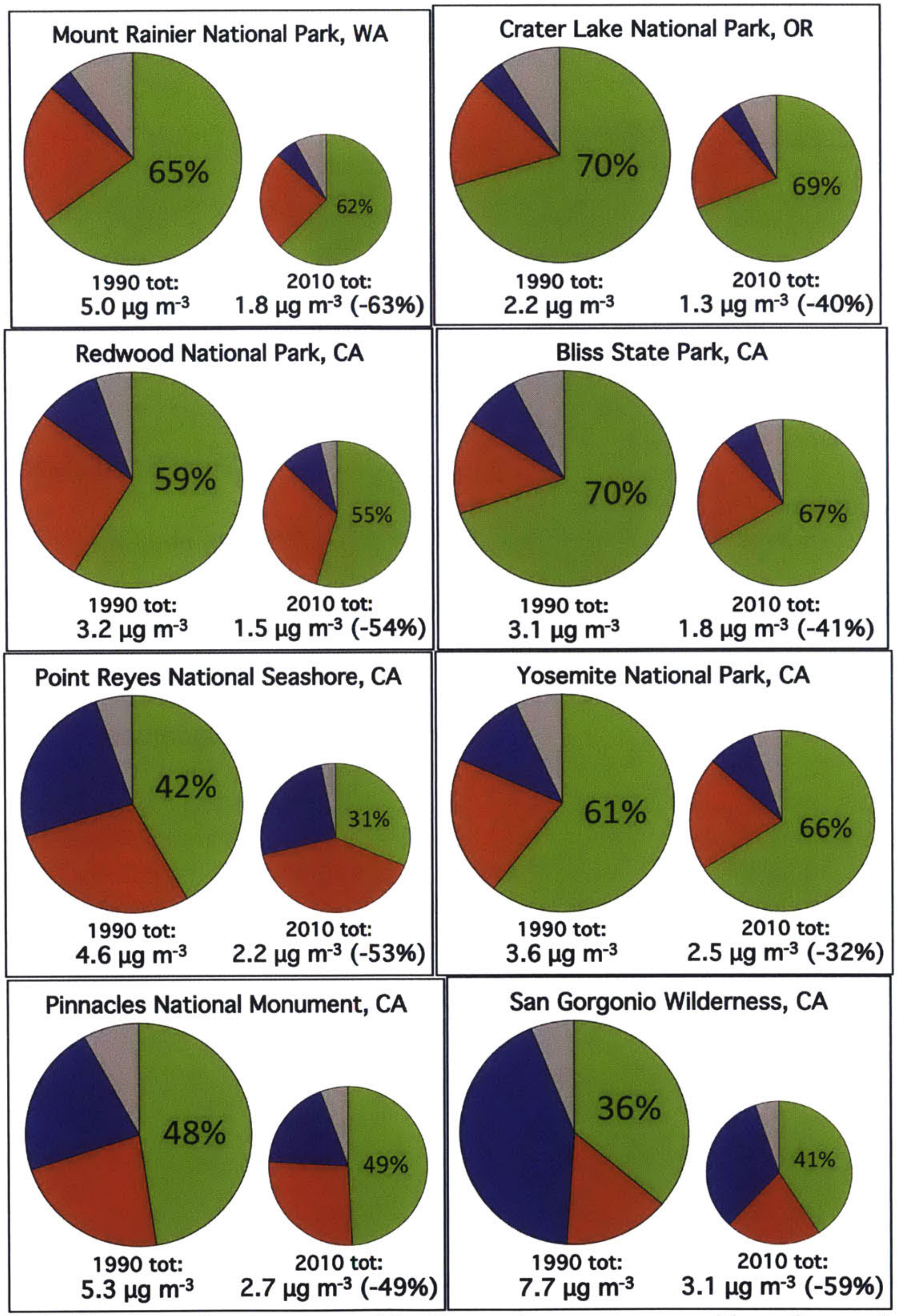
Appendix 1: Identifying site abbreviations for each of the IMPROVE locations used in this study.

Abbreviation	Name	Location
ACAD	Acadia National Park	Maine
BADL	Badlands National Park	South Dakota
BAND	Bandelier National Monument	New Mexico
BLIS	Bliss State Park	California
BRID	Bridger Wilderness	Wyoming
BRCA	Bryce Canyon National Park	Utah
CANY	Canyonlands National Park	Utah
CHIR	Chiricahua National Monument	Arizona
CRLA	Crater Lake National Park	Oregon
DENA	Denali National Park	Alaska
GLAC	Glacier National Park	Montana
GRSA	Great Sand Dunes National Monument	Colorado
GRSM	Great Smoky Mountains National Park	Tennessee
GUMO	Guadalupe Mountains National Park	Texas
HAVO	Hawaii Volcanoes National Park	Hawaii
INGA	Indian Gardens	Arizona
MORA	Mount Rainier National Park	Washington
PEFO	Petrified Forest National Park	Arizona
PINN	Pinnacles National Monument	California
PORE	Point Reyes National Seashore	California
REDW	Redwood National Park	California
SAGU	Saguaro National Monument	Arizona
SAGO	San Gorgonio Wilderness	California
SHEN	Shenandoah National Park	Virginia
TONT	Tonto National Monument	Arizona
WASH	Washington D.C.	Washington D.C.
WEMI	Weminuche Wilderness	Colorado
YOSE	Yosemite National Park	California

Western Region

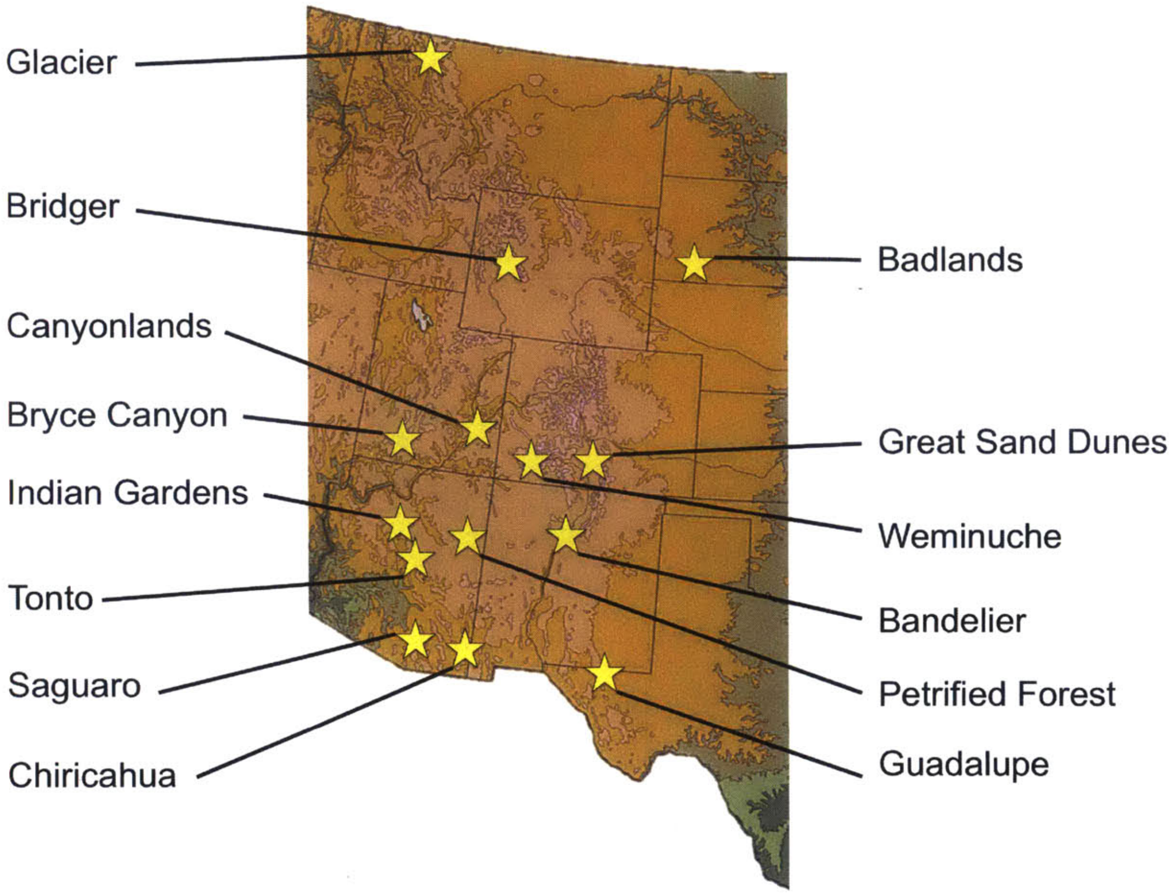


Appendix 2: The locations of the sites classified as Western United States in this work.



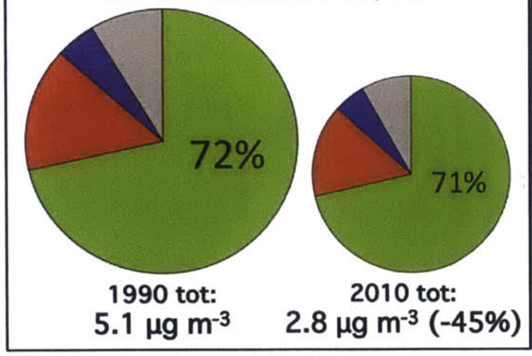
Appendix 3: Pie charts showing the total loading and average composition of aerosol at each western location in 1990 and 2010. The size of the 2010 pie chart is scaled by area relative to the 1990 chart to show average decrease in aerosol loading.

Mid-United States

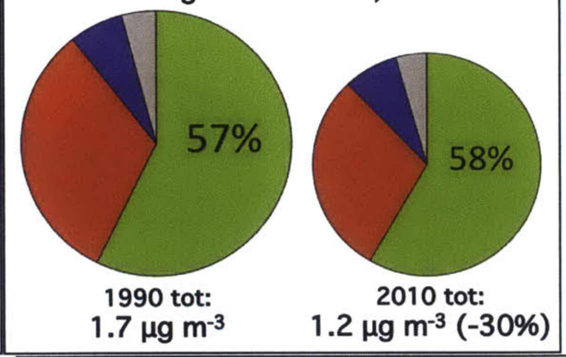


Appendix 4: The locations of the sites classified as mid-United States in this work.

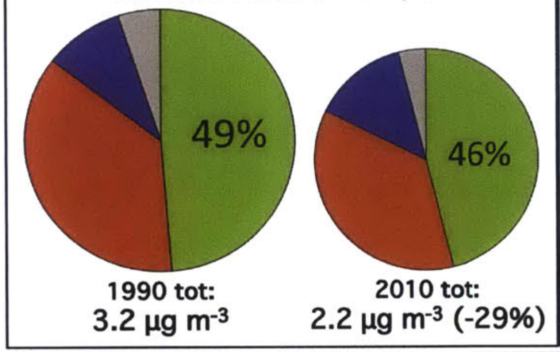
Glacier National Park, MT



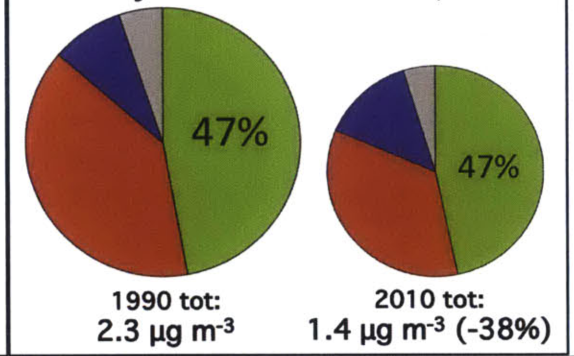
Bridger Wilderness, WY



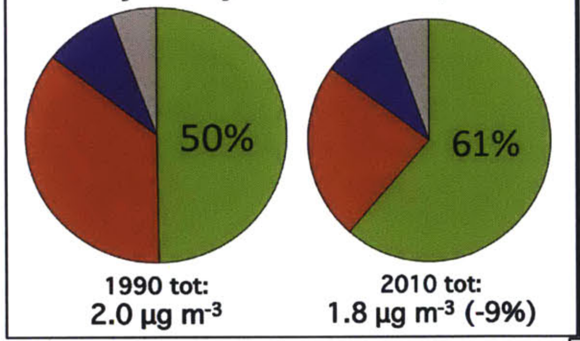
Badlands National Park, SD



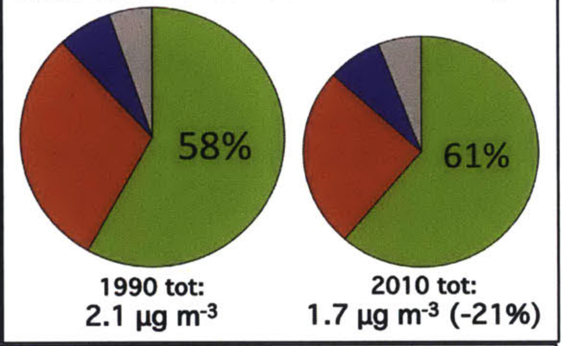
Canyonlands National Park, UT



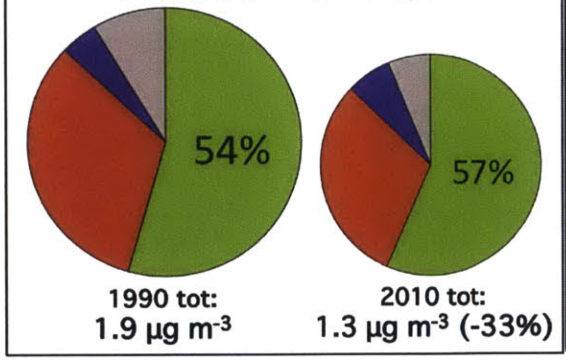
Bryce Canyon National Park, UT



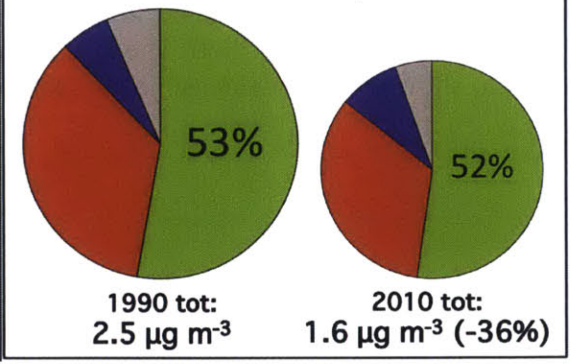
Great Sand Dunes National Monument, CO

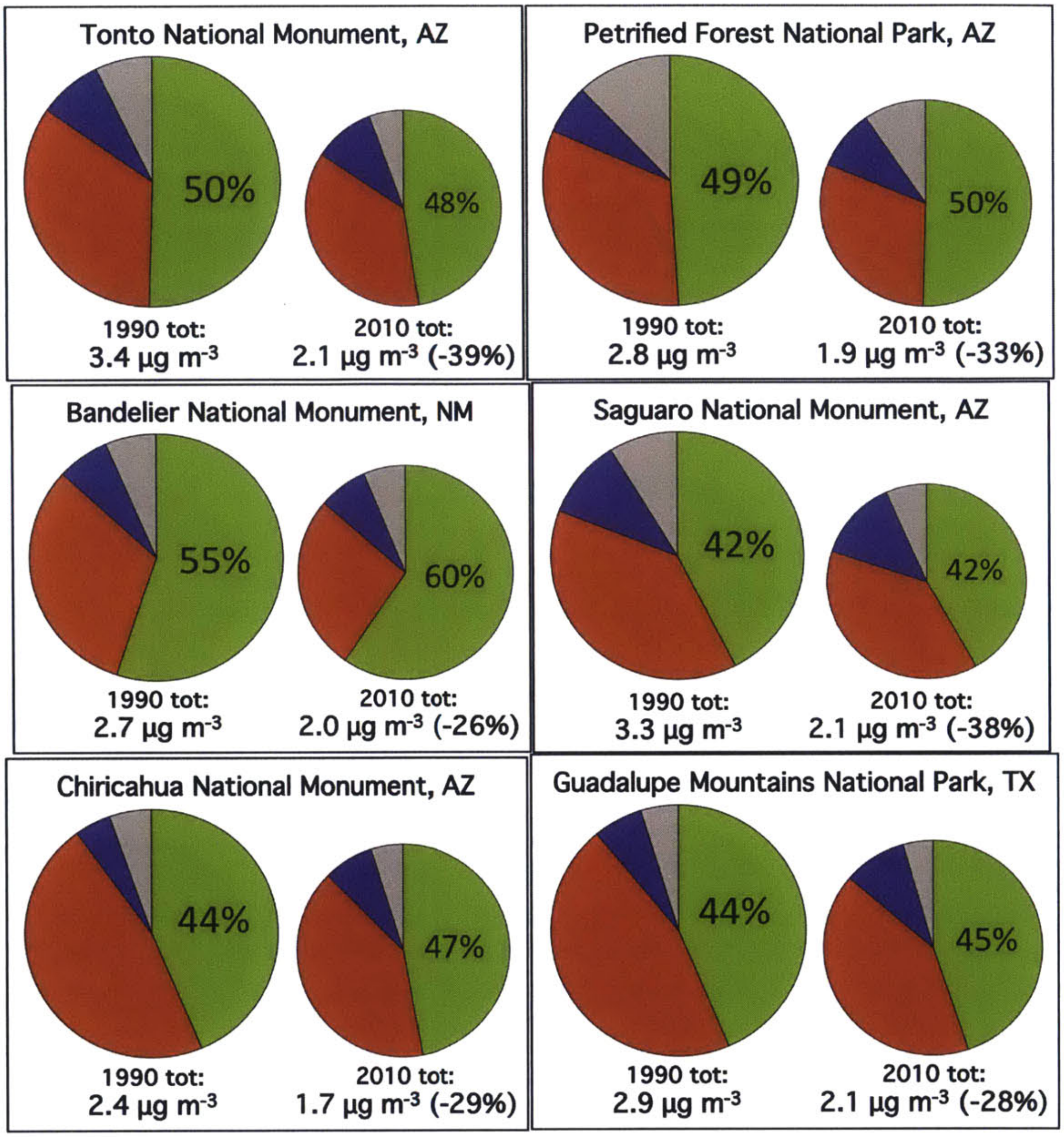


Weminuche Wilderness, CO



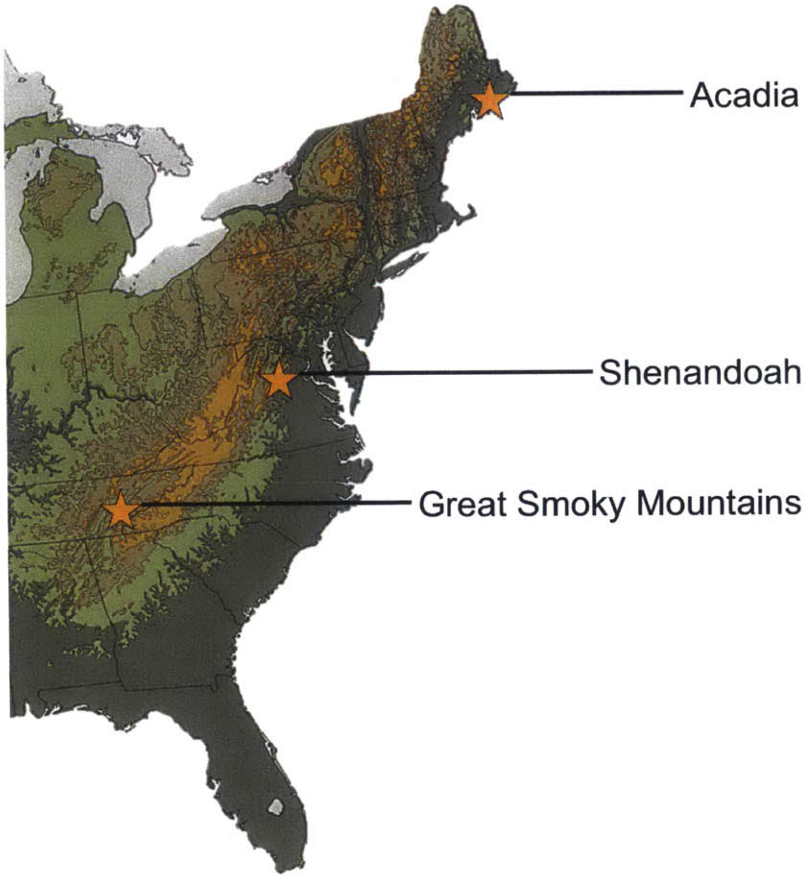
Indian Gardens, AZ



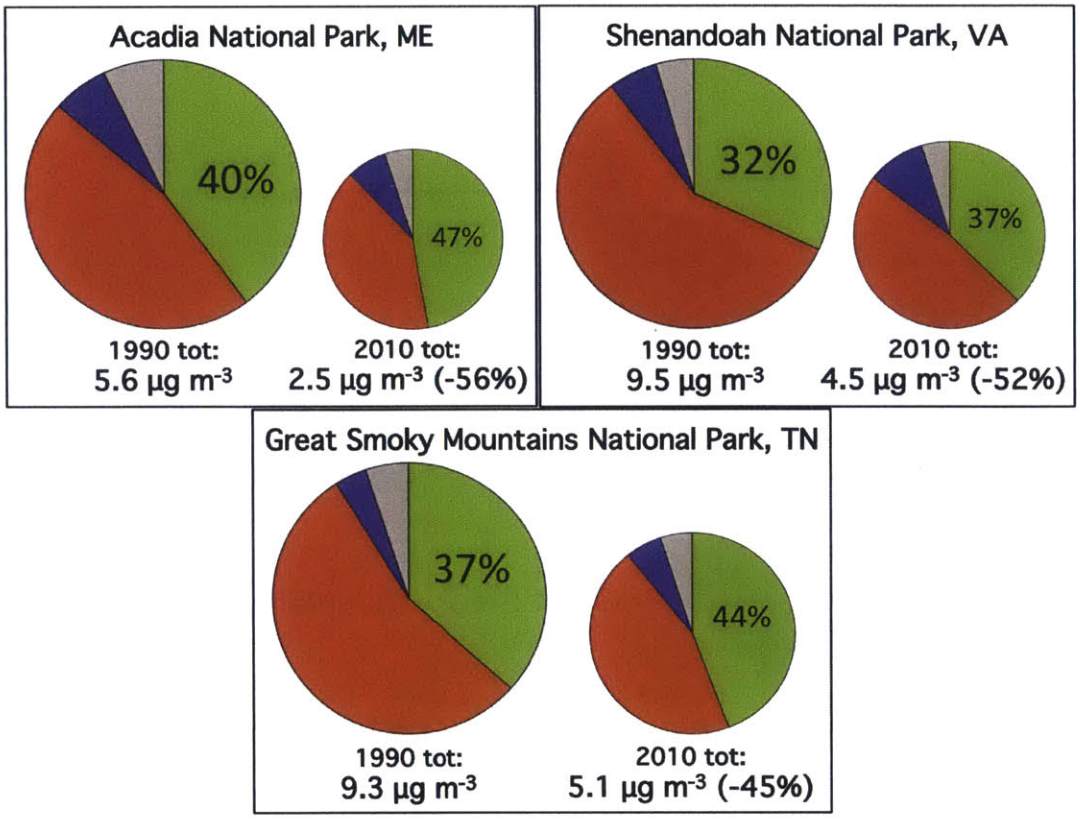


Appendix 5: Pie charts showing the total loading and average composition of aerosol at each mid-US location in 1990 and 2010. The size of the 2010 pie chart is scaled by area relative to the 1990 chart to show average decrease in aerosol loading

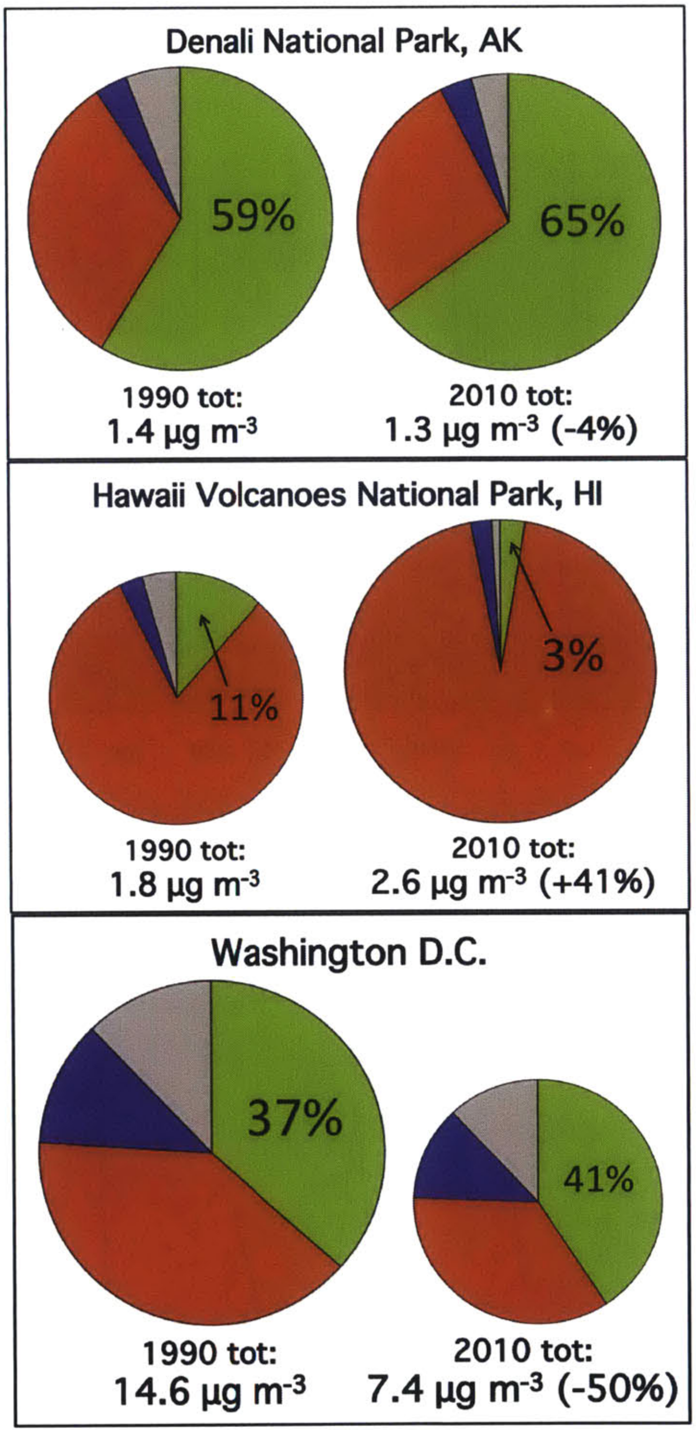
Mid-United States



Appendix 6: The locations of the sites classified as Eastern United States in this work.

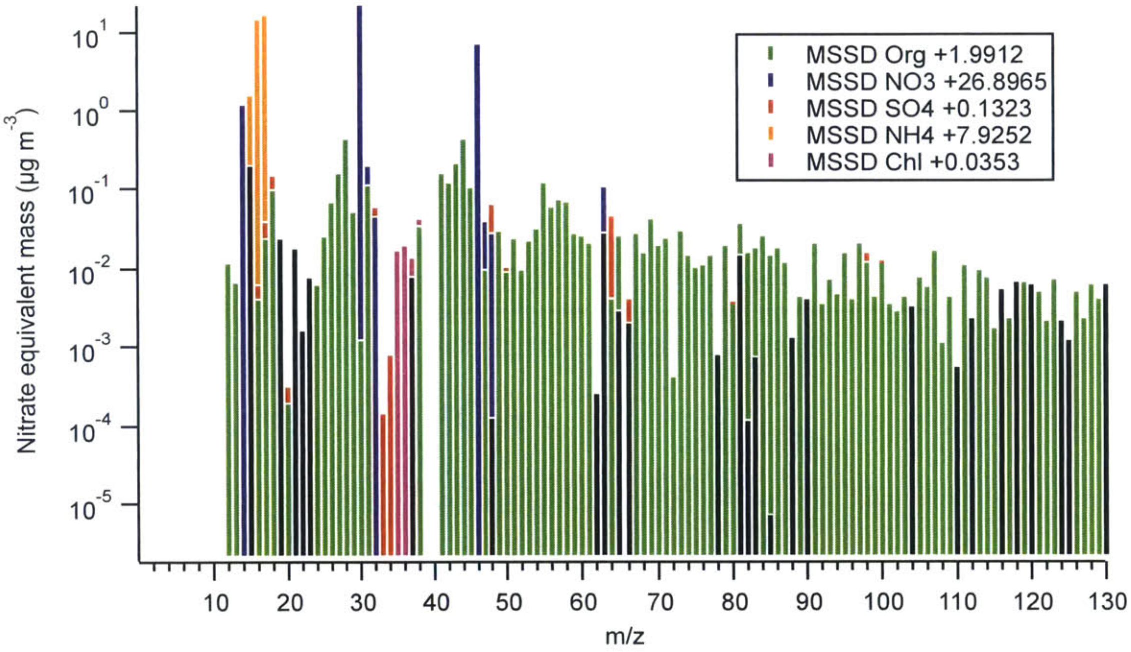


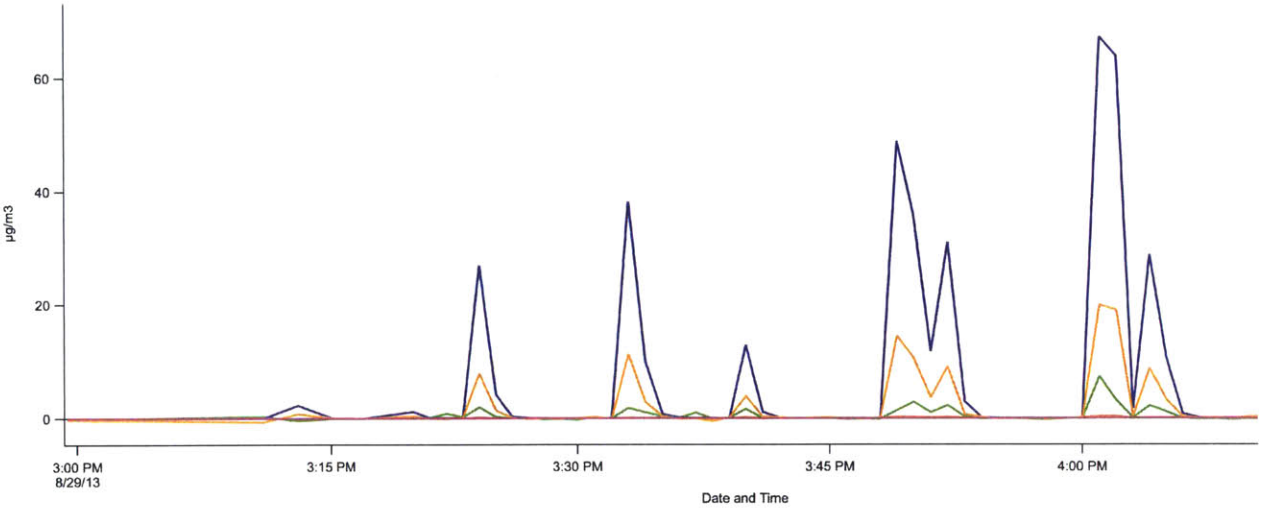
Appendix 7: Pie charts showing the total loading and average composition of aerosol at each Eastern US location in 1990 and 2010. The size of the 2010 pie chart is scaled by area relative to the 1990 chart to show average decrease in aerosol loading.



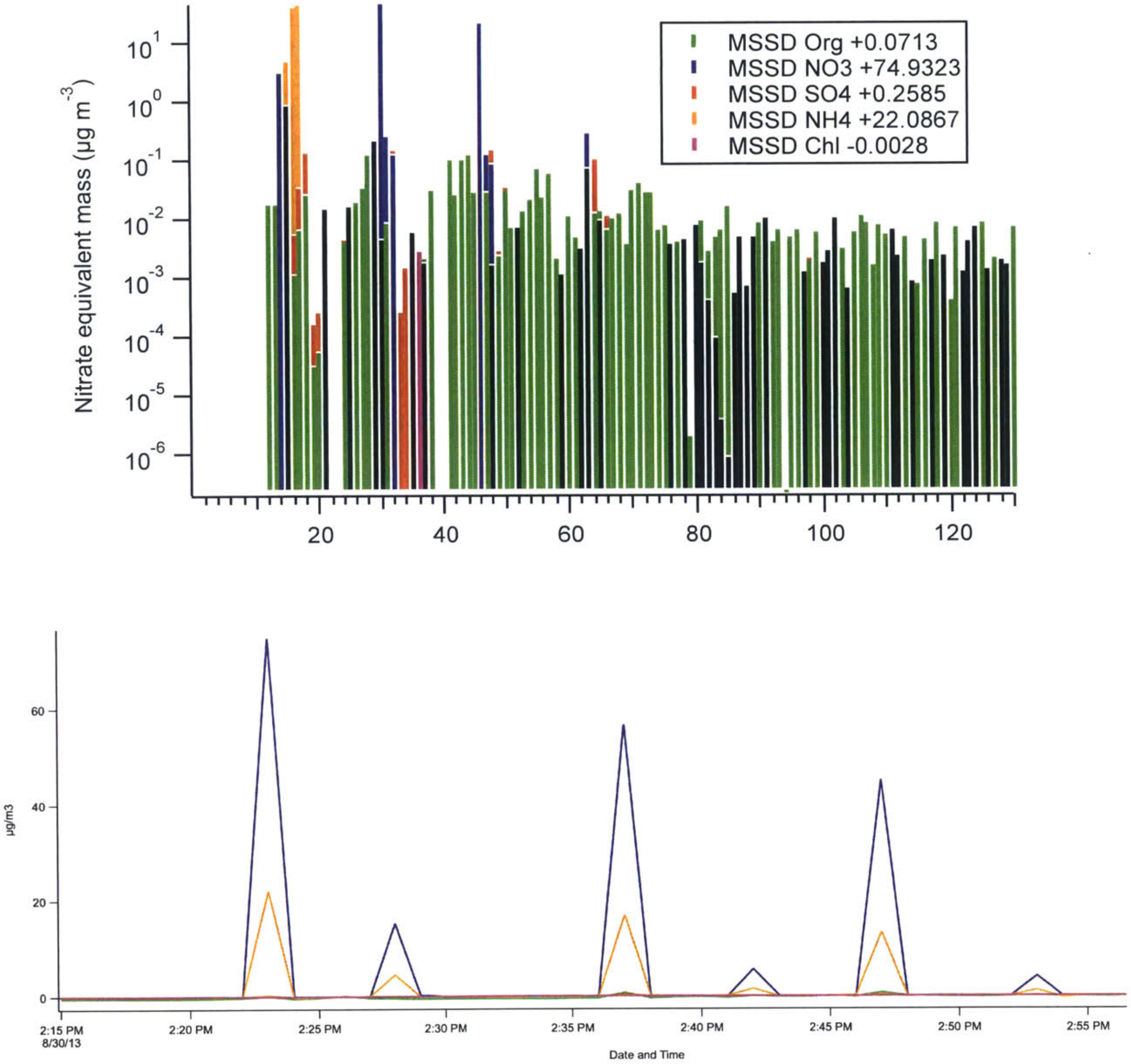
Appendix 8: Additional sites not included in the three regions due to their distance (Denali National Park in Alaska, Hawaii Volcanoes National Park in Hawaii) or non-rural location (Washington D.C.).

6.2 Comparing SVN Films

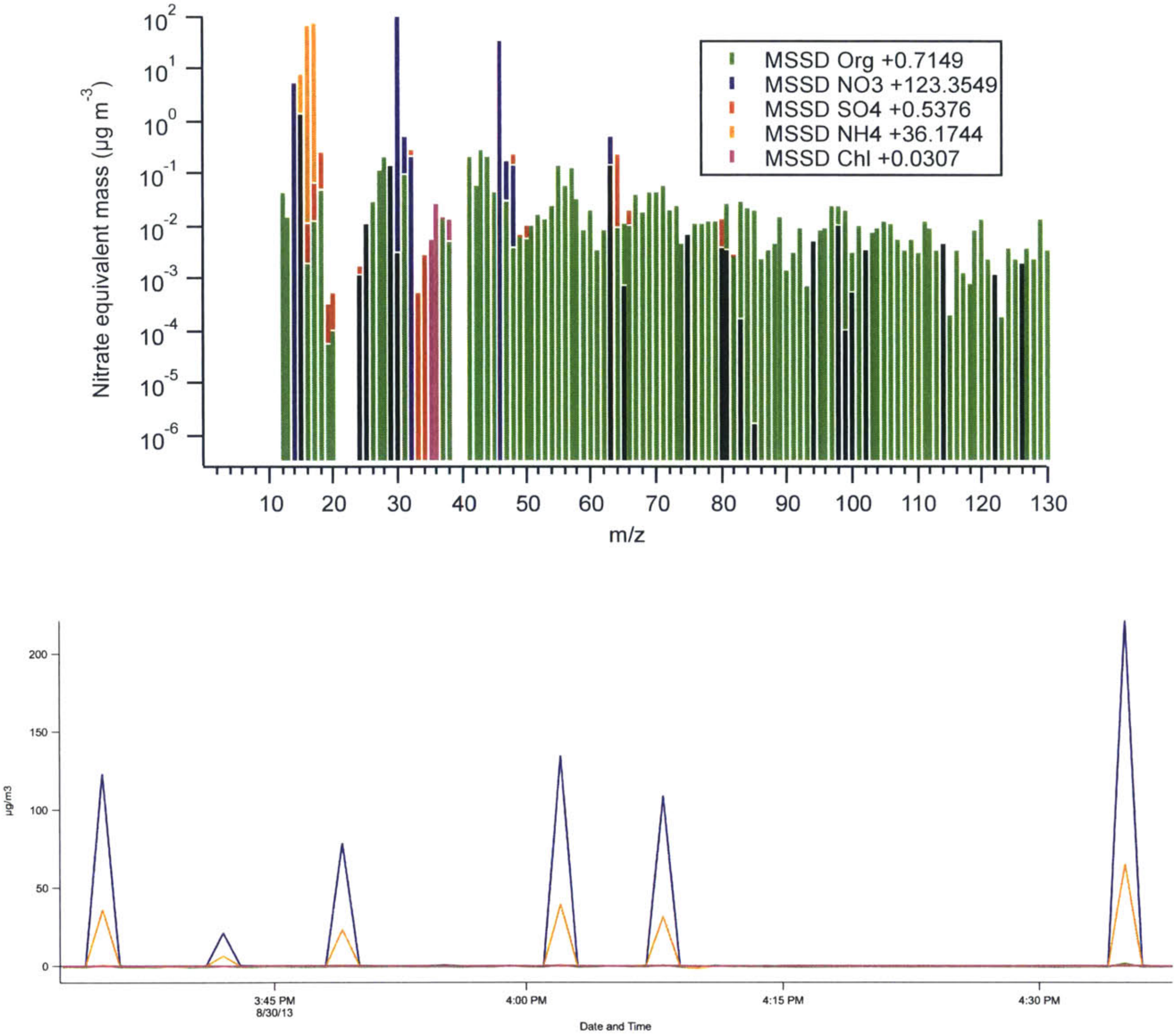




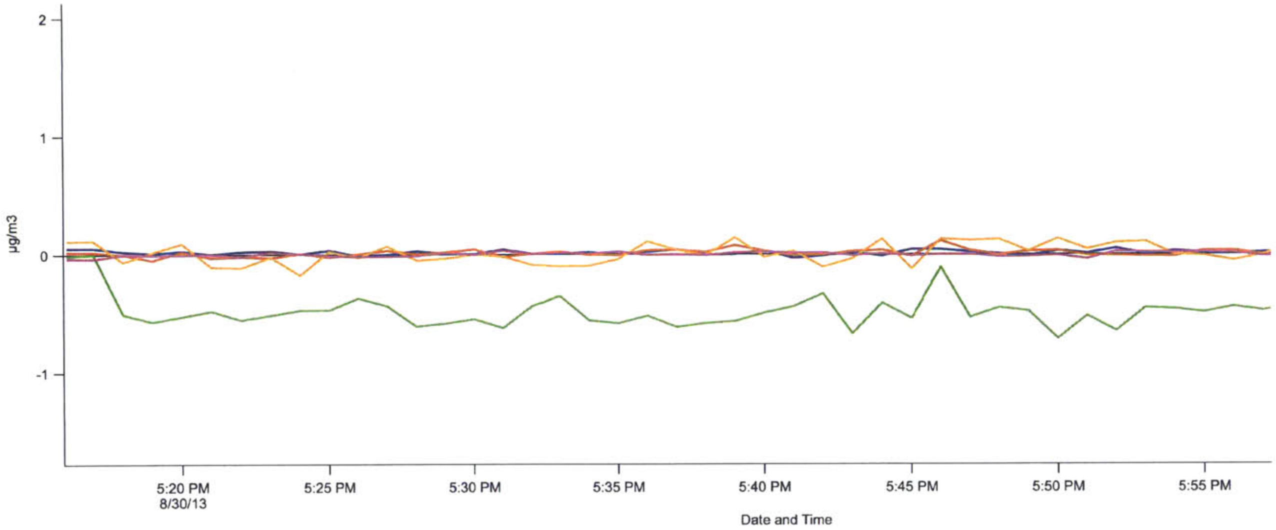
Appendix 9: The mass spectrum and signal time trace resulting from testing ammonium nitrate on the polyester film. The average organic-to-nitrate ratio was 0.10, indicating a high level of contamination.



Appendix 10: The mass spectrum and signal time trace resulting from testing ammonium nitrate on the FEP film. The average organic-to-nitrate ratio was 0.04, a 2.5x reduction in contamination relative to the polyester film.

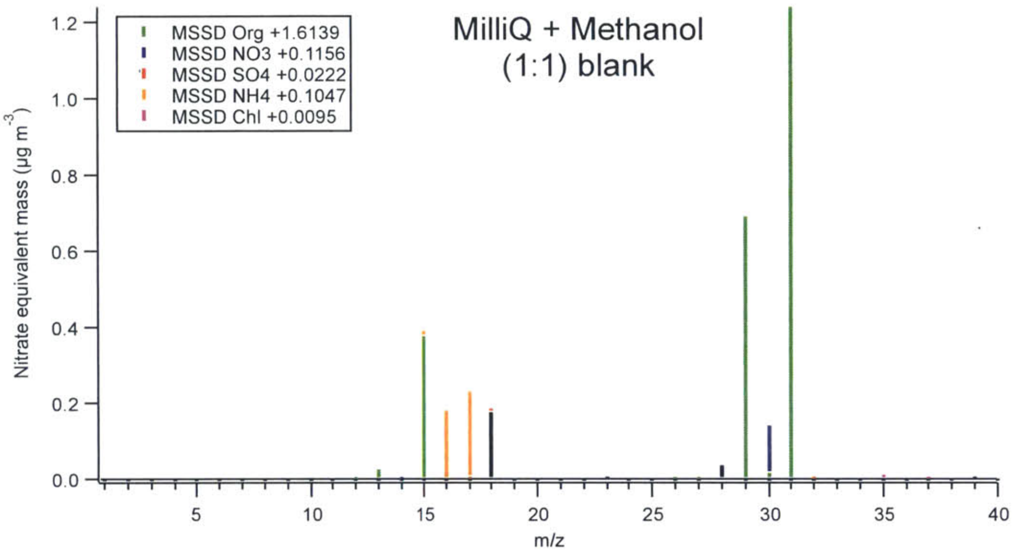


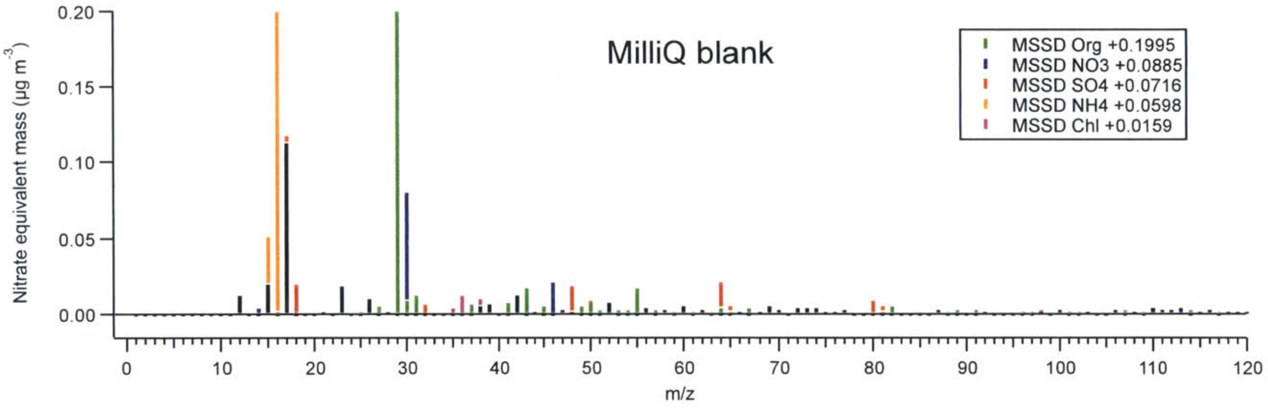
Appendix 11: The mass spectrum and signal time trace resulting from testing ammonium nitrate on the Kapton Polyimide film. The average organic-to-nitrate ratio was 0.025, a 5x reduction in contamination relative to the polyester film and a 1.6x reduction relative to the FEP film.

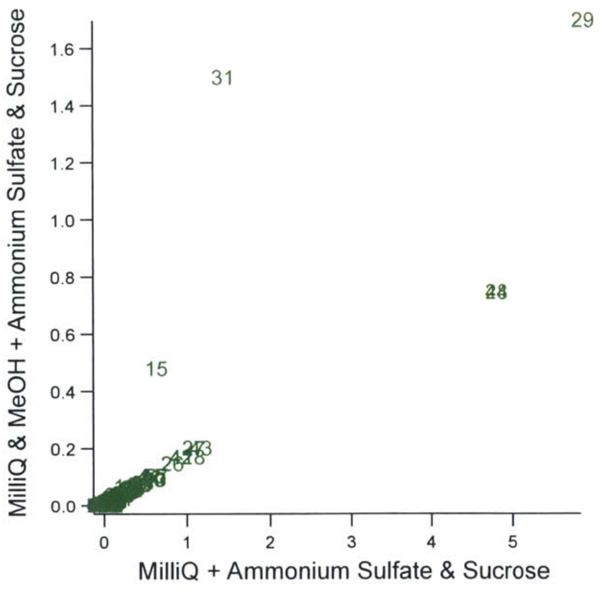


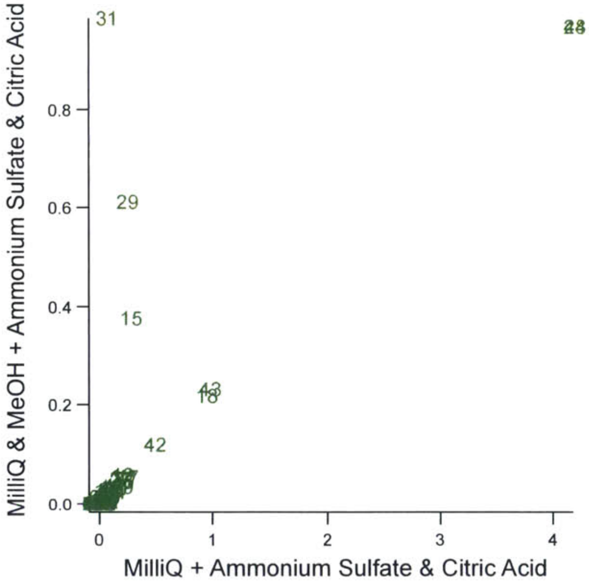
Appendix 12: Two attempts were made to atomize ammonium nitrate solution on the Teflon film, at 5:35pm and 5:52pm, but neither produced any signal. The film was determined to be too thick to transmit the nebulizing vibrations.

6.3 Comparing Extraction Solvents









Appendix 13: The top figure shows the mass spectrum for a MilliQ + methanol (1:1 by volume) solvent blank; the second figure shows the mass spectrum for a MilliQ only solvent blank. Organic peaks are clearly visible in the MilliQ + methanol spectra at mass-to-charge values 15, 29, and 31 due to the methanol. The bottom figures compare organic mass spectra peaks for Ammonium Sulfate + Organic (Sucrose or Citric Acid) solutions when they were made in pure MilliQ vs MilliQ + methanol. M/z values are plotted against one another, and the resulting line represents agreement in relative peak strengths. Methanol peaks 15, 29, and 31 are distinctly elevated in the MilliQ + methanol versions.