Variation, Patterns & Sources of Air Pollution:

A Study of Ambient $PM_{2.5}$ in Wisconsin

by

Chong-Le Li

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The dissertation is approved by the following members of the Final Oral Committee:

Jae K. Park, Professor, Civil and Environmental Engineering
Moo K Chung, Professor, Biostatistics and Medical Informatics
Gregory W Harrington, Professor, Civil and Environmental Engineering
James M Tinjum, Professor, Civil and Environmental Engineering
Chin-Hsien Wu, Professor, Civil and Environmental Engineering

ABSTRACT

Air quality is one of the high priority research areas identified by the United States (U.S.) Environmental Protection Agency (EPA) and research on the changing spatiotemporal patterns of $PM_{2.5}$ is part of the EPA's current focus. The U.S. EPA is looking for long-term prospective studies on relationship between long-term exposure to $PM_{2.5}$ and cardiovascular health effects in order to to reduce the uncertainty of the concentration – response relationships, especially at low ambient concentrations of $PM_{2.5}$. Several regions in Wisconsin have experienced $PM_{2.5}$ exceedance at all seasons. In this thesis, a comprehensive analysis on Wisconsin $PM_{2.5}$ data was performed to study the variations and the changes in patterns of ambient $PM_{2.5}$ and to establish a systematic approach for utilizing the broadely available ambient $PM_{2.5}$ data for long term health research.

In this study, the large volume of available $PM_{2.5}$ data sets collected at four different regions in Wisconsin from 2002 to 2013 were analyzed with different methods to explore the spatial and temporal variations of the characteristics, the patterns of the variations and the changes of the discovered patterns of ambient $PM_{2.5}$ from various angles. The same study was applied to the atmospheric aerosol acidity of $PM_{2.5}$ because of its role in the human health impacts and the formation of $PM_{2.5}$. In consideration of the health impacts of short-term high $PM_{2.5}$ exposure, the characteristics of elevated $PM_{2.5}$ events were analyzed to identify the trends in episode frequency and severity.

Differing from the traditional method of measuring the inorganic ions from the water extracts of $PM_{2.5}$, a thermodynamic principle-based new method used the deliquescent relative humidity (DRH) as a criterion to determine if the inorganic ions in $PM_{2.5}$ were in aqueous phase on the sampling day. If the relative humidity (RH) on the sampling day was higher than the DRH of the aerosol system, the inorganic ions were in aqueous phase and were selected for modeling. The Extended Aerosol Inorganic Thermodynamic Model (EAIM) was used to estimate the in-situ acidity of that day. Incorporating aerosol acidity, especially in-situ acidity, in studies of the health impacts of long-term exposure to low concentration of $PM_{2.5}$ can provide more accurate concentration – health responserelationships. The in-situ acidity calculated in this study had reasonable correlation with other aerosol acidity indexes used in the study.

The spatial and temporal variations of the characteristics and the changes of the discovered patterns of ambient $PM_{2.5}$ and the aerosol acidity of $PM_{2.5}$ were studied using statistical and graphical software. The changes in the concentrations of ambient sulfate, nitrate and OC highlights the need for changing $PM_{2.5}$ reduction strategies. A change in the ambient aerosol acidity trend was observed around 2009 and 2010. P value analysis indicated both the downward and upward trends were not insignificant. Further studies to determine if there is a permanent increasing trend is strongly recommended. An ascending trend of aerosol acidity was discovered during winter episodes in Milwaukee from 2002 to 2009, which need to be studied as well. Elevated $PM_{2.5}$ events were caused by both emission sources and meteorological conditions. Each episode was unique. There was no seasonal cap for the high concentrations of the episodes.

Patter changes in ambient $PM_{2.5}$ were observed. The periods when trends change direction provide valuable opportunities to study the underlying causes of the changes.

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CHAPTER 1. INTRODUCTION

1.1. Background

$PM_{2.5}$ is a complex mixture of extremely small particles (including dust, dirt, soot, smoke and small biogenic materials) and liquid droplets, which is either directly emitted from combustion (motor vehicles, power plants, smelters, biomass burning, etc.), industrial processes, agriculture activities and natural sources (volcanoes, dust storms, wild fires, biological species, and sea spray, etc.), or formed from its precursors through complicated atmospheric reactions. The major $PM_{2.5}$ components are sulfate (SO_4^{2-}), nitrate (NO_3^-), ammonium (NH_4^+), elemental carbon (EC), organic carbon (OC) and trace metals. Sulfate, nitrate, and ammonium are inorganic secondary $PM_{2.5}$, formed in the atmosphere from precursors of SO_2, NO_X and NH_3, which are emitted from both natural and anthropogenic sources. EC, also called black carbon, is predominately emitted from fossil fuel combustion processes due to incomplete combustion. OC is a mixture of hundreds to thousands of individual carbonaceous compounds with a wide range of chemical and thermodynamic properties (Polidori et al., 2006; Turpin, 2001). OC includes primary OC (POC) and secondary OC (SOC, also called secondary organic aerosol, SOA). The POC is directly emitted into the air as a solid or liquid particle, while SOA is formed in the atmosphere through a series of complicated reactions. The precursors of SOA are chemically active compounds emitted either from anthropogenic sources, such as automobile, power plant, industrial processes, or from biogenic emissions and wood burning (including wildfire) (Blanchard et al., 2008; Duncan et al., 1995; Jang et al., 2002; John H. Seinfeld, 2006; Liao et al., 2008; Robinson et al., 2007; Seigneur, 2001).

Numerous scientific studies have linked $PM_{2.5}$ exposure to severe health impacts. Children, old people and people having lung or heart troubles are the most likely to be affected by $PM_{2.5}$

pollution. The GBD (Global Burden of Disease) study (2015) claimed that air pollution accounts for 5.5 million deaths and 141.5 million DALYs (disability –adjusted life years) in 2013 (Mishamandani, 2015). $PM_{2.5}$ is also the main cause of reduced visibility and changes in atmospheric radiation balance. The deposition of $PM_{2.5}$ can make lakes and streams acidic, damage forests and farm crops, and affect the ecosystem diversity (U.S.EPA, 2013).

Global change and air quality are high-priority research areas identified by the EPA Office of Research and Development (EPA-G2014-STAR-G1). Specifically, research that seeks to characterize “the changing spatiotemporal patterns” is one of the EPA’s current interests. Climate change and the changes of the global economy (e.g., outsourcing, the decline of old industries) are expected to impact particulate matter air pollution. Studies have predicted that changes in temperature, relative humidity (RH), precipitation and air circulation patterns resulting from climate change could alter the pattern of spatial and temporal variations of $PM_{2.5}$ air pollution (Dawson et al., 2014b; Ervens et al., 2008; Mickley et al., 2004; Tsigaridis and Kanakidou, 2007).

Wisconsin has a diversified economy with industry and agriculture both playing significant roles. Wisconsin is known as "America's Dairyland" for it is one of the nation's leading dairy producers. Wisconsin is also home to a very large and diversified manufacturing economy, especially the paper products. However, the fast growing agriculture and industrial sectors have brought excess air pollution to the state.

Wisconsin’s diversified geography and long Great Lakes coastline, the northern bordering with Lake Superior and eastern bordering with Lake Michigan, not only provides uniquely abundant natural resources to the economy but also makes meteorology a complicating factor in air quality m anagement in the cities along the shoreline. Wisconsin air quality data provides a good opportunity to study the patterns of the variations and if there is change in pattern, how the change affects the air quality.

Wisconsin is the 23rd largest state by total area and the 20th most populous in US. Its gross state product was $248.3 billion (2010), making it 21st among U.S. states. However, the frequency of the elevated $PM_{2.5}$ and elevated O_3 events occurring in Milwaukee (the state's largest urban area) is similar or even higher than that occurring in larger industrial cities in Midwest, like Detroit, MI, Chicago IL and Cleveland, OH (Katzman et al., 2010). Several counties in the southeastern region of Wisconsin are nonattainment for 24-hourly $PM_{2.5}$ and 8-hour ozone NAAQS.

Many studies indicate the significant impact of meteorological changes on the daily air quality in the Midwest (LADCO, 2009; Mickley et al., 2004). Dawson et al. predicted that summertime episodes would happen more frequently, more severely and cover larger areas from present to 2050 in the Midwest (Dawson et al., 2014b; Dawson et al., 2009; Mickley et al., 2004).

Thus it is important to analyze daily episodes to enable us to characterize the worst-case scenario. This will provide useful information for efficient air quality management and health protection.

1.2. Problem Statement

1.2.1. The Spatiotemporal Variation of Ambient $PM_{2.5}$

Climate change and changes in the global economy are expected to impact particulate matter air pollution. Studies have predicted that changes in temperature, relative humidity (RH), precipitation and air circulation patterns resulting from climate change could alter the pattern of spatial and temporal variations of $PM_{2.5}$ air pollution (Dawson et al., 2014b; Ervens et al., 2008; Mickley et al., 2004; Tsigaridis and Kanakidou, 2007).

Like other states in the Upper Midwest, short-term elevated $PM_{2.5}$ events have occurred frequently in Wisconsin in all seasons and in both urban and rural areas. In addition, there are counties in Wisconsin that exceed the National Ambient Air Quality Standard (NAAQS) for $PM_{2.5}$ and O_3. Studies have linked the long-term and short-term exposure to air pollutants to severe human health impacts, especially for people with low socioeconomic positions.

Air monitoring data collected in Wisconsin reveale the spatiotemporal heterogeneities among urban and rural areas. The spatiotemporal variations of ambient $PM_{2.5}$ (including its components and precursors) and the variety of emission sources of ambient $PM_{2.5}$ make $PM_{2.5}$ reduction more difficult than other pollutants. The complicated meteorology conditions in Great Lake region adds more challenges in achieving a cost-efficient $PM_{2.5}$ reduction and human health protection plans.

The changes of pollution patterns will have ramifications for the management of ambient air quality and its impacts on the environment. Information about the variations of ambient $PM_{2.5}$, and the correlations between local meteorological conditions and $PM_{2.5}$ and its components is essential for lawmakers to formulate an optimum air quality management plan. For example, with the promulgation of the new NAAQS rules, if any counties in the state become non-attainment area by the new rules, Wisconsin will have to submit State Implement Plans (SIPs) to EPA for approval. The information from this study will help law makers in designing long-term, cost-effective pollution control strategies that balance controls across all relevant air pollutants to establish a realistic and feasible compliance plan to meet the NAAQS for $PM_{2.5}$ and O_3. Finally, the information will also provide useful data for making future exposure assessment and epidemiological analyses and climate change impact studies.

1.2.2. **Identification of Potential Emission Sources**

Epidemiological studies conducted to understand associations between $PM_{2.5}$ emission sources and human exposure have found that combustion particles in the fine fraction from mobile and stationary sources are associated with cardiovascular mortality and daily mortality (Laden et al., 2000; Mar et al., 2000; Tsai et al., 2000).

$PM_{2.5}$ is a regional pollutant that can travel long distances due to its relatively long residence time in the air. Studies on variations of characterization of ambient $PM_{2.5}$ from different regions (urban, agriculture, rural) in Wisconsin have revealed that the local air quality is influenced by both the background concentration as well as local and regional emission sources. Therefore, to have an effective $PM_{2.5}$ reduction and human health protection strategy, identifying and quantifying sources contributions to ambient concentrations of $PM_{2.5}$ is very important.

Source-oriented dispersion and chemical transformation models and receptor-oriented receptor models have been used in air quality management areas for source identification. Receptor models are mathematical or statistical procedures, which use the chemical and physical characteristics of gases and particles measured at source and receptor to identify and quantify the sources of air pollutants at a receptor location. Receptor models are most commonly used to investigate the sources of $PM_{2.5}$, since the speciated $PM_{2.5}$ collected by CSN program provides the chemical and physical characteristics of particles at the receptor site. There are several different kinds of receptor models. The receptor model used in this thesis is Positive Matrix Factorization or PMF. PMF does not require source profiles and is potentially capable of identifying previously unknown emission sources or chemical and physical processes. PMF is selected to identify the potential emission sources of ambient $PM_{2.5}$ monitored in different regions in Wisconsin.

1.2.3. **Atmospheric Aerosol Acidity**

Acidic aerosols are ubiquitous in the atmosphere and have significant implications for increasing the risk of human health, severe degradation of ecosystems and increasing climate forcing changes. The relative potency of toxics is likely related to the degree of acidic environment. Atmospheric acidic aerosols are more hygroscopic than their neutralized forms, and thus, more effective in reducing atmospheric visibility and disturbing the solar radiation balance (Khlystov et al., 2005; Zhang et al., 2007). Aerosol acidity is one of the most important parameters that influence atmospheric chemistry and physics. The acidity level of atmospheric aerosols is linked to secondary aerosol formation through its influence on the phases of the precursors, the heterogeneous reactions as well as the functions of the reactants and oxidants of photochemical reactions (Jang et al., 2002; John H. Seinfeld, 2006; Ziemba et al., 2007).

The level of atmospheric aerosol acidity is dynamic, varying by the composition of the aerosols, the season, time of day, and meteorology. Speciated $PM_{2.5}$ data collected in Wisconsin show that the aerosol acidity in the region has been increasing since 2002, despite decreasing sulfate emissions.

1.2.4. **Elevated $PM_{2.5}$ Episodes**

The American Lung Association's State of the Air 2007 report released a clear w arning to people living in the upper Midwest that the air quality was poor in both metropolitan areas and rural areas in the region. Many studies confirme the significant impact of meteorological changes on the daily air quality in the Midwest (LADCO, 2009; Mickley et al., 2004). Dawson et al. forecasted that the summertime episodes would happen more frequently, more severely, and cover larger areas from the present to 2050 in the Midwest (Dawson et al., 2014b; Dawson et al., 2009; Mickley et al., 2004).

Analyzing daily episodes enables us to characterize the worst-case scenario, thereby providing useful information for effective air quality management and health protection. The elevated $PM_{2.5}$ and O_3 data collected at stations in Milwaukee, Waukesha, Mayville and Perkinstown per CSN program from 2002 to 2013 (Mayville from 2002 to 2009 only) will be used in this study to examine the relationship between elevated air pollution events and the concurrent meteorological parameters to fully characterize elevated $PM_{2.5}$ events in Wisconsin.

1.3. Objectives

In this thesis, the ambient $PM_{2.5}$ data collected at four different regions in Wisconsin from 2002 to 2013 was analyzed with different methods from different aspects. A systematic approach was developed in analyzing the ambient $PM_{2.5}$ data collected in Wisconsin for the following objectives:

1) Describe the spatial and temporal characteristics and variability of ambient $PM_{2.5}$, its components and precursors at each station and the correlations among the air pollutants.
2) Explore the patterns of the variations of ambient $PM_{2.5}$ and its component and precursors at each station and the correlations among the air pollutants.
3) Investigate the changes of the discovered patterns and discuss what causes the change.
4) Use PMF to identify potential major emission sources or source categories that contribute to ambient $PM_{2.5}$ at different regions (urban, rural and forests area) within Wisconsin.

5) Distinguish emission sources by applying meteorological software and graphical software in source apportionment.
6) Investigate the characteristics and distribution of aerosol acidity in the different regions.
7) Study the major factors that determine the spatial and temporal variability in aerosol acidity.
8) Examine the trend and characteristics of short-term elevated $PM_{2.5}$ events.
9) Investigate the correlations between elevated $PM_{2.5}$ events and the meteorological conditions and identify trends in episode frequency and severity.
10) Discuss the application of these findings for air quality management and health protection planning.

This is the first comprehensive study done on Wisconsin $PM_{2.5}$ data to investigate the $PM_{2.5}$ problems in the state. Important trends are observed through this study. The systematic approach in data analysis developed during the processes of this study enables us to utilize the broadly available air quality monitoring data for future environmental management and human health protection researches.

1.4. Research Scope

Global change and air quality are high-priority research areas identified by the EPA Office of Research and Development (EPA-G2014-STAR-G1). Specifically, research that seeks to characterize "the changing spatiotemporal patterns" is one of the EPA's current interests.

In my thesis, the massive ambient $PM_{2.5}$ data collected at different region in Wisconsin from 2002 to 2013 was collected to explore and characterize the changing spatiotemporal patterns and the major factors that contributed to the changes for 1). $PM_{2.5}$; 2). Aerosol acidity; and 3).

Elevated $PM_{2.5}$ events, in Wisconsin. The 2) and 3) terms are $PM_{2.5}$ at different format. Air pollution from $PM_{2.5}$ is a complex, multifaceted problem, it requires multiple approaches to analyze and understand.

First, in Chapter 2 statistical and graphical techniques were used to examine the spatial and temporal variability of $PM_{2.5}$ mass and its components from four areas in Wisconsin that varies widely in geography, meteorology, and source influence. In Chapter 2, the ambient air quality data and local Meteorological parameters collected at Milwaukee, Waukesha, Mayville and Perkinstown, Wisconsin were analyzed to determine the characteristics of ambient $PM_{2.5}$ in the state, the variations of the $PM_{2.5}$ among different regions, the patterns of the variations and the changes on the discovered patterns. Chapter 2 has also included the data collection, analytical methods, the description of the study regions.

Next, in Chapter 3 a multivariate model known as Positive Matrix Factorization was applied with the techniques to derive source profiles from the speciated $PM_{2.5}$ data at each site and identify the potential local and regional emissions sources of the ambient $PM_{2.5}$ (including its major components) at the different regions in Wisconsin. New emissions source and different source strength are important factors that will affect the spatiotemporal patterns of air pollutants.

Due to the strong seasonality of sulfate and nitrate and the rapid growth in NH_3 emission sources, the aerosol acidity in the region becomes concern for its impact to human health and $PM_{2.5}$ formation. In Chapter 4, EAIM thermodynamic model was selected to estimate the in-situ acidity. For utilize the available long term speciated $PM_{2.5}$, a thermodynamic principle based method was developed to calculate the aqueous phase acid used for input in the modeling. Chapter 4 studies the characteristics of atmospheric acidity in Wisconsin. It includes the distribution of the aerosol acidity, the major contributors to the acidity variation, the effects of aerosol acidity on $PM_{2.5}$ formation and the correlations among atmospheric aerosol acidity and the local meteorological conditions. The change on trends of aerosol acidity were observed, which need to be further studied. Last, in Chapter 5 the statistical software and HYSPLIT were used to study the pattern of the elevated $PM_{2.5}$ events in past 10 years. Chapter 5 has also discussed the major contributions to the episodes.

1.5. References

Blanchard, et al. (2008). "Carbon in southeastern U.S. aerosol particles: Empirical estimates of secondary organic aerosol formation." Atmospheric Environment **42**(Compendex): 6710-6720.

Dawson, J. P., et al. (2014). "Understanding the Meteorological Drivers of us Particulate Matter Concentrations in a Changing Climate." Bulletin of the American Meteorological Society **95**(4): 520-532.

Dawson, J. P., et al. (2009). "Impacts of climate change on regional and urban air quality in the eastern United States: Role of meteorology." Journal of Geophysical Research-Atmospheres 114.

Duncan, B. N., et al. (1995). "ESTIMATED CONTRIBUTION OF POWER-PLANTS TO AMBIENT NITROGEN-OXIDES MEASURED IN ATLANTA, GEORGIA IN AUGUST 1992." Atmospheric Environment **29**(21): 3043-3054.

EPA, U. (2005). "Understanding Particle Pollution." Retrieved 09/16/2014, 2014, from http://www.epa.gov/airtrends/aqtrnd04/pmreport03/pmunderstand_2405.pdf.

EPA/600/P-99/002bF (2004). Air Quality Criteria for Particulate Matter. II of II**:** 1148.

Ervens, B., et al. (2008). "Secondary organic aerosol yields from cloud-processing of isoprene oxidation products." Geophysical Research Letters **35**(2).

Hidy, G. M., et al. (2011). Technical Challenges of Multipollutant Air Quality Management.

Jang, M. S., et al. (2002). "Heterogeneous atmospheric aerosol production by acid-catalyzed particle-phase reactions." Science **298**(5594): 814-817.

John H. Seinfeld, S. N. P. (2006). Atmospheric Chemistry and Physics: From Air Pollution to Climate Change, 2nd Edition**:** 1332.

Katzman, T. L., et al. (2010). "PM2.5 and PM10-2.5 Compositions during Wintertime Episodes of Elevated PM Concentrations across the Midwestern USA." Aerosol and Air Quality Research **10**(2): 140-U113.

LADCO (2009). Conceptual Model of PM2.5 Episodes in the Midwest _ Lake michigan Air Directors Consortium (LADCO)**:** 37.

Laden, F., et al. (2000). "Association of fine particulate matter from different sources with daily mortality in six US cities." Environmental Health Perspectives **108**(10): 941-947.

Liao, K.-J., et al. (2008). "Current and future linked responses of ozone and PM2.5 to emission controls." Environmental Science and Technology **42**(13): 4670-4675.

Mar, T. F., et al. (2000). "Associations between air pollution and mortality in Phoenix, 1995-1997." Environmental Health Perspectives **108**(4): 347-353.

Mickley, L. J., et al. (2004). "Effects of future climate change on regional air pollution episodes in the United States." Geophysical Research Letters **31**(24): 1-4.

Mishamandani, S. (2015). Global Burden of Disease Update Reveals Major Risk Factors for Death and Disability, National Institute of Environmental Health Science. December, 2015.

Polidori, A., et al. (2006). "Local and regional secondary organic aerosol: Insights from a year of semi-continuous carbon measurements at Pittsburgh." Aerosol Science and Technology 40(10): 861-872.

Robinson, A. L., et al. (2007). "Rethinking organic aerosols: Semivolatile emissions and photochemical aging." Science **315**(5816): 1259-1262.

Seigneur, C. (2001). Current status of air quality models for particulate matter, Air and Waste Management Association.

Tsai, F. C., et al. (2000). "An exploratory analysis of the relationship between mortality and the chemical composition of airborne particulate matter." Inhalation Toxicology **12**: 121-135.

Tsigaridis, K. and M. Kanakidou (2007). "Secondary organic aerosol importance in the future atmosphere." Atmospheric Environment **41**(22): 4682-4692.

Turpin, B. (2001). "Species Contribution to PM2.5 Mass Concentrations: Revisiting Common Assumptions for Estimating Organic Mass." Science and Technology **35**(1): 602-610.

U.S.EPA (2013). Particulate Matter (PM), U.S. EPA.

Ziemba, L. D., et al. (2007). "Aerosol acidity in rural New England: Temporal trends and source region analysis." Journal of Geophysical Research D: Atmospheres **112**(10).

CHAPTER 2.

SPATIOTEMPORAL VARIATIONS OF REGIONAL ATMOSPHERIC AEROSOL

2.1. Introduction

Numerous scientific studies have linked $PM_{2.5}$ exposure to a severe health impact. Children, old people and people having lung or heart troubles are the most likely to be affected by $PM_{2.5}$ pollution. GBD (Global Burden of Disease) study (2015) claimed that air pollution accounts for 5.5 million deaths and 141.5 million DALYs (disability –adjusted life years) in 2013 (Mishamandani, 2015). $PM_{2.5}$ is also the main cause of reduced visibility and changes in atmospheric radiation balance. The deposition of $PM_{2.5}$ could make lakes and streams acidic, damaging the sensitivity of forests and farm crops, and affecting the diversity of ecosystem (U.S.EPA, 2013). The Clean Air Act (CAA) requires EPA to set air quality standards in order to protect both public health and public welfare. On Dec. 14, 2012, the U.S. Environmental Protection Agency (EPA) strengthened the national air quality standards for fine particle pollution by revising the primary annual fine particle ($PM_{2.5}$) standard to 12 from 15 µg/m3 while retaining the 24-hour $PM_{2.5}$ standard at 35 µg/m^3.

Climate change and air quality are high-priority research areas identified by the EPA Office of Research and Development (EPA-G2014-STAR-G1). Specifically, the research that seeks to characterize “the changing spatiotemporal patterns” is one of the EPA’s current interests. Climate changes and the changes in global economy are expected to impact particulate matter air pollution. Studies have predicted that changes in temperature, relative humidity (RH), precipitation and circulation in air movement resulting from climate changes could change the pattern of spatial and temporal variations of $PM_{2.5}$ air pollutions (Dawson et al., 2014b; Ervens et al., 2008; Mickley et al., 2004; Tsigaridis and Kanakidou, 2007).

Like other states in Upper Midwest recently, short-term elevated $PM_{2.5}$ events have occurred frequently in Wisconsin in all seasons and in both urban and rural areas. In addition, there are counties in Wisconsin that exceed the National Ambient Air Quality Standard (NAAQS) for $PM_{2.5}$ and O_3. Studies have linked the long-term and short-term exposure to air pollutants to severe human health impacts, especially for people with low socioeconomic positions (Laurent et al., 2007). Air monitoring data collected in Wisconsin revealed the spatiotemporal heterogeneities among urban and rural areas. The spatiotemporal variations of ambient $PM_{2.5}$ (including its components and precursors) and the variety of emission sources of ambient $PM_{2.5}$ make $PM_{2.5}$ reduction more difficult than other pollutants. The complicated meteorology conditions in Great Lake region add more challenges in achieving a cost-efficient $PM_{2.5}$ reduction and human health protection plan.

Wisconsin has a diversified economy. Industry and agriculture both play a significant role in Wisconsin's economy. The diversified geography and long Great Lake coastline, the northern bordering with Lake Superior and eastern with Lake Michigan, not only provides uniquely abundant natural resources to economy but also makes the meteorology a complicating factor in air quality management in the cities along the shoreline. Wisconsin air quality data provides a good opportunity to study the patterns of the variations and how the change affects the air quality if there is a change in the pattern.

Most Midwest air quality studies were focused on the variations among major industrial cities such as East St. Louis, IL; Detroit, MI; Cincinnati, OH; Bondville, IL; and Northbrook, IL, Indianapolis, IN (Buzcu-Guven et al., 2007; LADCO, 2003, 2010; Lewandowski et al., 2008), or the variations between major cities in Midwest and major cities in California (Stone et al., 2009). The Lake Michigan Air Directors Consortium (LADCO) organized a series of studies on the air quality in the Upper Midwest (LADCO, 2003, 2004; Stanier et al., 2012). In a more recent study, Heo et al. (2013) analyzed the 24-hr CSN data collected in Madison, Milwaukee and Waukesha, Wisconsin from 2002 to 2010 and concluded that the changes of high $PM_{2.5}$ events were mainly driven by the variations from high emission sources at Ohio River Valley and adjacent states. Katzman et al. (2010) analyzed air quality data collected in 9 Midwestern states from 2000 to 2007, The study found winter episodes happened more often than summer episodes in northern Midwestern cities and there was a north south gradient exceeding the 35 $\mu g/m^3$ gradient in Midwest.

In this chapter, a systematic approach is developed to analyze the long-term ambient air quality and meteorological parameters collected at the four monitoring stations located in different regions within Wisconsin. This chapter examines the spatial and temporal characteristics of concentration and composition of ambient $PM_{2.5}$ and its components in Wisconsin. The major objectives of the study are to discover the patterns of variations at each station, the correlations among the air pollutants in these areas, and the changes of the discovered patterns. The causes of the variations are discussed.

The hypotheses of this study are:

1) The emissions associated with inorganic $PM_{2.5}$ components have been decreasing since 2005;
2) There are significant pattern changes in monitored ambient winter $PM_{2.5}$, ammonium and nitrate;

3) Both local and regional emission sources of precursors of $PM_{2.5}$ contributed to the winter high $PM_{2.5}$ and the major winter $PM_{2.5}$ components such as nitrate;
4) Non-fuel combustion related N-sources contributed to high $PM_{2.5}$ and high nitrate in winter;
5) The significance of the difference among the spatiotemporal variations of $PM_{2.5}$ and its major components at each station varies depending on the location and the seasons;
6) The significance of the impact of temperature and RH on the variations of $PM_{2.5}$, its major components and the composition of $PM_{2.5}$ varies depending on different seasons.

The changes of pollution patterns will have ramifications for the management of ambient air quality and its impacts on the environment. Information about the variations of ambient $PM_{2.5}$, and the correlations between local meteorological condition and $PM_{2.5}$ and its components is essential for lawmakers to formulate an optimum air quality management plan. For example, with the promulgation of the new NAAQS rules, if any counties in the state become non-attainment area by the new rules, Wisconsin will have to submit State Implement Plans (SIPs) to EPA for approval. The information from this study could help law makers in designing long-term, cost-effective pollution control strategies that balance control measurement across all relevant air pollutants to establish a realistic and feasible compliance plan to meet the NAAQS for $PM_{2.5}$ and O_3. Finally, the information will also provide useful data for making future exposure assessment and epidemiological analyses and climate change impact studies.

2.2. Literature Review

2.2.1. $PM_{2.5}$

$PM_{2.5}$, particles with an aerodynamic diameter of < 2.5 μm, has attracted more attentions in recent years due to its significant impact on human health and the environment (Avakian et al., 2002; Levy et al., 2009; Lippmann et al., 2003). $PM_{2.5}$ is a complex mixture of extremely small particles (including dust, dirt, soot, smoke and small biogenic materials) and liquid droplets. They are either directly emitted from combustion (motor vehicles, power plants, smelters, biomass burning, etc.), industrial processes, agriculture activities and natural sources (volcanoes, dust storms, wild fires, biological species, and sea spray, etc.), or formed from its precursors through complicated atmospheric reactions. The major $PM_{2.5}$ components are sulfate (SO_4^{2-}), nitrate (NO_3^{2-}), ammonium (NH_4^+), elemental carbon (EC), organic carbon (OC) and trace metals. Sulfate, nitrate, and ammonium ion that are inorganic secondary $PM_{2.5}$ are formed in the atmosphere from precursors of SO_2, NO_X and NH_3, which are emitted from both natural and anthropogenic sources. Black carbon (BC) is predominately emitted from fossil fuel combustion processes due to incomplete combustion. OC is a mixture of hundreds to thousands of individual carbonaceous compounds with a wide range of chemical and thermodynamic properties (Polidori et al., 2006; Turpin, 2001). OC includes primary OC (POC) and secondary OC (SOC, also called secondary organic aerosol, SOA). The POC is directly emitted into the air as a solid or liquid particle, while SOA is formed in the atmosphere through a series of complicated reactions. The precursors of SOA are chemically active compounds emitted either from anthropogenic sources such as automobile, power plant, and industrial processes, or from biogenic emissions and wood burning (including wildfire) (Blanchard et al., 2008; Duncan et al., 1995; Jang et al., 2002; John H. Seinfeld, 2006; Liao et al., 2008; Robinson et al., 2007;

Seigneur, 2001). Figure 2.1 illustrates $PM_{2.5}$ atmospheric processes. The species in green boxes are the precursors and the ones in red boxes are secondary $PM_{2.5}$.

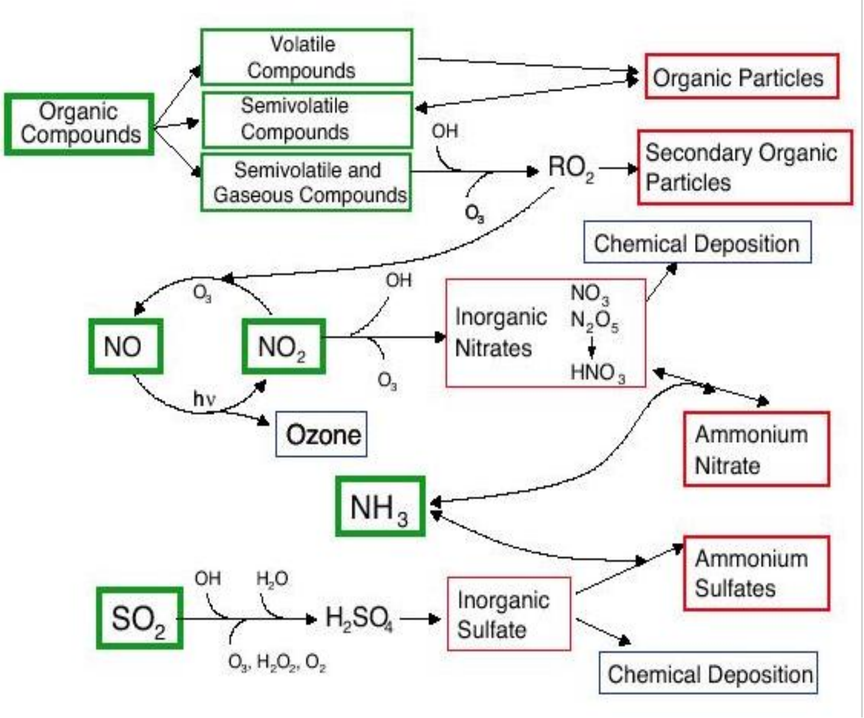

Figure 2.1 Atmospheric Aerosol Processes

(Source: PM Science for Policy Makers – A NARSTO Assessment, 2003)

Carbonaceous $PM_{2.5}$ [Total carbonaceous material (TC) = EC+OC] is a major component of fine particulate matter (ranging from 10 to 65% of total dry fine particle mass) (Andrews et al., 2000; Tolocka et al., 2001; Turpin and Huntzicker, 1995a; Turpin and Huntzicker, 1995b). However, we are currently unable to accurately measure the mass of organic $PM_{2.5}$. Organic and elemental carbon is usually measured by a thermal or thermal optical technique that quantifies the mass of the carbon collected on the sampling filter. Since the mass of organic compounds (OM) in atmospheric particulate matter include hydrogen, oxygen, and other element which combined with carbon, in traditional techniques, the concentration of particulate OM is consequently estimated by multiplying the measured concentration of organic carbon (μg of C/m^3 of air) by a factor in the range of 1.2–1.8. A conversion factor (OM/OC) of 1.4 for urban aerosol was first presented by White and Roberts (1977), based on the estimation of the average molecular weight per carbon weight for the organic aerosol. Since then many studies have been conducted for better estimates of the conversion factor from OC to OM. After considering molecular weight of broader types of OCs, Turpin (2001) suggested to use ratios of 1.6 ± 0.2 for urban aerosols and 2.1 ± 0.2 for nonurban aerosols. Russell (2003) used functional groups measured by FTIR spectroscopy to estimate composite OC and OM in ambient $PM_{2.5}$ and found more than 90% of the ratios of OM/OC lie between 1.2 to 1.6. The limitation of these two approaches is that only about 10–30% of the organic compounds in ambient aerosol samples can be identified by techniques currently available and organic aerosols vary across locations and across seasons.

One method that has been widely used is using reconstructed mass to estimate the OM. In this method, it is assumed that all of the measured mass not accounted for by sulfate ion, nitrate ion, ammonium ion, EC, and metal oxides are associated with organic compounds. The weakness associated with this method could be the unmeasured water content of $PM_{2.5}$ and the varying absorption or desorption artifacts at different samples. However, if a larger dataset is available, the sampling errors can be compensated. This method could provide reliable OM/OC ratio that reflects the local characteristics with local meteorological influences.

In addition to improving the accuracy in estimating ambient $PM_{2.5}$, the OM/OC ratio can also be used to help determine the origin of the pollutants. During low biogenic emission seasons, a higher OM/OC ratio usually indicates that the OC is either highly oxidized or significantly aged (Xing et al., 2013). Examination of concentration ratios could help to determine if the SOA is formed locally (fresh) or regionally transported (aged) (Polidori et al., 2006).

2.2.2. **The Mechanism of $PM_{2.5}$ Formation**

Most of the ambient $PM_{2.5}$ is secondary, such as sulfate, nitrate, ammonium and OC. They are formed through complex physicochemical processes in the atmosphere.

2.2.2.1. **Sulfate (SO_4^{2-})**

SO_2 is the precursor of sulfate. SO_2 is very soluble and can be converted to sulfate by reactions in the gas, aerosol, and aqueous phases. The major anthropogenic point sources of SO_2 are fossil fuel combustion at electric utilities (approximately 66%), industrial facilities (approximately 29%) and sulfur containing fuels by mobile sources and non-road diesel equipment. The majority of aerosols in the atmosphere are created through gas phase oxidation of SO_2 in the air (Hewitt, 2009):

$$\mathrm{OH} + SO_2 + \mathrm{M} \longrightarrow \mathrm{HOSO_2} + \mathrm{M}$$

$$\mathrm{HOSO_2} + \mathrm{O_2} \longrightarrow \mathrm{SO_3} + \mathrm{HO_2}$$

$$\mathrm{SO_3} + \mathrm{H_2O} + \mathrm{M} \longrightarrow \mathrm{H_2}SO_4 + \mathrm{M}$$

where M is a reaction chaperone. H_2SO_4 is highly hygroscopic (Seinfeld, 2006) and the most significant condensable molecules in the troposphere, which plays important role in atmospheric nucleation. The gas-phased SO_2 becomes aqueous SO_2 ($SO_{2(g)}$= K_H×$SO_{2(aq)}$) and is governed by Henry's Law:

$$K_{\mathrm{H}}(\mathrm{SO_2}) = [SO_2(\mathrm{aq})]/P(\mathrm{SO_2})$$

where K_H is the Henry's Law constant for SO_2 and $p(SO_2)$ is the pressure of SO_2. Once gaseous SO_2 becomes aqueous SO_2, the following heterogeneous, aqueous phase oxidation occurs:

$$\mathrm{SO_2}(aq) \leftrightarrow \mathrm{H^+} + \mathrm{HSO_3}^-$$

$$\mathrm{HSO_3}^- \leftrightarrow \mathrm{H^+} + \mathrm{SO_3}^{2-}$$

Due to the formation of bisulfite $[HSO_3^-]$ and sulfate $[SO_3^{2-}]$ ions, effective Henry's Law coefficient (K_{Heff}) is more commonly used (Hewitt, 2009):

$$k_{\mathrm{Heff}}(\mathrm{SO_2}) = ([\mathrm{SO_2(aq)}] + [\mathrm{HSO_3}^-] + \left[\mathrm{SO_3}^{2-}\right])/P(\mathrm{SO_2})$$

$$k_{\mathrm{Heff}}(\mathrm{SO_2}) = k_{\mathrm{H}}(\mathrm{SO_2})(1 + \mathrm{K_1}/[\mathrm{H^+}] + \mathrm{K_1K_2}/[\mathrm{H^+}]^2)$$

From above equations, we can see that the solubility of SO_2 is related to the pH of aqueous phase and decrease when $[H^+]$ is high. Sulfate (SO_4^{2-}) originates partially from the dissociation of sulfuric acid (H_2SO_4). The neutralized sulfates are very stable in the aerosol phase at atmosphere.

2.2.2.2. **Nitrate (NO_3^-)**

The primary source of man-made nitrogen oxides (NOx = NO + NO_2+N_2O) is from the burning of fossil fuels, and the oil and gas industries. For most emission sources, NOx is emitted as NO. The lifetime for NOx could be several hours, while the lifetime for individual NO_2, or N_2O, is in the order of seconds. The longer lifetime of NOx allows it to have diurnal and seasonal cycles.

Daytime pathway: $\mathrm{NO_2} + \mathrm{OH} \rightarrow \mathrm{HNO_3}$

Relatively slow but important night-time oxidation: $\mathrm{NO_2} + \mathrm{O_3} \xrightarrow{1} \mathrm{NO_3} + \mathrm{O_2}$

Nitrate can be formed in low winter sunlight. At acidic condition, the following night-time reaction occurs and generates N_2O_5. N_2O_5 (Dinitrogen pentoxide) can react heterogeneously with water to yield HNO_3:

$$\mathrm{NO_2 + NO_3 + M \underset{3}{\overset{2}{\rightleftarrows}} N_2O_5 + M} \qquad K_{2,3} = \frac{[\mathrm{N_2O_5}]}{[\mathrm{NO_2}][\mathrm{NO_3}]}$$

$$\mathrm{N_2O_5 + H_2O}(s) \xrightarrow{4} \mathrm{2HNO_3}$$

Nitrate is not as stable as sulfate (Tang, 1980). NH_4NO_3 dissociation is a function of temperature and RH. The variation of ammonium nitrate also depends on the availability of ammonia and is favored by low temperatures and high relative humidity (see Figure 2.1) (Blanchard et al., 2008; Stelson and Seinfeld, 1982; Tsimpidi et al., 2008). At higher temperature, nitrates are partitioned to its gaseous phase.

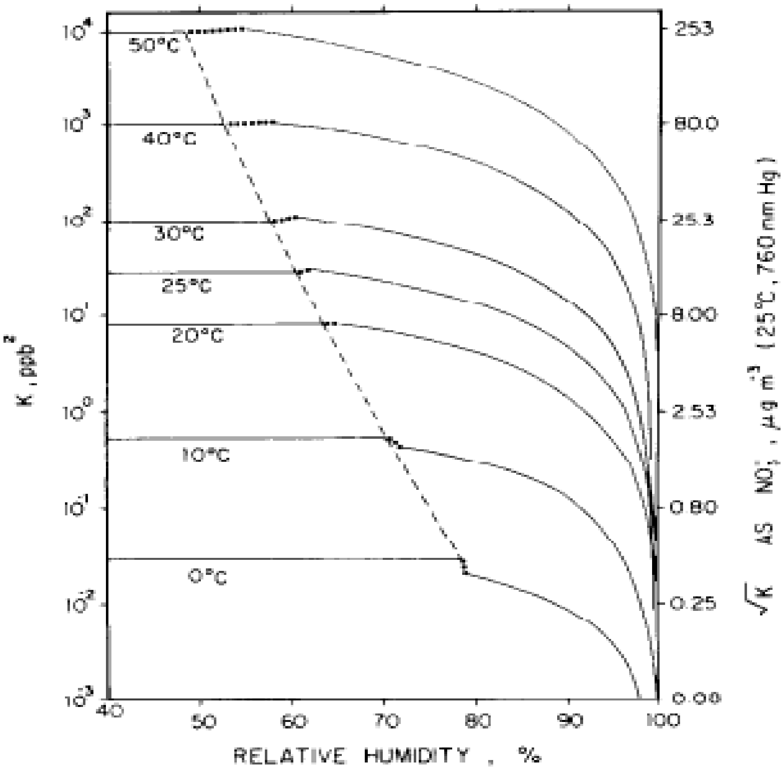

Figure 2.2 NH_4NO_3 dissociation constant

2.2.2.3. **Ammonium Ion (NH_4^+)**

Ammonia (NH_3) is a highly reactive and soluble alkaline gas. The major emission sources for the ammonia are agricultural activities, such as, domestic animals (40.3%), synthetic nitrogen fertilizers (16.9%) and biomass burning (including forest fires) (Bouwman et al., 1997; Erisman et al., 2007). Ammonia is also emitted at a lesser extent from a range of non-agricultural sources such as catalytic converters in cars, landfill sites, sewage works, composting of organic materials and combustion processes.

Under the catalyst of a specific manure enzyme, the release of NH_3 from livestock manure is assumed to depend on the following major factors:

1) The difference between [NH3gas] in air above manure surface and the [NH3gas] at the surface of manure. The release of NH3gas from the surface of manure to the air is governed by the diffusion constant;

7) The equilibrium between [NH3aq] and [NH3gas] in manure is governed by Henry's law;

8) The chemical equilibrium between [NH4+aq] in manure and [NH3aq] in manure, which is governed by the dissociation coefficient of [NH4+]. The dissociation coefficient depends on pH and temperature (see Figure2.2) (Behera et al., 2013). The dissociation occurs at wider pH range. However, higher temperature and high pH contributes to [NH4+aq] dissociation.

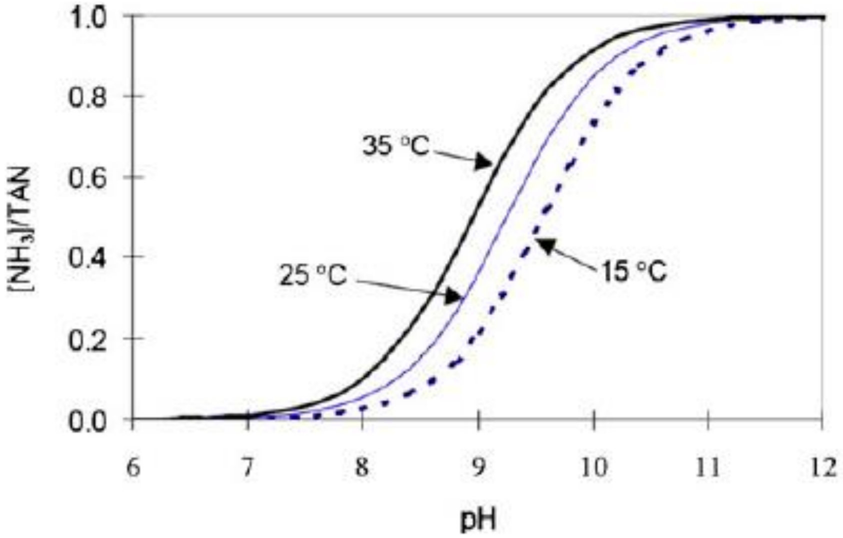

Figure 2.3 Effect of pH and temperature on equilibrium between NH_4+ and NH_3 in aqueous solution

NH_3 concentration has spatial and temporal distribution. High NH_3 spots are near agricultural activities areas. The concentration varies temporally with the changes in agricultural practice. Ammonia (NH_3) and Ammonium (NH_4^+) are the major bases available to neutralize sulfuric acid aerosol and nitric acid aerosol:

$$\mathrm{NH_3} + \mathrm{H_2SO_4} \longrightarrow \mathrm{NH_4}HSO_4 + \mathrm{NH_3} \longrightarrow (\mathrm{NH_4})_2SO_4$$
$$\mathrm{NH_3} + \mathrm{HNO_3} \Leftarrow\Rightarrow \mathrm{NH_4NO_3}$$

The products of neutralization, NH_4HSO_4 and $(NH_4)_2SO_4$, are more stable in the aerosol phase compare with the NH_4NO_3 in aerosol phase. In a low NH_3 environment, sulfuric acid exists in the aerosol phase in the form of H_2SO_4. As NH_3 increases, H_2SO_4 is converted to HSO_4^- and its salts (Seinfeld, 2006).

Higher summer temperature enhances the photochemical reactivity that produces elevated OH, O_3 and H_2O_2 concentrations and results in higher sulfate production (John H. Seinfeld, 2006). Unlike H_2SO_4, NH_3 and HNO_3 are relatively volatile and may transfer between the gaseous phase and aqueous phase, in the suspended solution droplets.

2.2.3. **The impact of meteorological condition**

Most of the air pollutants are released into the atmosphere in the lower level of troposphere, the planetary boundary layer, where the transport and dispersion of air pollutants are significantly influenced by meteorological parameters. The variability of the concentration, the “clean” or “polluted” ambient air in an area with almost constant emissions, is determined by the meteorology (Seinfeld, 2006).

Tai et al. found that daily variation in temperature, relative humidity (RH), precipitation, and circulation could explain up to 50% of $PM_{2.5}$ variability (Tai et al., 2010) and the sensitivity of $PM_{2.5}$ to these meteorological parameters indicates that changes in climate could have significant impacts on $PM_{2.5}$ concentrations (Dawson et al., 2007). By examining the influence of the complex meteorology in the vicinity of Great Lakes region on air quality, it was concluded in two separate studies that lake breeze increased the formation of aerosols and as a result enhanced the impact of local important anthropogenic emissions (Brook et al., 2013; Fosco and Schmeling, 2006).

Tsigaridis and Kanakidou (2007) suggested that temperature and precipitation induced changes in biogenic emissions of VOCs could increase organic aerosol concentrations appreciably over the U.S. VOCs from biogenic emissions could be the precursors of the formation of SOA; however, the role of many biogenic VOCs in forming organic aerosol is either not well understood or may generally be underestimated in chemical transport model (Dawson et al., 2014a; Ervens et al., 2008). Due to the multiple complex links among air quality, emission sources and the variations of most relevant meteorological parameters such as temperature, RH, precipitation and mixing height, their impact on longer-term (monthly, seasonal, and annual) averages might negate one another. It is important to take a close look at the correlations between the $PM_{2.5}$ and meteorological parameters in each region at different seasons.

Mickley et al. (2004) indicated that the severity and duration of summertime regional pollution episodes in the Midwestern and northeastern United States would increase significantly relative to present due to the reduced cyclone frequency in future warmer climate. Mickley et al further suggested that statistical analysis of observed correlations between pollutant concentrations and meteorological parameters might provide a useful tool to predict pollution trends.

For better understanding of the future air quality and better projection of the effects of climate change on $PM_{2.5}$ air quality, it is essential to have a good understanding of the dependence of $PM_{2.5}$ on meteorological variables.

2.2.4. **Prior Work on Air Quality Variation**

Most Midwestern air quality studies have so far focused on the variations of emission sources and characteristics of $PM_{2.5}$ of major industrial cities such as, East St. Louis, IL; Detroit, MI; Cincinnati, OH; Bondville, IL; and Northbrook, IL, Indianapolis, IN (Buzcu-Guven et al., 2007; Lewandowski et al., 2008; Snyder et al., 2010). Receptor models were used in these studies to estimate the potential major emission sources. After comparing samples collected at Cleveland, OH and Detroit, MI in the Great Lake region with samples collected at Riverside, CA of the Los Angeles Air Basin, Stone et al. (2009) found that the summertime SOA at the two regions was substantially different from each other and warned to exert caution if generalizing the source and nature of SOA in different regions.

LADCO has organized a series of studies on the air quality in Midwest, U.S. Speciated $PM_{2.5}$ collected from 1999 to 2001 in six Upper Midwest states, Minnesota, Wisconsin, Michigan, Illinois, Indiana and Ohio were analyzed to determine the spatial, temporal, and chemical variations in $PM_{2.5}$ concentrations. The annual average $PM_{2.5}$ from 1999 to 2001 showed a gradient in $PM_{2.5}$ concentrations, with higher values to the south (i.e., Illinois, Indiana, Ohio, southern Michigan, and southern Wisconsin) and lower values to the north (i.e., Minnesota, central/northern Wisconsin, and central/ northern Michigan). The Classification and Regression Tree (CART) analysis indicated that in these urban areas, high $PM_{2.5}$ concentrations are associated with low wind speeds, generally southerly wind directions, and higher relative humidity (LADCO, 2003). In Upper Midwest urban air quality study, it was found that the annual average of nitrate and OC from Wisconsin is similar to that from the big industrial towns near Chicago (LADCO, 2004). To better understand wintertime episodes of elevated $PM_{2.5}$ concentrations in the Midwest, the elevated $PM_{2.5}$ and meteorology data collected from Jan.1 to

March 31, 2009 at the Milwaukee and Mayville sites were analyzed. This study pointed out the remaining biggest uncertainties: the variation of ammonia emissions from episode to episode, the nitrate production, and how to control the N compound to achieve the best $PM_{2.5}$ reduction goal (Stanier et al., 2012).

Heo, et al (2013) applied Potential Source Contribution Function (PSCF) analysis to the 24-hr CSN data collected at Madison, Milwaukee and Waukesha, Wisconsin from 2002 to 2010. The study concluded that the changes of high $PM_{2.5}$ events were mainly driven by the variations of the mass movement originating from the high emissions sources and the enhanced nitrates and sulfates were strongly influenced by the high emission sources at Ohio River Valley and adjacent states. They proposed that in order to reduce ambient $PM_{2.5}$ concentration it is necessary to consider both pollutant transport and local emissions. Katzman et al. (2010) compared the composition of $PM_{2.5}$ on days when it exceed 35 $\mu g/m^3$ with the annual average composition of $PM_{2.5}$ collected at 9 Midwestern states from 2000 to 2007 and found winter episodes happened more often than summer episodes in northern Midwestern cities, and vice versa for the episodes that happened in south of Great Lakes. Based an analysis of the speciated $PM_{2.5}$ data collected from Monday, January 31, 2005 through Saturday, February 6, 2005, a winter episode that covered entire Midwestern 9 states, they discovered a north-south gradient exceeding 35 $\mu g/m^3$ in Midwest. Therefore, they suggested adopting a different control strategy for each city at different seasons depending on how far north or south the city is located in the Midwest.

2.2.5. **Summary**

$PM_{2.5}$ is a complex mixture of extremely small particle and liquid droplets. The collected ambient concentration of $PM_{2.5}$ and its major components revealed the heterogeneities of ambient air pollutants in both urban and nonurban areas in United States. The variations in air quality distribution have impacts on air quality management practices and associated human health studies. The complex and interrelated factors contributing to these heterogeneities include:

1) The variety of local or long distance transported, anthropogenic and natural emission sources of the primary $PM_{2.5}$ and the precursors of secondary $PM_{2.5}$.
2) The complicated $PM_{2.5}$ formation mechanism.
3) The thermodynamic properties of the precursors and $PM_{2.5}$ components.
4) Meteorological conditions.

Global economy and global warming have brought in new factors that can influence the heterogeneities of ambient air pollutions. Analyzing long-term available air quality data collected in one state, relying on the formation theory and thermodynamic properties of $PM_{2.5}$ to discover the spatial and temporal variations of the ambient $PM_{2.5}$, the patterns of the variations, changes in the patterns and causes of the changes is essential for an efficient air quality management plan.

2.3. Methods

2.3.1. **Site Description**

Since 1979 the EPA required each state to operate a network of monitoring sites designated as State and Local Air Monitoring Sites (SLAMS) that measure the ambient concentration of air pollutants that have NAAQS. The SLAMS network includes Ozone and Photochemical Assessment Monitoring Stations (PAMS), $PM_{2.5}$ Chemical Speciation Network (CSN), National

Air Toxics Trends Stations (NATTS) and National Core Multi-Pollutant Monitoring Stations (NCore). The CSN program is part of an effort to monitor concentration trends and to assist state and local air monitoring agencies with meeting the NAAQS for $PM_{2.5}$ and to support the ongoing studies on health effects. Figure 2.3 is a map that indicates the locations of the monitoring stations.

Seven CSN stations have been installed in Wisconsin at different period. Their locations are: Milwaukee, Waukesha, Mayville, Horicon, Green Bay, Perkinstown and Chiwaukee.

Four monitoring stations (Milwaukee, Waukesha, Mayville and Perkinstown) with different geographical settings in Wisconsin and having longest continuously collected speciated $PM_{2.5}$ data were selected for this study. Table 2.1 shows details of the parameters collected at each of these four stations. These four stations are all State and Local Air Monitoring Station (SLAMS).

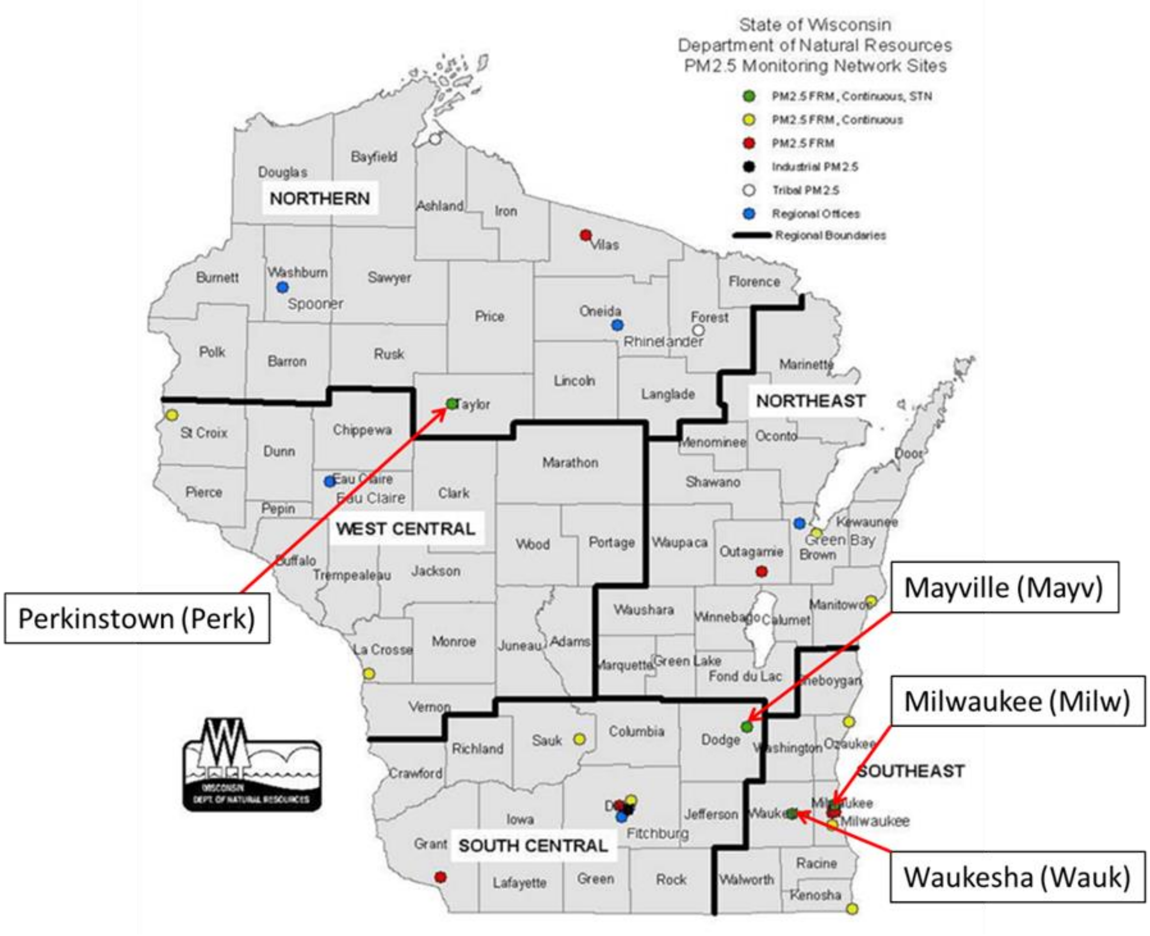

Figure 2.4 Map of the monitoring stations (with the four stations used in this study indicated)

2.3.1.1. Milwaukee, WI (Milw, latitude: 43.000, longitude: -87.735)

Milw station is about 1.6 km (1 mile) north of Downtown Milwaukee, 3.2 km (2 miles) west of Lake Michigan, and about 0.8 km (0.5 mile) east of highway I-43 (a major north-south roadway). The surrounding area is primarily commercial and residential. Natural gas is the most widely used fuel for cooking and heating. Local traffic emissions from cars idling, stopping, and accelerating are all year long. This station is also a PAMS site. The Monitoring objectives of this station are: population exposure, maximum precursor emissions and to detect elevated levels of $PM_{2.5}$ and Ozone to determine compliance with NAAQS. See Table 2.1 for details about the parameters collected at this station.

2.3.1.2. Waukesha, WI (Wauk, latitude: 43.020, longitude: -88.215)

Wauk station is located in a fenced area in an industrial area in city of Waukesha, Waukesha County. The Monitoring objectives of this station are to monitor urban population exposure, to detect elevated O_3 and $PM_{2.5}$ to determine compliance with NAAQS and to provide pollutant level for daily air quality index reporting. See Table 2.1 for details about the parameters collected at this station.

2.3.1.3. Mayville, WI (Mayv, latitude: 43.439, longitude: -88.528, removed in 2009)

Mayv station is located in an agricultural field. This station also serves as a special Purpose Monitoring Station (SPMS) used to monitor urban transport. A limestone quarry is located to the northwest of the site on the northeast corner of Highway 33 and 67. The Monitoring objectives of this station are urban population exposure related, to detect elevated pollutant levels of $PM_{2.5}$ and O_3 to determine compliance with NAAQS and to provide pollutant levels for daily air quality index reporting. See Table 2.1 for details about the parameters collected at this station.

2.3.1.4. Perkinstown, WI (Perk, latitude: 45.204, longitude: -90.600)

Perk station is also a National trend network (NTN) used for regional background information. The station is located in a private property about 1.61 km (1mile) east of the town of Perkinstown, in the middle of a hilly grass field surrounded by heavily wooded Chequamegon National Forest. The closest industry site is a coal fired power plant, about 80 km (50 miles) southwest in Wausau, WI. This station is a CASTnet monitoring site as well as a National Atmospheric Deposition Program (NADN) site. The Monitoring objectives of this station are welfare related, detecting elevated pollutant levels of $PM_{2.5}$ to determine compliance with NAAQS and to provide pollutant levels for daily air quality index reporting. Table 2.1 shows the parameters collected at this station.

2.3.2. **Sampling and Sample Analysis**

CNS, PAMS, NMOC network's operation, sampling and measurement methods for $PM_{2.5}$, O_3, NO_3^{2-}, SO_4^{2-} , NH_4^+, EC, OC, SO_2, NOx, etc are documented in EPA website. Table 2.1 lists the parameters collected at each station. The sampling starting date at each station varies. Meteorological data is obtained from the Midwestern Regional Climate Center (MRCC, http://mrcc.isws.illinois.edu/)[1].

Table 2.1 Parameters collected at each station:

Air Parameters	MILW	WAUK	MAYV	PERK
FRM $PM_{2.5}$	x	x	x	
CSN $PM_{2.5}$	x	x	x	x
IMPROVE $PM_{2.5}$				x
O_3	x	x	x	
PAMS/1-hr NMOC	x			
PAMS/24-hr NMOC	x			
SO_2	x	x		
NOx, NOy, NO,	x			
CO	x			
Meteorology	x	x	x	x

RTI International, an EPA contractor laboratory since 1999, is in charge of the CSN $PM_{2.5}$ program. The Sample Handling and Archiving Laboratory (SHAL) at RTI prepares sampling

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[1] The MRCC is a cooperative program between the National Centers for Environmental Information (NCEI) and the Illinois State Water Survey in Champaign, Illinois. Its center is a partner in a national climate service program that includes NCEI, five other Regional Climate Centers, and State Climate Offices. The NCEI is part of the Department of Commerce, National Oceanic and Atmospheric Administration (NOAA).

modules for each sampling event. The sampling modules are fitted with three filters and shipped to the field. The laboratory also provides denuders coated with magnesium oxide or sodium carbonate as needed. A Teflon filter is used to collect $PM_{2.5}$ for measurement of total mass by gravimetry, elements by X-ray fluorescence, and in some cases, anions and cations by ion chromatography. A nylon filter is used to collect $PM_{2.5}$ for measurement of anions and cations by ion chromatography, and a quartz filter is used to collect $PM_{2.5}$ for measurement of organic, elemental, carbonate, and total carbon. After 24-hour sampling, the modules are retrieved from the sampler, placed in ice chests and shipped back to RTI laboratory. In RTI, the received filters are distributed to the appropriate speciation laboratories for chemical analysis [RTI, http://www.epa.gov/ttn/amtic/]. Sample results are entered in the EPA's Air Quality System (AQS) database. Before October 2009, the Speciation Trend Network (STN) used a Thermal Optical Transmittance (TOT) method to measure OC and EC in $PM_{2.5}$. The thermal Optical Reflectance (TOR) technique is currently used in CSN program to measure OC and EC since October 2009.

Sampling in Wisconsin is performed by Wisconsin Department of Natural Resources' Air Program (WDNRAP). After receiving the sampling modules and the denuders, the WDNRAP staff places them in the sampler before scheduled sampling time and retrieve them when the cycle is over. SASS samplers (MetOne) are used for sample collection at the stations. Samples are collected on a set of three different filters over a 24-hour sampling period at an interval of every third day at Milwaukee and Mayville stations and every sixth day at the other stations.

2.3.3. **Data Preparation**

2.3.3.1. **Missing Data and Below Detection Limit (BDL) Data**

The data used in this study was downloaded from AQS website (http://www.epa.gov/ttn/airs/airsaqs/). In the obtained raw data, the samples with values below the detection limit (BDL) were reported as "0". In this study, these below-detection-limit data were replaced by half of the associated "alt" (minimum detection limit (MDL) for that day). The species with more than 50% of BDL were removed from the calculation, unless the species could be used as an index for a specific emission source. In the correlation analyses, the data with below detection limits were treated as no-data (Nan). In the descriptive analysis, the data with below detection limits were replaced by half of the associated individual minimum detection limit (MDL).

2.3.3.2. **Outliers**

Many factors contribute to the outliers. Studies have indicated that there are seasonal discrepancies between FRM $PM_{2.5}$ and CSN $PM_{2.5}$ mass (Tolocka et al., 2001). It is not reliable to use either FRM $PM_{2.5}$ or CSN $PM_{2.5}$ as a final measurement. FRM $PM_{2.5}$ does not capture all the ambient particles and has significant analytical problems caused by evaporation of ammonium nitrate and some volatile compounds, and adsorption of particle bound water (EPA Manual 2000). In this study, the measured CSN $PM_{2.5}$ (Mass) and reconstructed $PM_{2.5}$ (SUM) were compared to determine the outliers following the approach proposed by (Klemm RJ, 2000). It is assumed that the reconstructed $PM_{2.5}$ is comprised by the sum of sulfate (SO_4^{2-}), ammonia (NH_4^+), nitrate (NO_3^-), organic matter, elementary carbon and oxidized metals:

Reconstructed $PM_{2.5}$ (SUM) = $SO_4^{2-} + NH_4^+ + NO_3^- + OM + EC + MetOx + Others$

where MetOx = 2.2 AL + 2.49 Si + 1.63 Ca + 2.42 Fe + 1.94 Ti;

OM = 1.4 x OC; and

Si, Ca, Fe, Ti, SO_4^{2-}, NH_4^+, NO_3^-, EC and OC = concentrations of speciated $PM_{2.5}$ measured by CSN, in unit of μg/m^3.

The outliers are then defined as the points that lie outside of the range of 60~140% of the "(Mass/Sum)/Sum" ratio (Baumann et al., 2008) as shown in Figure 2.5.

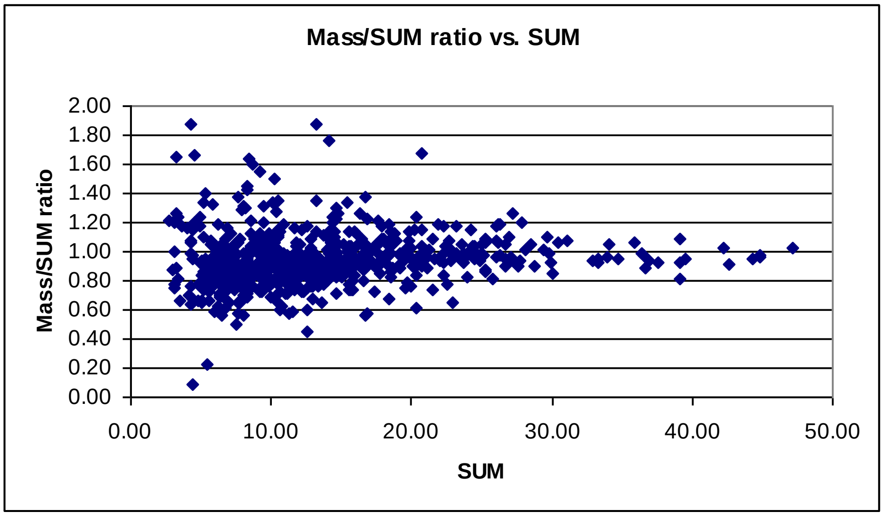


Figure 2.5 Mass/sum ratio vs. Mass

Without considering the field blank, the blank correction and simply using a uniform number to convert OC to OM adds significant bias to the data collected at different geographical settings. Taking advantage of the large dataset of CSN speciated $PM_{2.5}$ available, linear regression is used in this study to estimate the seasonal blank correction value and OC to OM conversion factors at each station. The four seasons are defined as:

Winter: January, February and December

Spring: March, April and May

Summer: June, July and August

Fall: September, October and November

2.3.3.3. **OC and Blank correction and OC to OM Conversion**

In CSN program, quartz-fiber filters are used to collect air samples for testing OC and EC contents in $PM_{2.5}$ by Thermal Optical Transmittance (TOT) method (before 2009). It has been found that the adsorption of organic vapors onto quartz-fiber filters and evaporation of the organics between the filter and air during $PM_{2.5}$ sampling cause the discrepancies in reported organic carbon measurements (John G. Watson, 2008; John G. Watson∗, 2005). The Chemical Speciation Network (CSN) measures field blanks. However, due to the differences in handling the blanks throughout the network, the field blank is not reported with the NAQ data. The U.S. EPA has recommended a sampler specific, field averaged measurement, 1.53μg/m^3, as the "blank correction" for OC collected by MetOne SASS samplers in the entire network.

1. OC Blank Correction

With the advantage of the large sized data set, a simple regression method was used to estimate the OC blanks (see Figure 3.3). It is assumed that if the mass of $PM_{2.5}$ is zero, then the OC should be zero. If OC can be described as: $OC = a + b \times (Mass)$,

Then the intercept "a" can be considered as the integrated blank correction value for the OC.

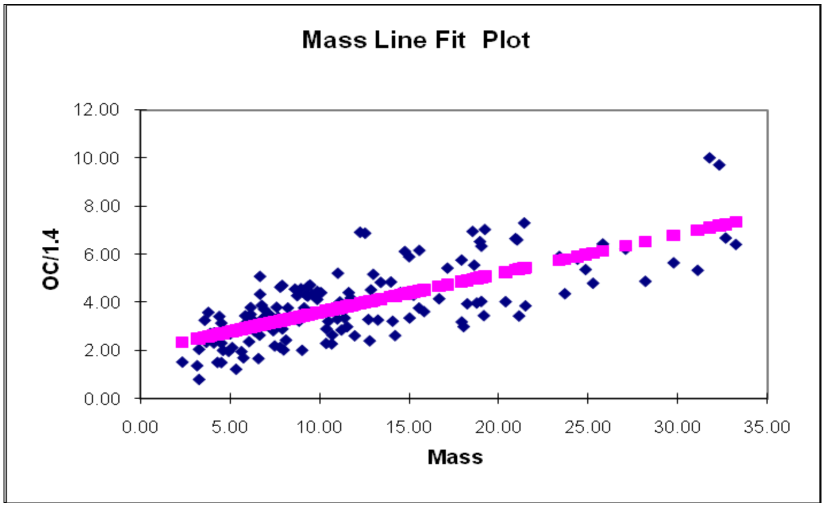


Figure 2.6 OC regression over mass

2. Estimating OC to OM (OM/OC) Conversion Factor

Taking advantage of the large dataset, ordinary least square regression was used to estimate the conversion factors (b) and the mass contributed by non-OM (a) at each station at different seasons as defined in Equation 1 (Lim and Turpin, 2002). The hypothesis is that organic matter (OM) varies with the OC.

Assuming OM can be described as:

$OM = a + b \times (OC)$ (Lim and Turpin, 2002)

where: a = (interceptor), the mass associated with non-OM;

b = OM/OC, when “a” is negligible.

$OM = [CSN\ PM_{2.5}\ mass] – ([EC] + [Sulfate] + [Nitrate] + [Ammonium] +$

$[Soil] + [\sum Other\ metals]) + OC$

$Soil = Al_2O_3 + SiO_2 + CaO + Fe_2O_3 + TiO_2$

$= 2.2Al + 2.49\ Si + 1.63\ Ca + 2.42\ Fe + 1.94\ Ti$;

where Al, Si, Ca, Fe, Ti, SO_4^{2-}, NH_4^+, NO_3^- and EC are the speciated $PM_{2.5}$ collected by CSN program, in unit of μg/m^3.

It is assumed that all of the measured mass not accounted for by sulfate ion, nitrate ion, ammonium ion, EC, and metal oxides is associated with organic compounds. The mass of oxides of unknown trace metals is negligible. The estimated OC to OM conversion factors will be summarized and discussed in "Results and Discussion" Section.

2.3.4. **Methods of Analysis**

2.3.4.1. **Statistical analysis**

In this chapter, the mass of $PM_{2.5}$ and Speciated $PM_{2.5}$ (μg/m^3) collected at the four stations were analyzed on daily, seasonal, yearly and yearly seasonal time scale for the 8-year period (2002 to 2009) to discover the patterns of spatiotemporal variations and the changes of the discovered patterns at the four regions. The 12-year data (2002 to 2013) from stations of Milw, Wauk and Perk are also examined for the long-term trends of air quality changes in these three regions. The statistical significance of the changes in concentration and composition of $PM_{2.5}$ and speciated $PM_{2.5}$ among the four regions, and the two contrasts, Urban vs nonurban, and Lakeshore/inland (Milw vs. Wauk, Mayv and Perk), were determined using descriptive statistical analysis, Kolmogorov-Smirnov Test (KS-Test) and Kruskal-Wallis tests.

The following specific spatiotemporal variations are studied to find the patterns of the variations and the change of the patterns. Emission inventories and meteorological data were used to investigate the following:

1. Long-term (2002 to 2009) mean concentration and composition of $PM_{2.5}$ and the major $PM_{2.5}$ components at the four stations;

2. Annual variations for mean concentration and composition of $PM_{2.5}$ and major $PM_{2.5}$ components;
3. For studying the trend for the past 9 years and the contributors to the change Seasonal Variations and yearly seasonal variations;
4. The table of episodes at the four stations

2.3.4.2. **Meteorological data**

Meteorological data for the four stations, including wind speed, wind direction, ambient temperature and relative humidity (RH) were downloaded from Midwestern Regional Climate Center's website (MRCC, http://mrcc.isws.illinois.edu/). These data were recorded at hourly intervals. The dominant wind direction and wind speed at each station and each season are illustrated in wind roses.

The relative humidity (RH) were also analyzed. Refer to the plots in Appendix Figure AA4.7 to Figure AA4.11 for the plots of wind roses and the RH and temperature distributions (see Appendix_ch3 for plots and tables).

2.4. Results and Discussion

2.4.1. **Spatial Variations**

The monitoring station at Mayville was removed to Horicon at the end of 2009 and the analytical method for OC was modified since then. Therefore, $PM_{2.5}$ and speciated $PM_{2.5}$ from 2002 to 2009 were studied for special and temporal variations among four regions.

2.4.1.1. **Spatial Variations (2002 to 2009) at the Four Regions**

Table 2.2 (Mean concentration (µg/m^3) of PM$_{2.5}$ (2002~2009)) summarizes the long-term average concentrations of PM$_{2.5}$, NO$_3^-$, SO$_4^{2-}$, NH$_4^+$ and OC collected from Milw, Wauk, Mayv and Perk from 2002 to 2009. These concentrations reflect the combination of primary emitted, formed in the air through atmospheric physical and chemical reactions and long distance transported PM$_{2.5}$, organic and inorganic secondary PM$_{2.5}$ components. Figure 2.7 is the box-plot graph for the PM$_{2.5}$ collected at the four stations from 2002 to 2009. Each station has many days when the concentrations were higher than the upper whiskers. Figures 2.7 and 2.8 illustrate the long-term mean concentration and mean composition of the major PM$_{2.5}$ components from each station.

Table 2.2. Mean concentration (µg/m^3) of PM$_{2.5}$ (2002~2009)

Station	PM$_{2.5}$	NH$_4$	NO$_3$	SO$_4$	EC	OM	Al	Ca	Si	Fe	K
MILW	12.61	1.65	2.69	2.72	0.50	3.83	0.02	0.04	0.06	0.08	0.07
WAUK	13.75	1.53	2.68	2.59	0.57	4.07	0.03	0.05	0.14	0.14	0.08
PERK	8.55	0.95	1.53	1.81	0.20	2.63	0.02	0.03	0.06	0.03	0.04
MAYV	11.02	1.56	2.67	2.45	0.28	2.80	0.02	0.03	0.05	0.03	0.05

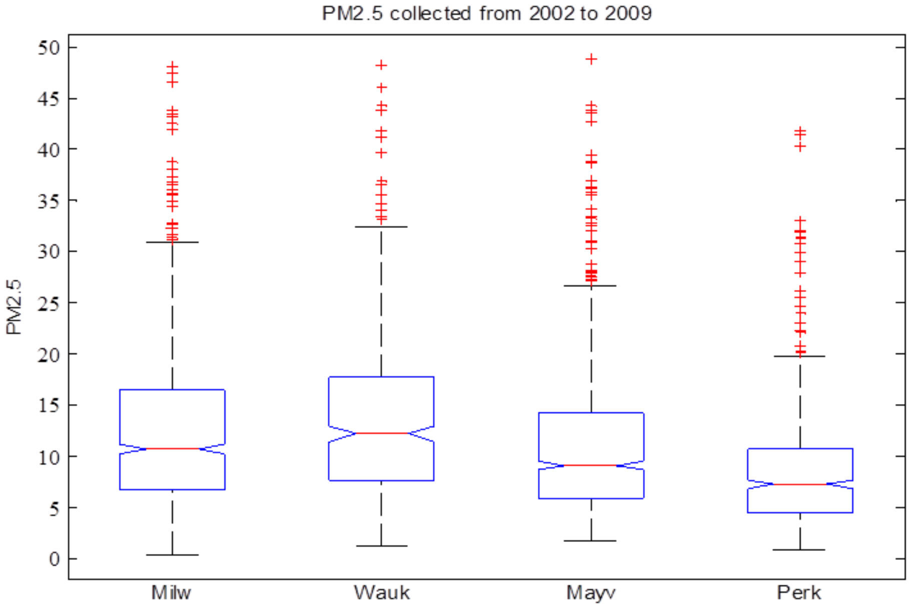


Figure 2.7 Box Plot for $PM_{2.5}$ (2002 ~ 2009)

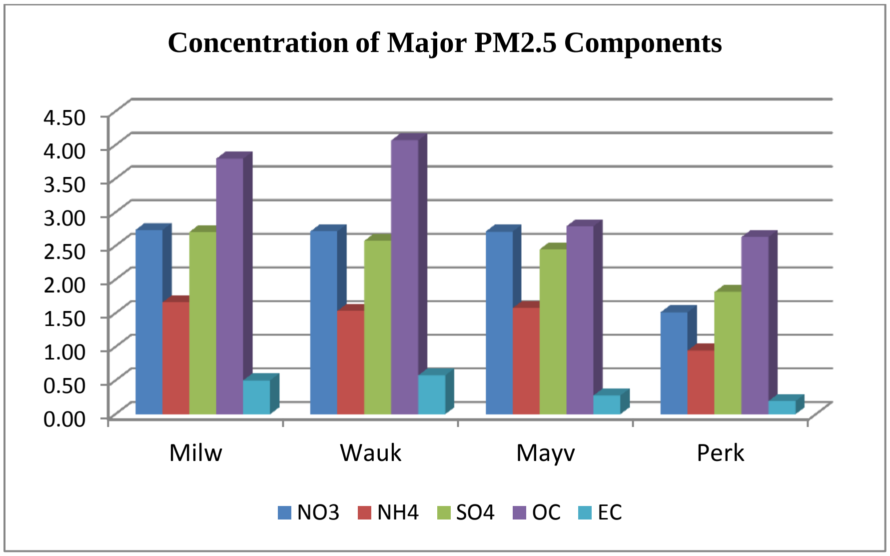


Figure 2.8 Mean Concentration of major components from the Four Stations

From Table 2.2 and Figure 2.8, the long-term average concentrations of $PM_{2.5}$, NO_3^-, SO_4^{2-} and NH_4^+ from each station vary. The long-term means of $PM_{2.5}$, NO_3^-, SO_4^{2-} and NH_4^+ observed at

Perk were significantly lower than those observed at urban, industrial and agricultural areas, represented by Milw, Wauk and Mayv, respectively. The long-term means of EC were higher at urban and industrial stations. The means of OM at each station showed similar trend as that of EC at each station, higher at MILW and Wauk, lower at Mayv and lowest at Perk. As expected, the higher concentration of $PM_{2.5}$ was found in industrial and urban areas. OC is the highest single component (both in concentration and in composition) of ambient $PM_{2.5}$ collected at the four stations. Wauk has the highest average concentration of $PM_{2.5}$, EC, OM and individual trace metals among the four stations. Mayville monitor station is located in a farmland and surrounded by agricultural field. The average concentration of $PM_{2.5}$ and major inorganic components at Mayv, like Ammonium and nitrate, were very close to that from the urban and industrial stations.

Table 2.3 lists the long-term all season mean composition of major primary and secondary $PM_{2.5}$ components at each station. Figure 2.9 shows the composition of major $PM_{2.5}$ components, composition of the major components = concentration of the major $PM_{2.5}$ components divided by the concentration of the $PM_{2.5}$ at the same day. The highest composition of NO_3^- and NH_4^+ was observed at Mayv, while the lowest was observed at Perk. Milw and Wauk had higher EC composition, while Perk had the lowest EC composition. EC is mainly associated with direct emissions from fossil fuel combustion (both stationary and mobile). It is obvious there were more EC sources in urban and industrial area than in a rural area which is surrounded by forests. OM not only has the highest mass content in $PM_{2.5}$ but also has the highest composition in $PM_{2.5}$, compare with other component of $PM_{2.5}$. The OM composition at Perk (36.9%) was close to the highest composition of OM at Wauk (38.8%), while Mayv had only 29.8%. The Perk station in is located on the edge of the heavily wooded Chequamegon National Forest.

Wisconsin county road M is about 450 yards south of the site. The closest industry is a coal fired power plant, which is about 50 miles southwest in Wausau. The relatively less industrial emissions impact and higher biogenic emissions from the forest flora in the area contributed to the high OC composition in the ambient $PM_{2.5}$ collected at Perk station.

Table 2.3. Mean composition ($\mu g/m^3$) of the major $PM_{2.5}$ components (2002~2009)

Station	NH_4	NO_3	SO_4	EC	OM	Al	Ca	Si	Fe	K
MILW	0.131	0.214	0.215	0.040	0.317	0.002	0.003	0.005	0.007	0.005
WAUK	0.111	0.195	0.186	0.042	0.388	0.002	0.003	0.010	0.010	0.006
PERK	0.111	0.178	0.212	0.023	0.369	0.002	0.003	0.006	0.003	0.005
MAYV	0.142	0.242	0.221	0.025	0.298	0.002	0.002	0.004	0.003	0.004

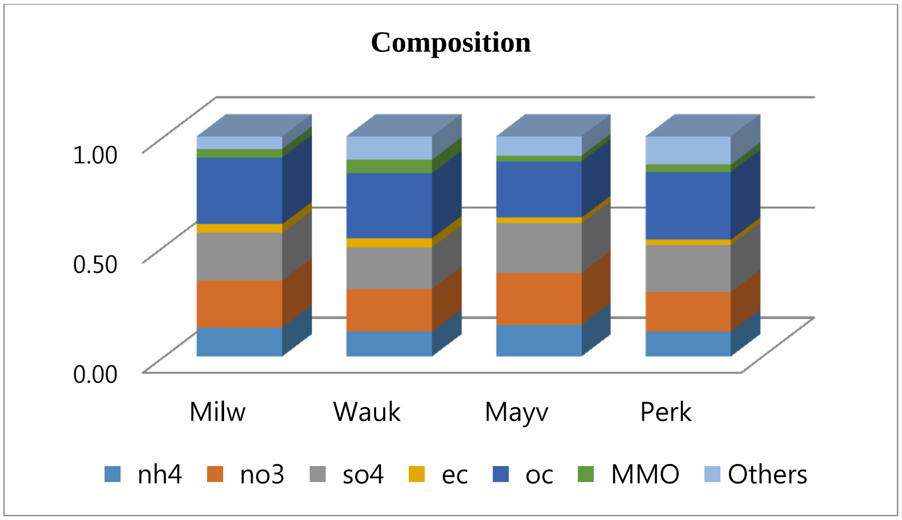


Figure 2.9 Mean Composition from the Four Stations (2002~2009)

About 90% of Wisconsin's industries are located in southeast and east region of Wisconsin. Big foundries and metal processing facilities are located in Milwaukee County, The Menomonee River Valley, a heavily industrial area which hosts a variety of industries, is about two miles western of downtown Milwaukee. Lake Michigan exerts a strong effect on the weather in Milwaukee. The Fox River Valley, famous for its largest concentration of paper manufacturing facilities in the world, is about 120 miles northwest of Milwaukee and 120 miles north of Waukesha, and 70 miles north of Mayville. In addition to paper industry, Fox River Valley is also famous for its metal products and food processing. Large coal-fired power plants are located along Lake Michigan shoreline. Checking the wind roses for Milw, Wauk and Mayv, the emissions from these neighboring counties could have exerted big impact on the ambient air quality, especially in winter time, when the domain wind directions are north and northwest. In addition, the Columbia Energy Center is only about 80 km west of Mayville station. The SO_2 and NOx emitted from the power plant, paper mill and other industries in Columbia County are the major contributors to the $PM_{2.5}$ observed at Mayv station.

Considering the shared sources of precursors of secondary $PM_{2.5}$ and the prolonged residence life after the gaseous precursors become ions, Kruskal-Wallis (K-W) analysis is applied to the $PM_{2.5}$ data collected at the four stations from 2002 to 2009 to test if the differences among the four stations are significant. K-W test indicated that the variations of $PM_{2.5}$ at Milw are significantly different from the variations at the stations of Perk, Mayv and Wauk (see Figure. 2.10).

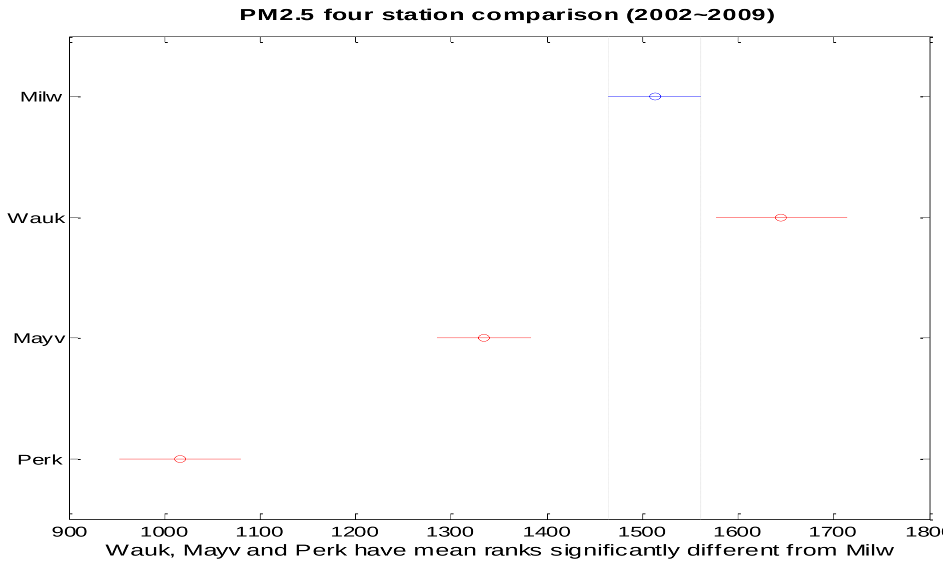


Figure 2.10 K-W analysis for significant changes of $PM_{2.5}$ among the four stations

The above K-W test results plot also indicates that the variations of $PM_{2.5}$ at Mayv, Wauk and Perk are significantly different from each other.

2.4.1.2. **Shoreline vs inland and Urban vs non-urban**

The inland stations are the same as the non-urban stations in this study. They are: Waukesha (industrial), Mayville (agricultural) and Perkinstown (rural and forests). Mayville and Perkinstown are frequently under the influence of emissions from major industries.

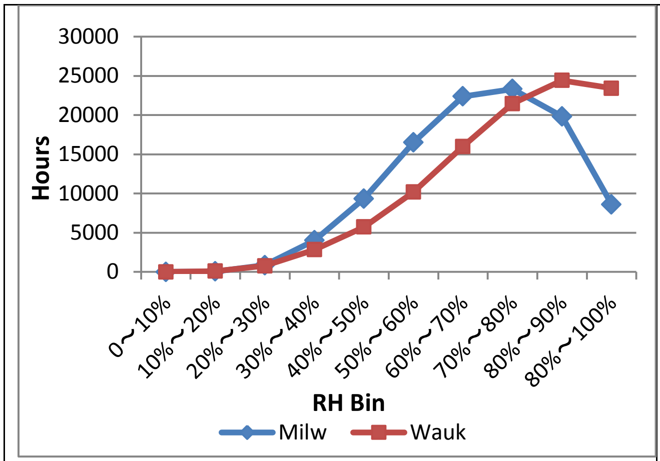


Figure 2.11-1. RH _ Milw vs Wauk

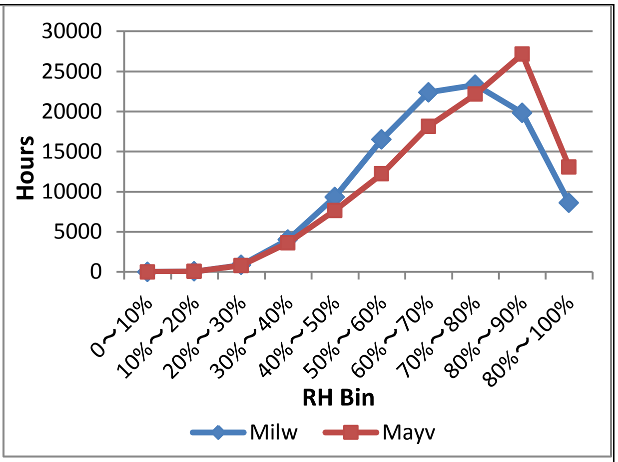


Figure 2.11-2. RH _ Milw vs Mayv

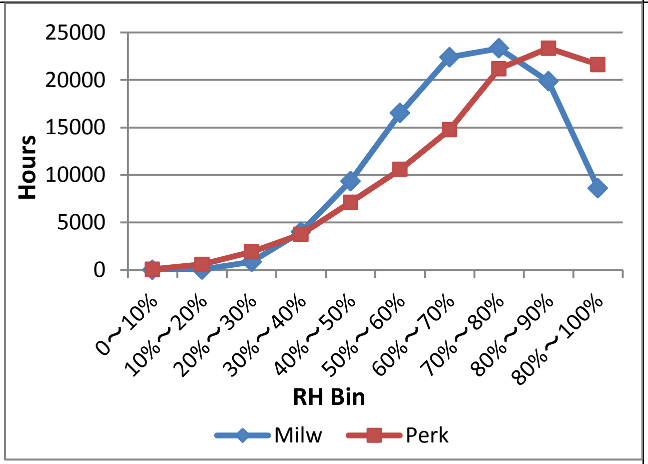


Figure 2.11-3. RH _ Milw vs Perk

Figure 0.11. RH at Different Stations

Milwaukee and Waukesha are located in Milwaukee metropolitan area, in the Great Lakes Region with a humid continental climate with cold, windy, snowy winters, and warm, humid summers. Since it is located adjacent to Lake Michigan, Milwaukee is periodically affected by "Lake Breeze" between the months of March and July. At daytime the onshore flow causes air with cooler temperatures and higher relative humidity to move inland. After sun sets, the convection current reverses and an offshore flow creates a land breeze. After the land breeze develops warmer temperature flows east toward the lakeshore. From Figures 2.11, Milw has more hours of RH in the range between 20~30% to 70~80%, compare with Wauk; more hours of RH in the range between 30~40% to 70~80%, compare with Mayv; and more hours of RH in the range between 30~40% to 80~90%, compare with Perk. The higher RH enhanced the $PM_{2.5}$ formation. The lake or land breezes can transport pollutants in three dimensions and recirculate the pollutants several times over the near-shore area (Lyons, 1972). The offshore and onshore circulation traps the pollutants inside the air and transport the air pollutants inland is highly correlated with the high occurrence of elevated concentration of $PM_{2.5}$ in Milwaukee County (Lyons and Cole, 1976).

2.4.2. **Annual Variations**

Figure 2.12 illustrates the concentration of annual $PM_{2.5}$, ammonium, nitrate, sulfate, OC and EC from 2002 to 2009, respectively. Two different trends were clearly seen for $PM_{2.5}$ and the inorganic secondary $PM_{2.5}$, ammonium, nitrate and sulfate at the four regions from 2002 to 2009. The annual concentration of $PM_{2.5}$ and the inorganic secondary $PM_{2.5}$ increased from 2002 to 2005 (Period 1) and then slowly decreased after 2005. At all sites, $PM_{2.5}$ emissions in 2002 and 2005 were higher than that in other years. The concentrations for EC at Milw and Wauk showed similar upward and downward trends with highest at 2005. However, the different sources of EC at the Mayv and Perk region made the concentration of EC kept increasing slowly till 2007, then decreasing. No significant annual changes on concentration of OC at the four stations.

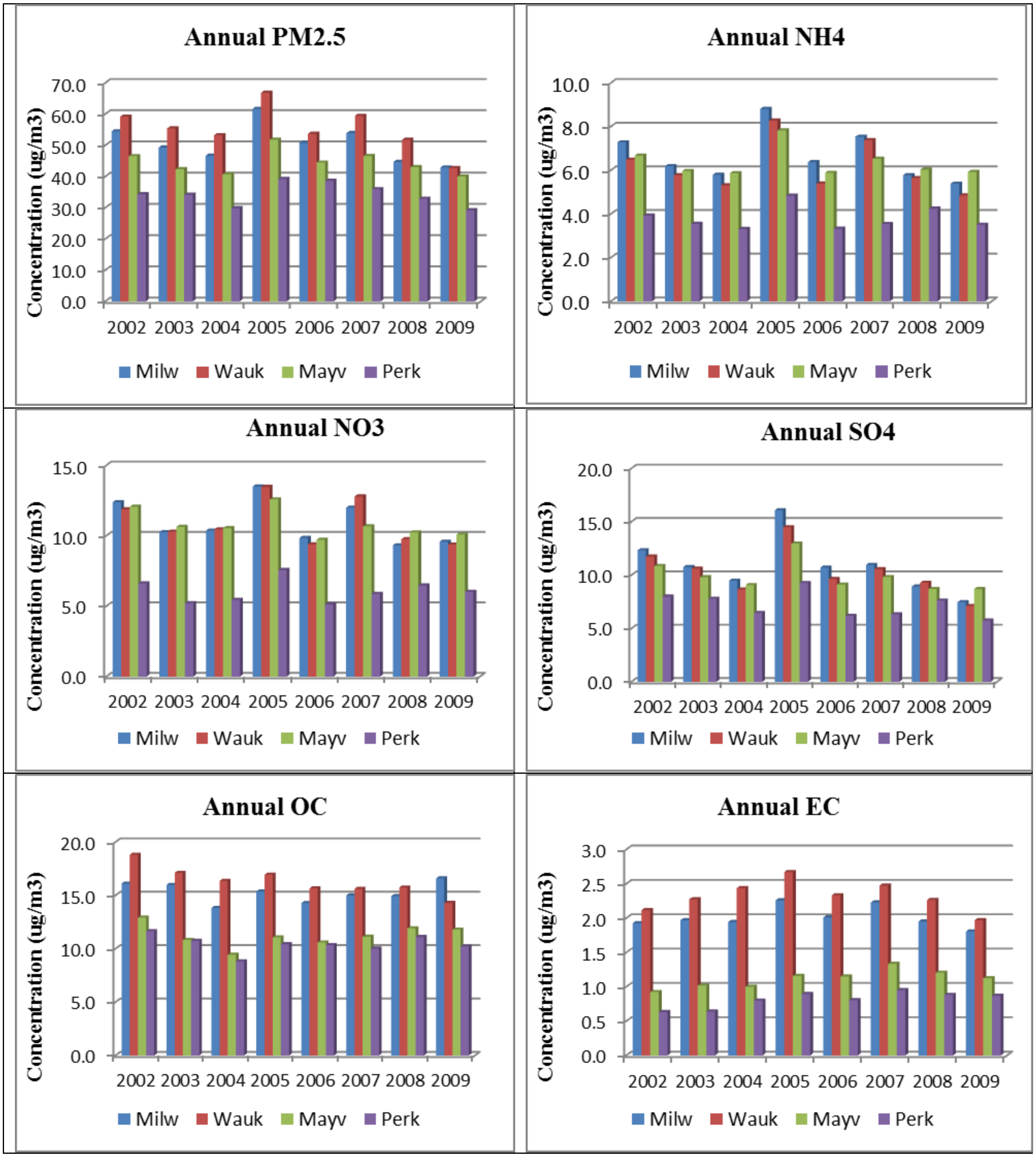


Figure 2.12. Annual Concentration of $PM_{2.5}$, NH_4^+, NO_3^-, SO_4^{2-}, OC and EC

Krustal-Wallis analysis (Figure 2.13) indicated that the upward variations in Period I is significantly different from the downward variations from Period II.

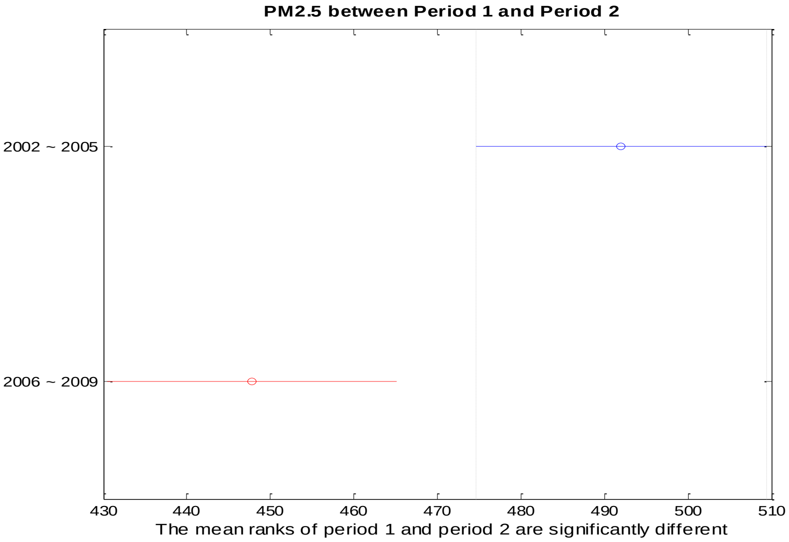


Figure 2.13. K-W test result for difference between the two periods of $PM_{2.5}$

There are many factors that could cause air pollution in a region. The major factors are anthropogenic emission sources and meteorology conditions (Seinfeld, 2006). K-W analysis indicated that the meteorology conditions were not significantly different between these two periods

Emission inventory (EI) from 2002 to 2004 is not available. The 2005 to 2014 emission inventory for SO_2, NOx and VOC from Wisconsin sources is used to discuss the annual trend in this study (see Figure AA4, Figure AA5 and Figure AA6 for emissions inventory of NOx, SO_2 and VOC, respectively).

Sulfate (SO_4^{2-}) and nitrate (NO_3^-) are secondary $PM_{2.5}$ formed in the air through complex photochemical reactions of SO_2 and NOx. Even though it is hard to relate SO_2 and NOx emissions from one region to the ambient SO_2 and NOx observed in that region, it is clear that SO_2 and NOx emissions have been decreasing significantly since 2005 and the emission drop is the major contributor to the decreasing ambient sulfate and nitrate. VOCs are the precursors of OC. The OC is the highest single $PM_{2.5}$ component (see Figure 2.8). From VOC EI plot, the stationary source emissions of VOC in Wisconsin had been dropping steadily since 2005 (883 tons/yr) until 2009 (772 tons/yr). Since the ambient OC concentrations were relatively stable from 2002 to 2009, there must be other VOC sources that were not reported in the emission inventory. Biogenic VOCs are another major VOC sources. At eastern U.S., biogenic VOC contributed about 90% of OC of $PM_{2.5}$. Biogenic VOC emissions are not required to report in the emission inventory and are the significant VOC sources in Wisconsin too.

2.4.3. **Seasonal Variations**

2.4.3.1. **Seasonal Variations in Concentration and Composition**

A strong seasonality was clearly observed cross all the stations for $PM_{2.5}$ and its major components (Figure 2.14). It could be seen from Figure 2.14 that the winter has the highest $PM_{2.5}$ mass at all stations, except for Perk. MILW and WAUK have similar seasonal trends: winter $PM_{2.5}$ is higher than that in summer and spring has the lowest $PM_{2.5}$. At MAYV, winter $PM_{2.5}$ was almost 20% higher than the $PM_{2.5}$ observed at other seasons. Summer concentration of $PM_{2.5}$ is similar to the concentration at spring and fall. PERK had highest $PM_{2.5}$ in summer and the second in winter.

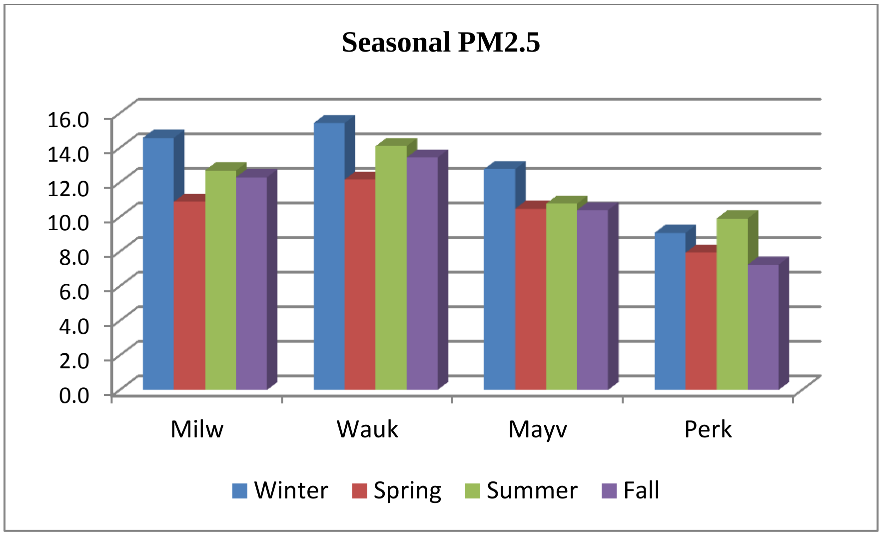


Figure 2.14. The Seasonality of PM2.5 at each station

Figure 2.15 shows the statistics of the $PM_{2.5}$ at each season for the four stations.

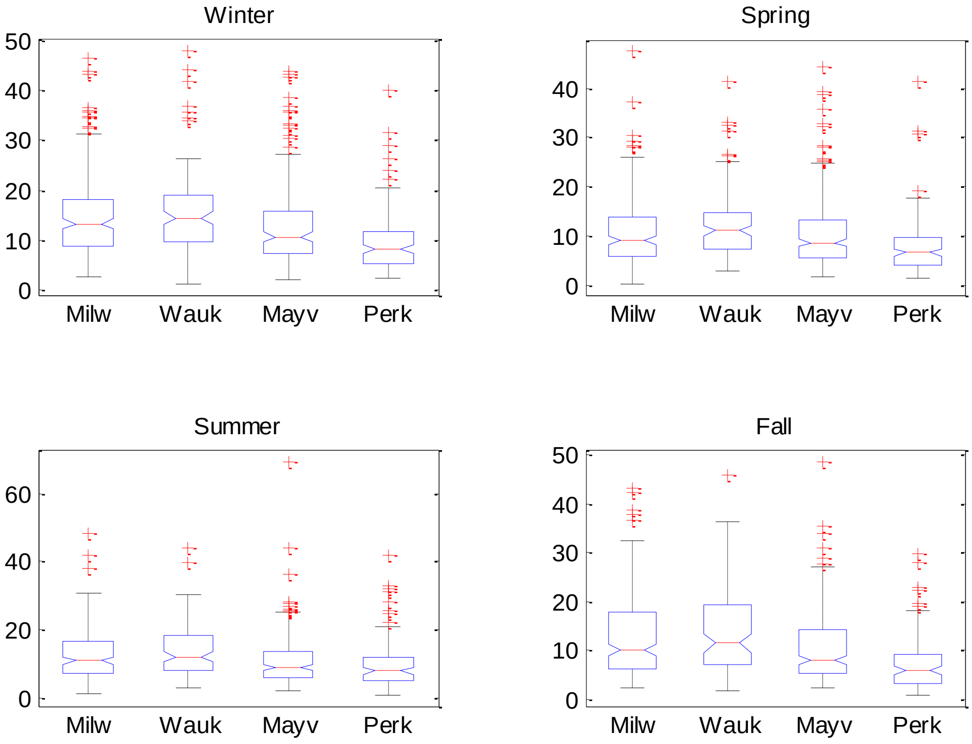


Figure 2.15. $PM_{2.5}$ collected at the four stations at each season (2002 ~2009)

From Figure 2.15, we can see that at each season and at each station, there are many days when the concentrations of $PM_{2.5}$ were above the upper whisker. The study on elevated $PM_{2.5}$ events in Wisconsin indicated winter has the highest number of exceedance (> 35 µg/m^3) at all the four stations. Milw has the highest number of elevated $PM_{2.5}$ episodes. The rank for other three stations is Wauk > Mayv > Perk. The concentration, composition and causes of the episodes will be discussed in another chapter. It could be seen from Figure 2.16 that the largest composition in winter $PM_{2.5}$ is nitrate, and the largest composition in summer $PM_{2.5}$ are sulfate and organic matter (OM).

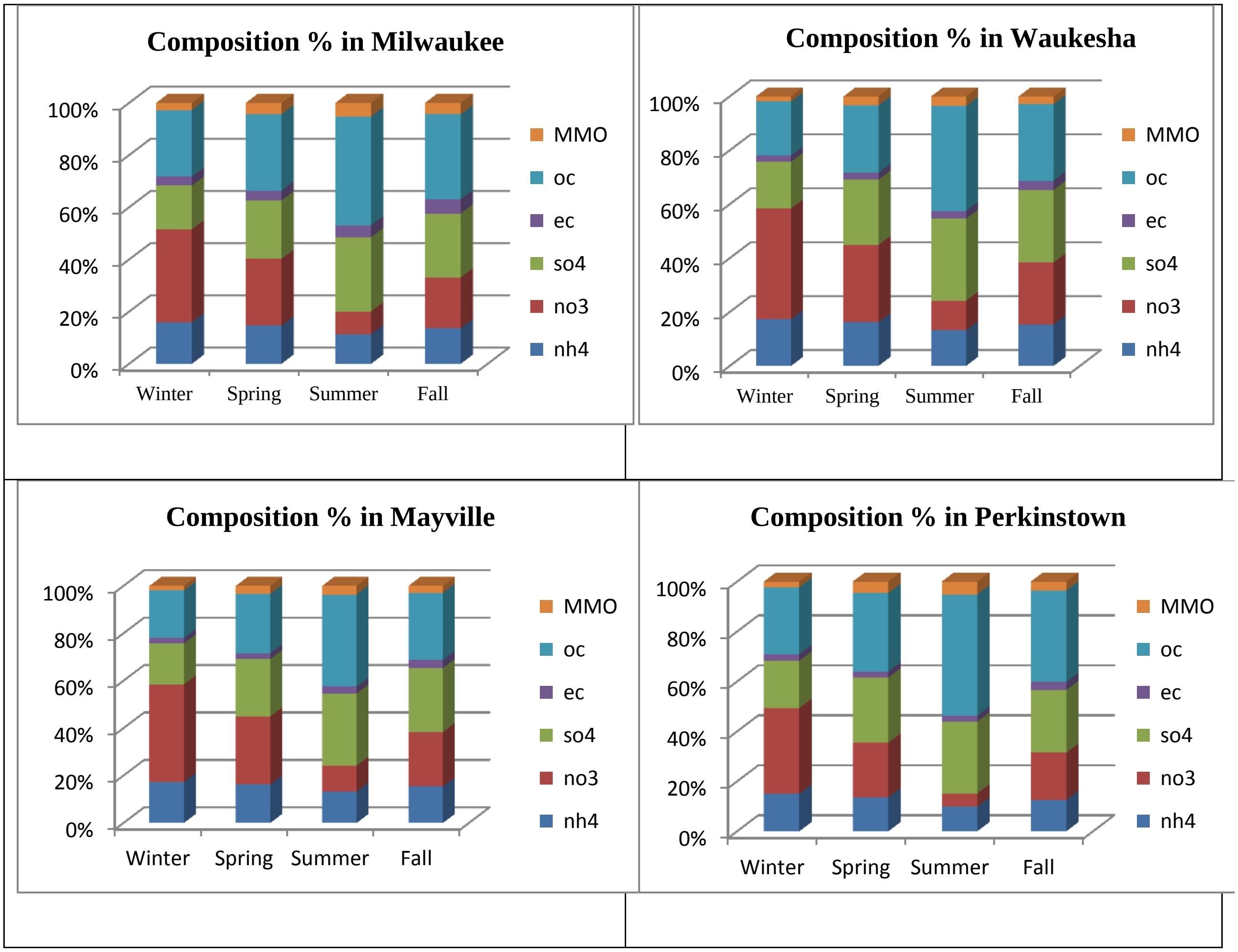


Figure 2.16. Average seasonal composition at each station (2002 ~2009)

Table AA2.8 lists the seasonal compositions of major $PM_{2.5}$ components from the four stations (see Appendix A). Nitrate contains the highest composition of $PM_{2.5}$ in winter while lowest (except for EC) composition in summer at the four stations. Sulfate and OC composition are higher in summer and lower in other seasons. The major components of $PM_{2.5}$ (such as ammonia, nitric acid and organics) can exist in both gas and aerosol phases in the atmospheric. Thus, in order to understand the seasonality in the ambient $PM_{2.5}$ concentration, it is essential to understand the thermodynamic properties of these species in both vapor and particulate phases.

Through homogeneous and/or heterogeneous photochemical reactions, SO_2 and NOx are converted to sulfuric acid (H_2SO_4) and nitric acid (HNO_3), respectively. Higher summer temperature enhances the photochemical reactivity that produced elevated OH, O_3 and H_2O_2 concentration and resulted the higher sulfate productions (John H. Seinfeld, 2006). Not like H_2SO_4, NH_3 and HNO_3 are volatile and may transfer between the gaseous phase and aqueous phase in the suspended aqueous particles. Since sulfuric acid is a strong acid, NH_4^+ reacts with sulfuric acid first, then the remaining reacts with nitric acid. The variation of ammonium nitrate concentration depends on the availability of ammonia and favors low temperatures, and high relative humidity (Blanchard et al., 2008; Tsimpidi et al., 2008). HNO_3 has strong affinity for ice and liquid water, not depending on H_2O_2, which allows nitrate be formed at low winter sunlight. At higher temperature, nitrates are portioning to its gaseous phase.

The solubility of SO_2, HNO_3 and NH_3 are also related to the pH of aqueous phase, decrease when $[H^+]$ is higher for SO_2 and NOx, increase when $[H^+]$ is higher for NH_3.

$$\mathrm{k_{Heff}(SO_2) = k_H(SO_2)(1 + K_1/[H^+] + K_1K_2/[H^+]^2)}$$

$$\mathrm{k_{Heff}}(NO_3^-) = \mathrm{k_H}(NO_3^-)(1 + \mathrm{K}_{n1}/[\mathrm{H}^+])$$

$$\mathrm{k}_{\mathrm{Heff}}(\mathrm{NH}_3) = \mathrm{k}_{\mathrm{H}}(\mathrm{NH}_3)(1 + \mathrm{K}_{a1}[\mathrm{H}^+]/\mathrm{K}_w)$$

The Henry's Law coefficient (K_{Heff}) is the function of Henry's Law coefficient (K_H). The K_{Heff} is always larger than K_H. K_H is governed by Van't Hoff equation and generally increases in value when temperature decreases (Seinfeld, 2006).

The variations of the composition at each station can be affected by the source strength and the atmospheric acidity at the region and the impact of transported air pollutions. From Figure 2.16, the winter nitrate composition varied from 30.9% (Wauk) to 37.2% (Mayv). Summer OM composition varied from 39.4% (Milw) to 55.2% (Perk) and summer SO_4^{2-} composition varied from 21.9% (Perk) to 26.3% (Mayv). Perk is surrounded by forests. The biogenic VOC emissions from the forests could contribute to the higher OC concentration in summer time.

2.4.3.2. **Kruskal-Wallis (K-W) Analysis and the Variations**

K-W analysis had also been applied to seasonal variations at each station to determine if the seasonal variations of the major components at each station are significantly different. The test results indicate that the significance of the variations varies depends on seasons and components. For example, the mean rank of $PM_{2.5}$ in spring at Mayv was not significantly different from Milw, while it was significantly different from Milw at the other three seasons (see Figure 2.15-2). These observations indicated that Milw and Mayv have been impacted by the emissions from different sources. The different sources impact can be caused by the seasonal wind direction and strength change (see wind roses for Milw and Mayv).

K-W analysis can be used as an initial analysis to examine if there are significant differences between the parameters collected at different stations, then further analyzing what caused the differences. For example, $PM_{2.5}$ variations at Perk and Mayv are significantly different from the variations at Milwaukee in winter, summer and fall, except spring. In spring, only the variation in Perk is significantly different from that in Milw. PERK has entirely different wind pattern compare with the other three stations (Figure AA7 for wind roses, Appendix A). In addition to the difference caused by seasonal wind direction change, Perk can also be impacted by its own local sources, such as forests, and long distance transported air pollutions.

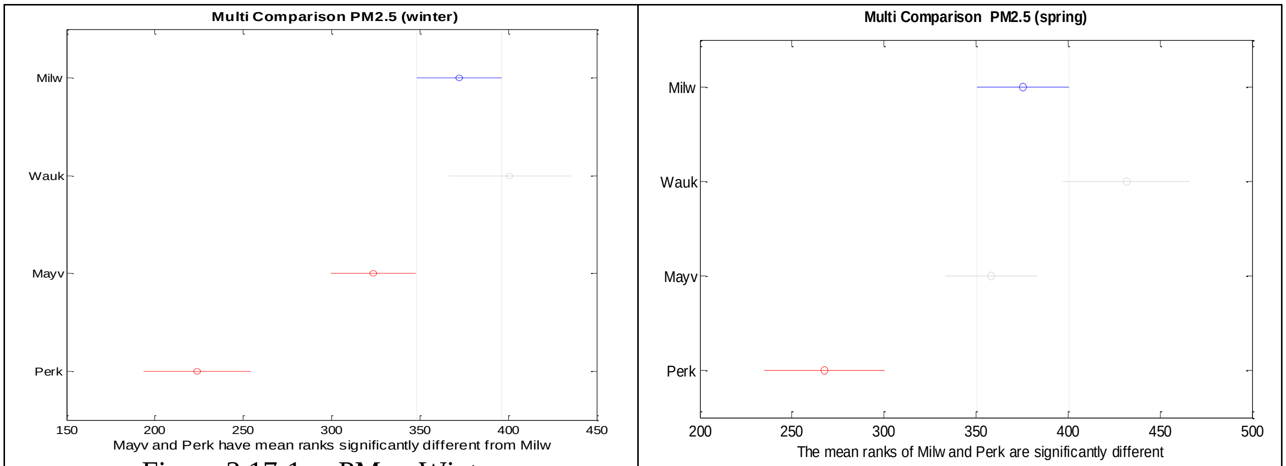


Figure 2.17-1. $PM_{2.5}$_Winter

Figure 2.17-2. $PM_{2.5}$_Spring

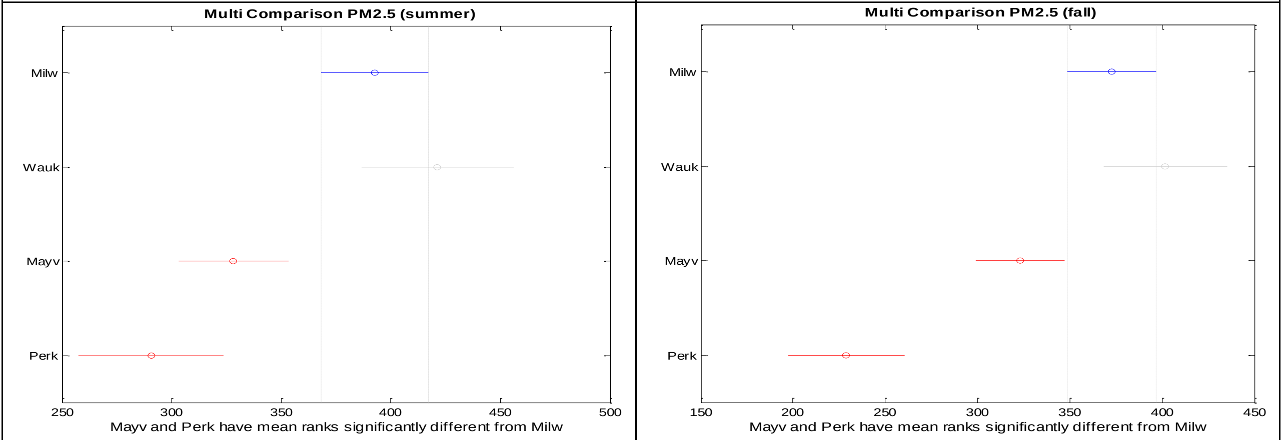


Figure 2.17-3. $PM_{2.5}$_Summer

Figure 2.17-4. $PM_{2.5}$_Fall

Figure 2.17. K-W test for significant changes of Seasonal $PM_{2.5}$

K-W analysis found that the variation of $PM_{2.5}$ at Mayv and Perk stations are significantly different from that at Wauk station. Wauk station is only about 24 km away from Milw station. Wauk may have same pattern of $PM_{2.5}$ as Milw station. The variations of sulfate, nitrate and ammonium at Perk are significantly different from those in Milw at all seasons. The variations of sulfate, nitrate and ammonium among Milw, Wauk and Mayv are not insignificantly different (see Figure AA1 for nitrate). Sulfate, nitrate and ammonium are regional air pollutants. Milw, Wauk and Mayv can be influenced by the same regional sources of the precursors of sulfate, nitrate and ammonium. At each season, the variations of OC at Mayv and Perk are significantly different from that in Milw and Wauk (see Figures Figure AA2). EC is mainly associated with the emissions from fuel combustions. In non-industrial area the emissions can be from traffic or local machinery operations. In spring and summer, the variations of EC are different from each other among the four stations. The difference between Milw and the other three stations is significant. For fall and winter, only the variations at Mayv and Perk are different from that at Milw. There is no significant difference between the variations at Milw and Wauk (see Figure AA3).

$PM_{2.5}$ consists of primary and secondary particles. The emission sources of primary $PM_{2.5}$ and precursors for secondary $PM_{2.5}$ can be both local and regional. When the regional sources are dominating, the mean ranks of the secondary $PM_{2.5}$ from neighboring stations do not show significantly differences, such as winter time $PM_{2.5}$ and nitrate. Nitrates are formed by the reactions between NH_4 and NOx. NH_3 -> to NH_4^+. The difference of $PM_{2.5}$, nitrate and ammonium among Milw, Mayv and Wauk are usually not significantly different, as the K-W test indicates.

2.4.4. Temperature and Variations

2.4.4.1. Temperature Impact and Nitrate Concentration

The emissions of NH_3 and VOCs vary depending on the temperature. Higher emissions when the temperature is higher. Emission of NH_3 also depends on agricultural activities that are more active when temperature is warmer. The biogenic VOCs are the major sources of precursors of OC. The biogenic VOC emission is high in warm seasons. The release of NH_3 from agricultural activities is controlled by thermodynamics and kinetic equilibrium, which is controlled by atmospheric pH and temperature. The formation speed of nitrate and sulfate depends on the thermodynamics and the kinetics of associated photochemical reactions, which are temperature, humidity and pH dependent. High temperature and humidity increase hydroxyl radicals and induce more rapid oxidation of SO_2 and NOx in the air. Figure 2.18 shows NO_3 decrease as temperature rose and the difference of the variation in Milw and in Mayv.

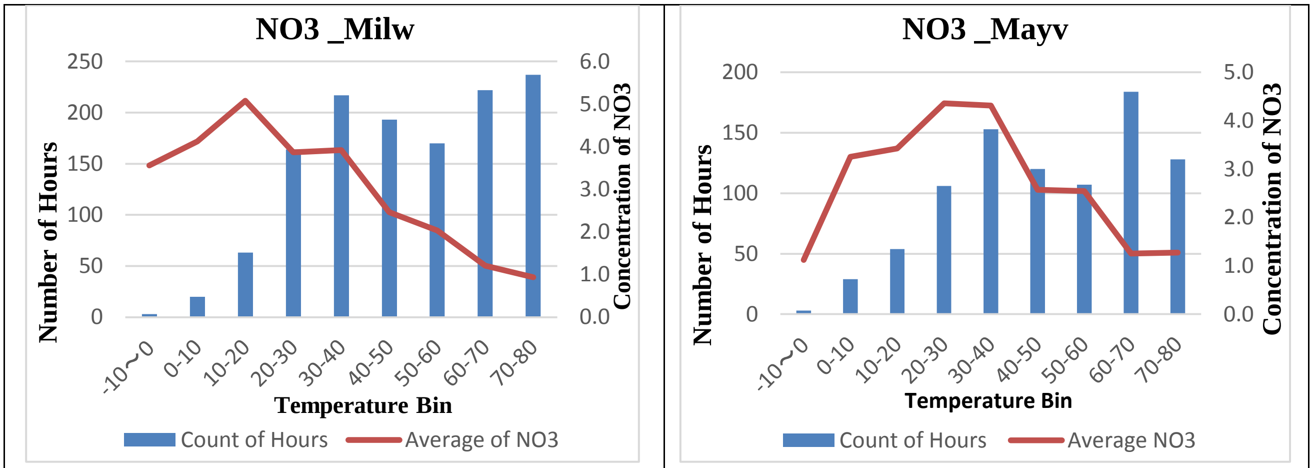


Figure 2.18 -1. NO_3 vs Temperature changes_Milw

Figure 2.18-2. NO_3 vs temperature changes_Mayv

Figure 2.18. NO_3^- Change vs Temperature

2.4.4.2. **Temperature and OC Concentration**

As discussed in the previous sector that OC is sensitive to temperature change. Figure 2.19 to Figure 2.22 are the linear polynomial model for OC over temperature (^oK) at the four stations. Table 2.4 listed the linear polynomial regression results.

Table 2.4. The linear polynomial equations for OC over Temperature at each station:

Station	Linear Regression (polynomial)	R^2
Milw	$f(x) = 0.0049 \times (\ln T)^2 - 2.715 \times (\ln T) + 375.3$	0.58
Wauk	$f(x) = 0.0061 \times (\ln T)^2 - 3.363 \times (\ln T) + 467.4$	0.45
Mayv	$f(x) = 0.0038 \times (\ln T)^2 - 2.084 \times (\ln T) + 287.6$	0.59
Perk	$f(x) = 0.0039 \times (\ln T)^2 - 2.124 \times (\ln T) + 290.3$	0.70

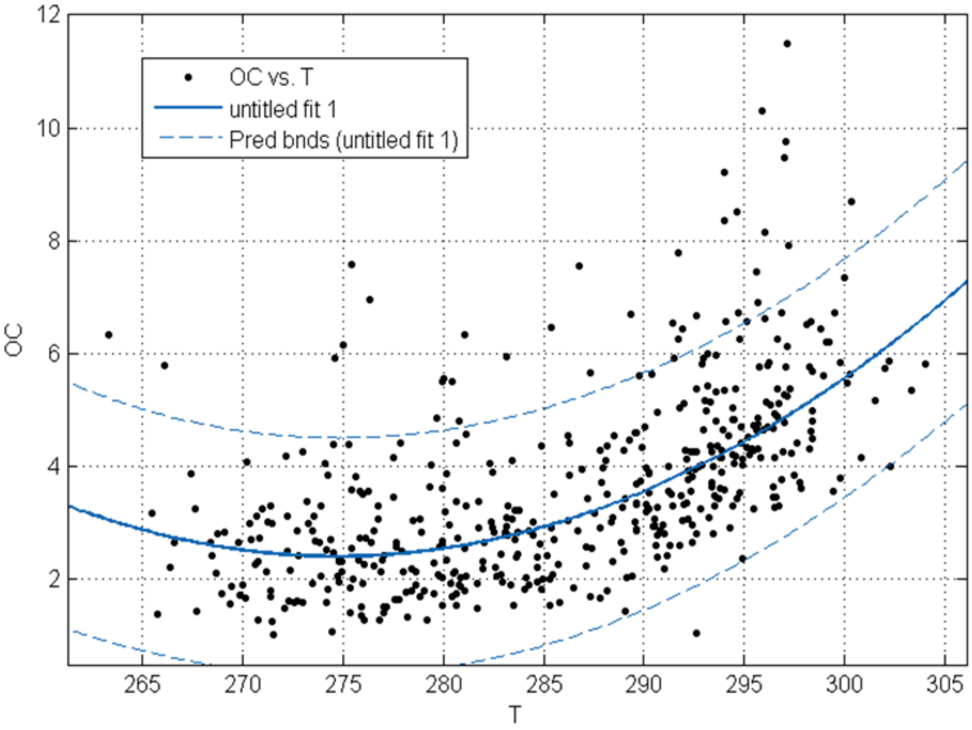


Figure 2.19. OC vs Temperature_Milw

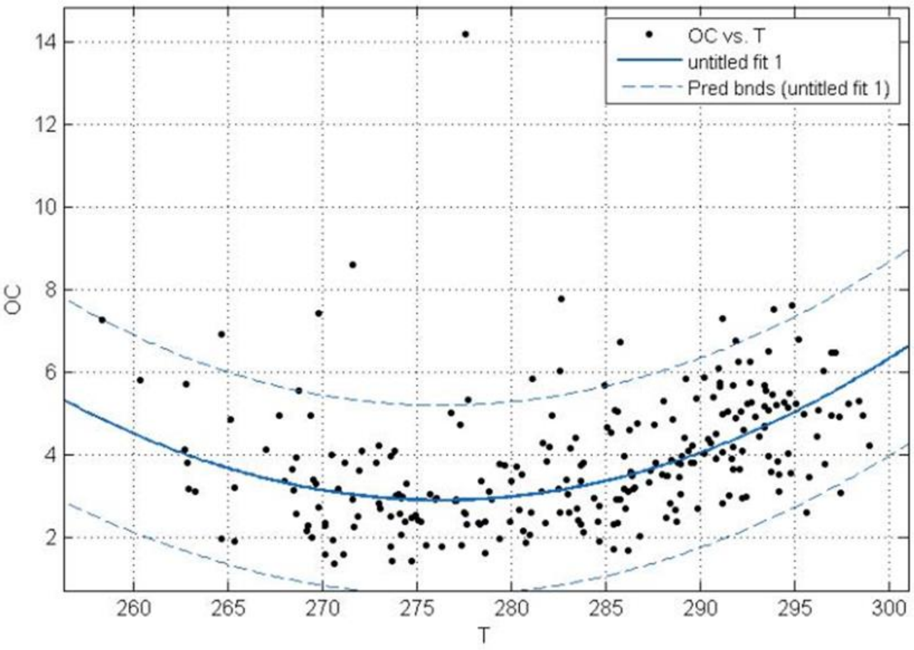


Figure 2.20. OC vs Temperature_Wauk

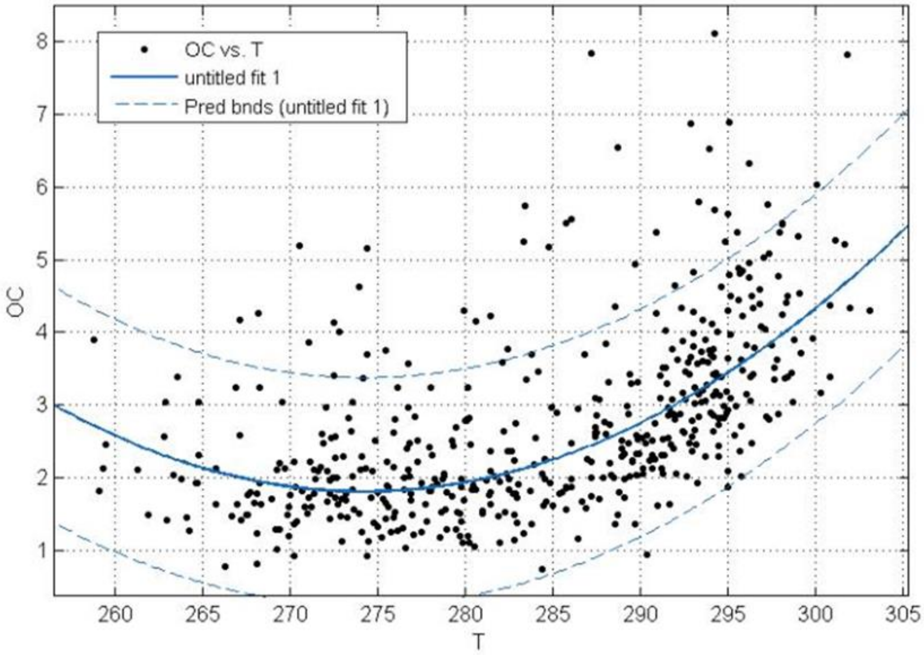


Figure 2.21. OC vs Temperature_Mayv

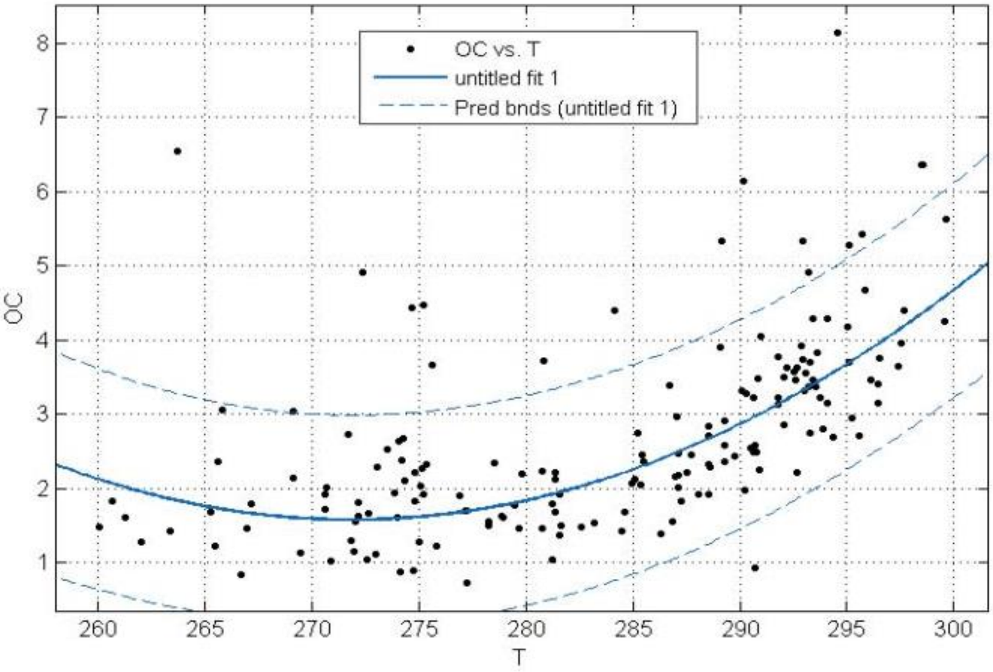


Figure 2.22. OC vs Temperature_Perk

At all the four stations, the concentration of OC increases when temperature is above around 275 °K.

2.4.4.3. **Blank Correction for OC and OC to OM Conversion Factors**

The mass ratios of organic matter (OM) to organic carbon (OC) at the four stations from 2002 to 2009 were analyzed to assess the relative influence of biogenic and anthropogenic organic sources on the ambient organic $PM_{2.5}$ at the four regions. In a low biogenic emission season, a higher OM/OC ratio usually indicates that OC is either highly oxidized or significantly aged. The ratio of OM/OC was calculated using speciated $PM_{2.5}$ data collected at the four stations from 2002 to 2009. Taking the advantage of the large dataset, ordinary least square regression was used to estimate the OC blank correction (OC_BC) and OC to OM conversion factors (OC/OM) at each season at the four stations. The hypothesis of using speciated $PM_{2.5}$ to estimate the OM to OC ratio is that all of the measured mass that is not accounted for by sulfate ion, nitrate ion, ammonium ion, EC, and metal oxides was associated with organic compounds and OM varies with OC. The method was described in details in the "Method" section. Table 2.5 lists the regression results for blank correction for organic carbon (OC_BC) and OC to OM conversion factors at each season for each station.

Table 2.5. Blank Correction for OC and OC to OM Conversion Factors

Factors	Season	Milwaukee	Waukesha	Mayville	Perkinstown
OC_BC	Winter	0.4969 (H)	0.8656 (H)	0.6508 (L)	0.4374 (H)
	Spring	0.5758 (H)	0.2061 (H)	0.5299 (H)	0.4374 (H)
	Summer	1.3893 (H)	1.3885 (H)	0.7437 (H)	0.6826 (H)
	Fall	0.646 (L)	0.4214 (H)	0.3785 (H)	0.6826 (H)
OC/OM	Winter	1.2376 (191)	1.0391 (98)	1.4675 (195)	0.9517 (113)
	Spring	1.3670 (193)	1.5313 (110)	1.5371 (191)	1.2240 (112)
	Summer	1.5942 (226)	2.0691 (114)	1.6613 (210)	2.0194 (123
	Fall	1.3563 (104)	1. 4530(93)	1.4469 (171)	1.7457 (108)
	Average	1.3888	1.5465	1.5282	1.4852

The OC to OM conversion factors at the four stations all exhibit the following pattern: winter < spring < summer > fall, with the highest in the summer. The four season average conversion factors range from 1.3888 to 1.5465, very close to the default conversion factor used by EPA (1.4). The conversion factors are also in the range introduced by Turpin and Lim in 1995: 1.6±0.2 for urban organic aerosol and 2.1±0.2 for rural organic aerosol (Turpin and Huntzicker, 1995b).

2.4.5. **Changes in Patterns**

Tables AA2.4 to AA2.7 tabulate the yearly seasonal mean concentrations of $PM_{2.5}$ and major $PM_{2.5}$ components at the four stations (see Appendix A). Tables AA2.1 to AA2.3 (see Appendix

A) list the yearly seasonal composition changes of major $PM_{2.5}$ components, with the number of sample and its 5th and 95th percentile. Figures 2.23 and Figure 2.24 showed the annual seasonal concentration of $PM_{2.5}$ and its major components and the annual seasonal composition of major $PM_{2.5}$ components in Milwaukee, respectively.

2.4.5.1. **The first pattern change**

From Figures 2.23 we can see that yearly average concentration of $PM_{2.5}$ and its major components had a peak in 2005 for $PM_{2.5}$, NO_3^-, NH_4^+, SO_4^{2-} and EC, except for OC. We can also see that since 2005, the winter $PM_{2.5}$ and major winter $PM_{2.5}$ components, like NH_4^+ and NO_3^-, had increased significantly and the differences of $PM_{2.5}$, NO_3^- and NH_4^+ between the winter and spring were higher than those in previous years. However, sulfate, EC and OC did not show these trends. Sulfate concentration was high in winter 2005, but decreased to the level close to previous years in 2006. Concentration of EC and OC remained relatively flat.

The compositions of NH_4^+ and NO_3^- were relatively flat from 2005 to 2009, while the composition of SO_4^{2-} was decreasing since 2005. The composition of OC had been increasing

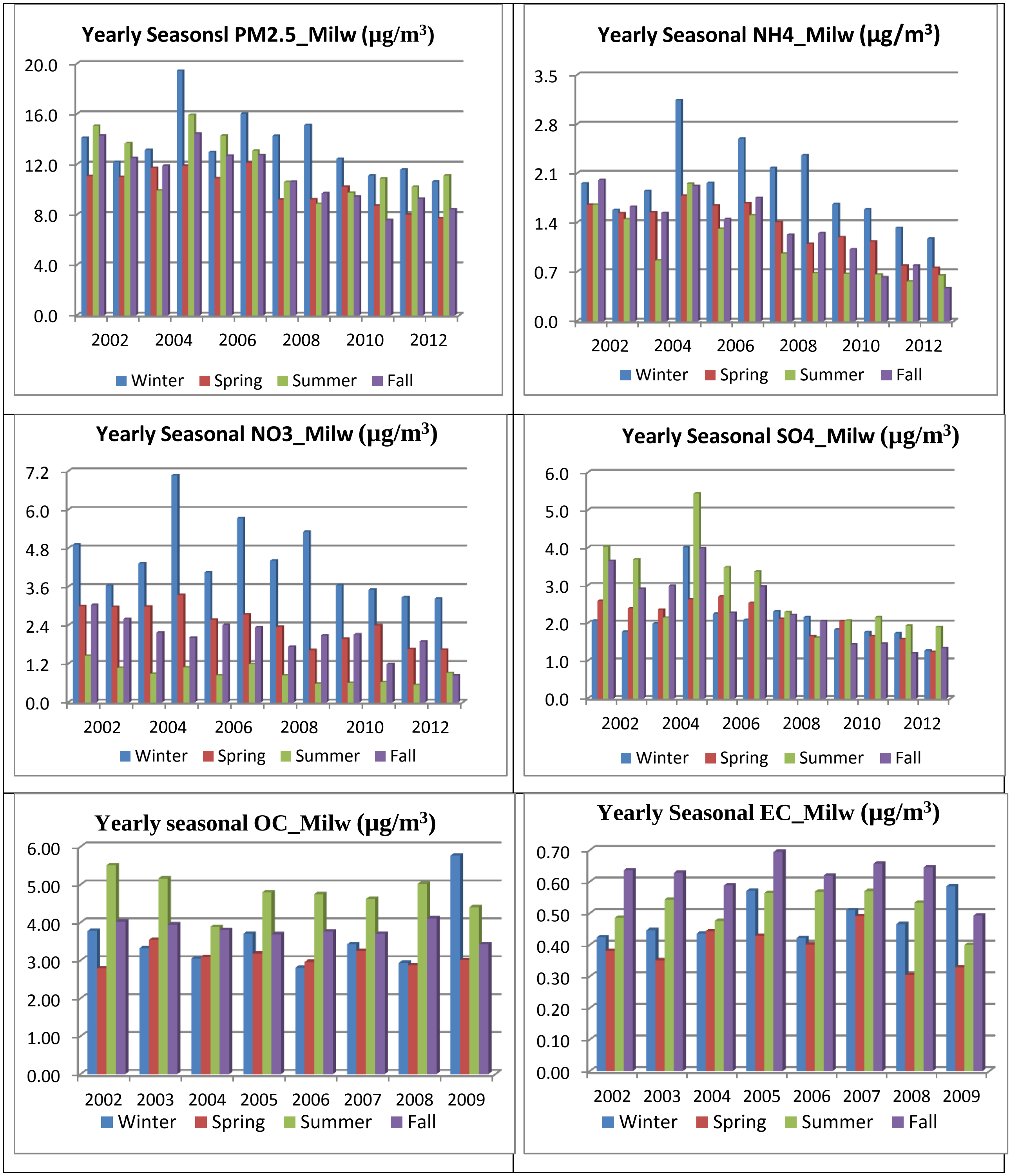


Figure 2.23. The annual seasonal concentration of $PM_{2.5}$ and its major components

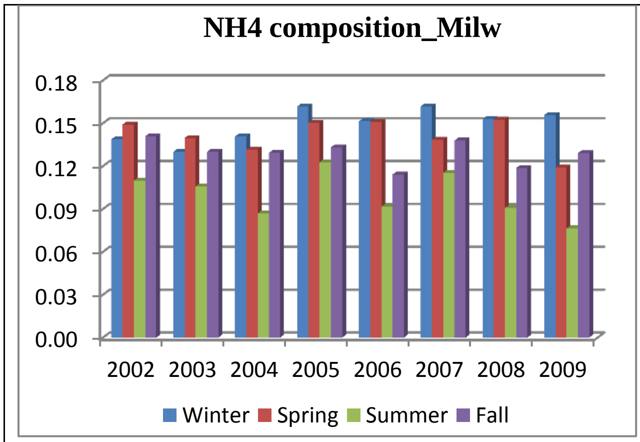


FIGURE 2.28-1

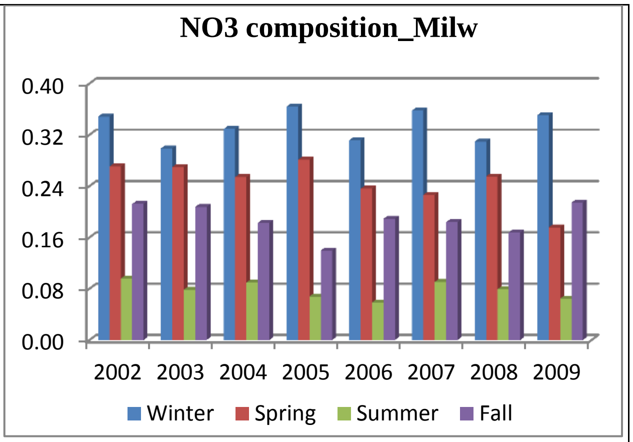


FIGURE 2.28-2

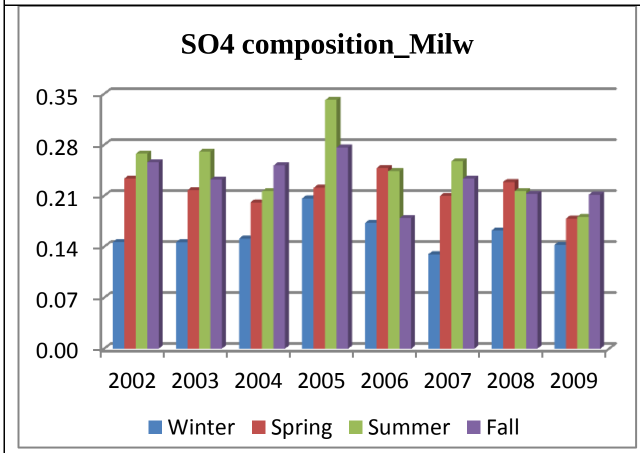


FIGURE 2.28-3

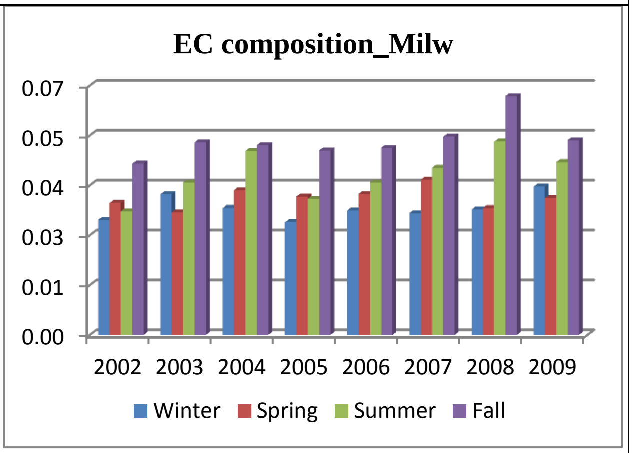


FIGURE 2.28-4

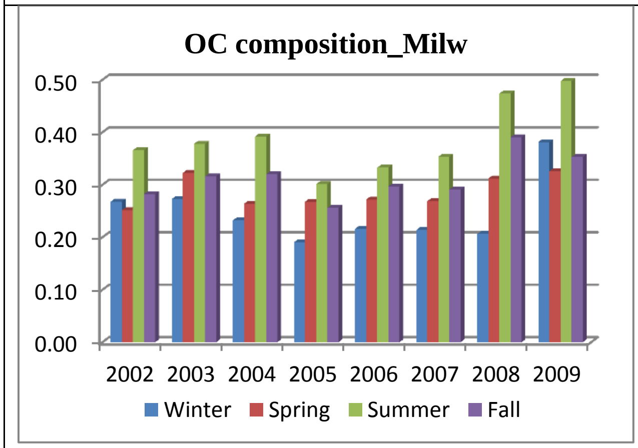


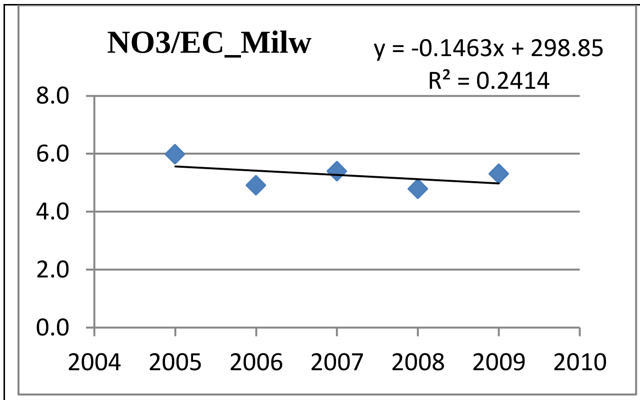
FIGURE 2.28-5

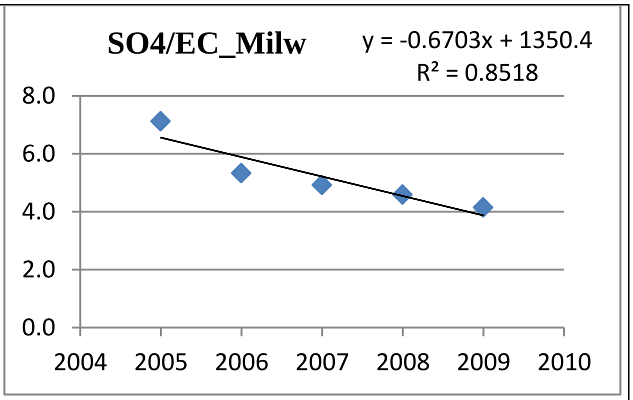
Figure 2.24. The annual seasonal composition of major $PM_{2.5}$ components

every year since 2005. The summer OC composition was 55.1% in 2009, 50% higher than the composition in 2005 (36.5%). The composition of EC had no big variations.

Fuel combustion processes are the major anthropogenic sources of NOx and SO_2. Agricultural activities are the major sources of NH_3. EC emission is mainly associated with fuel combustion and frequently used as index of fuel combustions. Following plots show the linear regression of NO_3^-, SO_4^{2-} , NH_4^+ and $PM_{2.5}$ over EC based on Milw data. It can be seen that SO_4^{2-} and $PM_{2.5}$ have very good correlation with EC, R^2=0.85 and 0.78, respectively. However, R^2 for correlation between NO_3^- and EC is only 0.2414. This indicates that fuel combustion to nitrates is not as important as it to sulfate. If the increase of $PM_{2.5}$ and nitrate in winter was due to increasing usage of fuel, sulfate emission would have to increase too, which was not the case.

Formation of NH_4NO_3 is limited by the availability of NH_4^+ after $(NH_4)_2SO_4$ is formed. The warm winter temperature created favorable conditions for NH_4NO_3 formation . If there is sufficient NH_4^+, the NH_4^+ remaining after reaction with all available SO_4^{2-} can react with NOx to form NH_4NO_3. Low temperature does not affect the oxidation of NOx as much as it does the oxidation of SO_2. Instead, low temperature would decrease gas-phase partitioning of NH_4NO_3.





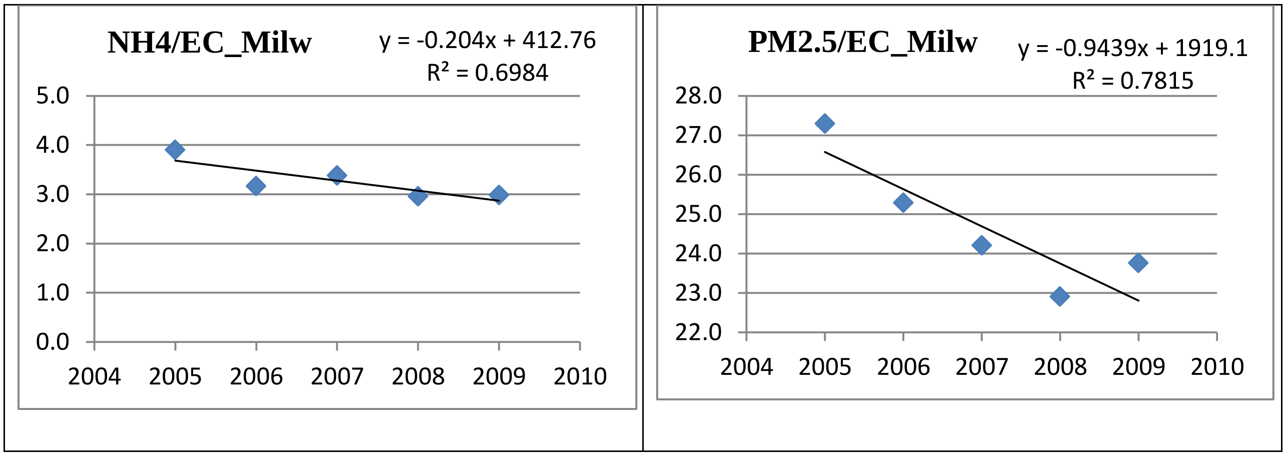


Figure 2.25. Linear regression of $PM_{2.5}$ and its components over EC

Table 2.6 summarized the linear regression results for $PM_{2.5}$, NO_3^-, SO_4^{2-} and NH_4^+ over EC and the ratio of NO_3^- /EC, SO_4^{2-} /EC, $PM_{2.5}$/EC and NH_4^+/EC at the four stations.

Table 2.6 Summary of linear regression of inorganic ions and $PM_{2.5}$ over EC

	NO_3^-/EC			SO_4^{2-}/EC			$PM_{2.5}$/EC			NH_4^+/EC		
	Slope	R^2	Medn	Slope	R^2	Medn	Slope	R^2	Medn	Slope	R^2	Medn
Milw	-0.1463	0.24	5.305	-0.6703	0.85	4.919	-0.9439	0.78	24.21	-0.204	0.70	3.168
Wauk	-0.0283	0.01	4.763	-0.3666	0.75	4.139	-0.6817	0.73	23.03	-0.109	0.24	2.492
Mayv	-0.3712	0.27	8.505	-0.7593	0.53	7.738	-2.1202	0.68	35.72	-0.307	0.40	5.110
Perk	-0.2067	0.13	6.949	-0.6489	0.43	7.682	-3.0969	0.74	37.83	-0.205	0.23	4.127

The correlations between NO_3^- and EC are lower, less than 27%, while the correlations between SO_4^{2-} and EC are higher, from 43% to 85%. The correlations between $PM_{2.5}$ and EC are higher, from 68% to 78%. This shows that the ambient concentrations of sulfate and $PM_{2.5}$ are closely correlated with the fuel combustion. The lower correlations between nitrates and EC and the higher winter $PM_{2.5}$ and nitrate indicate that there is a non-fuel related N emission source that contributed significant amount of N precursor to the formation of nitrates.

2.4.5.2. **The second pattern change**

The second pattern change observed is the increasing OC composition in $PM_{2.5}$ since 2005 (see Figure 2.24-5). From Figure 2.27-3 and Figure 2.27-4, we can see that the annual concentrations of NO_3^- and annual SO_4^{2-} are decreasing since 2005, while the annual OC concentration maintained relatively unchanged. As a consequence, the composition of OC has steadily increased since 2005. From Table AA2.1, Yearly Seasonal Composition _ Milwaukee, the OC composition increased by 100%, 22%, 65% and 38% for the season of winter, spring, summer and fall, respectively. The following two figures illustrate how the OC varies with different temperature ranges at Milwaukee and Mayville station, respectively.

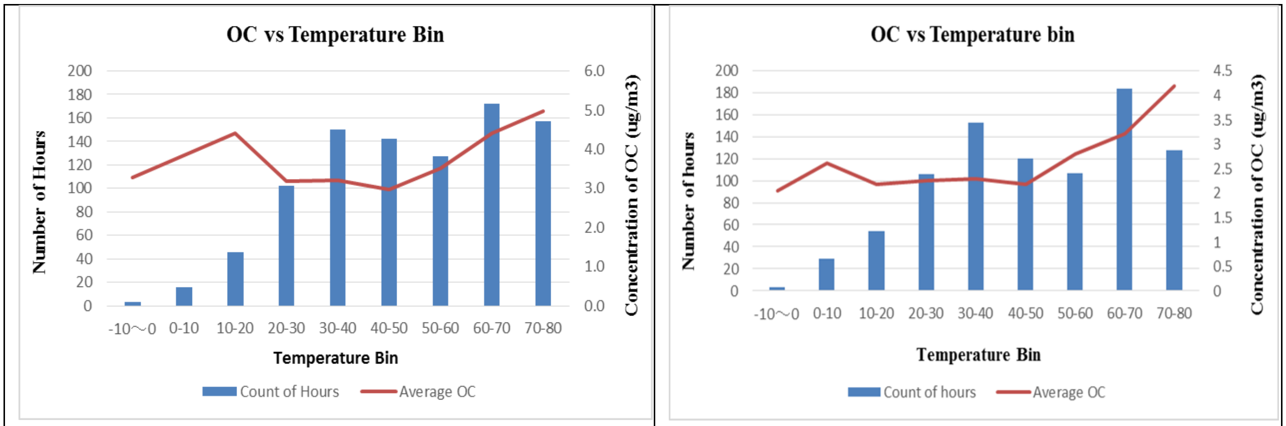


Figure 0.26-0.1 OC vs Temperature_Milwaukee

Figure 0.26-2 OC vs Temperature_Mayville

Figure 2.26. OC vs. Temperature (Milw and Mayv)

OC consists of primary OC (POC) and secondary OC (SOC). The emission sources of their precursors are fuel combustion (stationary and mobile), fuel industry (such as refinery), chemical industry and biogenic reactions. In eastern US, the OC formed by biogenic VOC constitutes about 92% of total ambient VOCs [ref]. Emissions of biogenic VOC are very sensitive to temperature. In general, the emissions will be higher when the temperature is higher. The peaks at the lower temperature range were very likely caused by winter heating (such as, wood burning) and cold start of automobile in the winter.

Studies have forecasted the temperature increasing in Midwest and possible extreme weathers (Dawson et al., 2007). As indicated from Table 2.3, the OC is the largest single $PM_{2.5}$ component. The increasing OC composition means $PM_{2.5}$ would become more sensitive to the temperature changes. Therefore, the impact of global warming to ambient $PM_{2.5}$ becomes more severe.

This discovery is another good example how global warming is affecting the air quality in Upper Midwest. Due to changes in economy, the production and the fuel usage will change. To develop a cost-efficient $PM_{2.5}$ reduction plan, policy maker need to shift focuses from inorganic $PM_{2.5}$ reduction to paying more attentions to controlling VOC emissions.

2.5. Conclusion and Recommendation

1) The significance of spatial variations among Milw, Wauk, Mayv and Perk depends on the air pollutant, location and seasons. The variations between Perk and other three stations are significant for all elements and at all seasons. Local emission sources and meteorological conditions are the major contributors to the significance of the variations.

2) Lake Breeze is the major cause of the contrast between shoreline and inland regions. The relative humidity and temperature difference between Milwaukee and other regions have contributed to the higher frequency of elevated $PM_{2.5}$ events in Milw than other stations.

3) Ambient concentration of $PM_{2.5}$ at the four stations has clear seasonal variations. Like many Midwest areas, winter has higher nitrate, summer has higher sulfate and OC.

4) The downward trend of ambient concentration of $PM_{2.5}$, nitrate and sulfate in the period of 2005 to 2009 was mainly due to the decreasing emissions associated with the reduced fuel combustion. During the same period, the relatively flat ambient OC concentration and increasing OC composition were observed. This change in pattern highlighted the need for changing $PM_{2.5}$ reduction strategies.

5) Another observed change on the variation pattern is the increase of ambient concentration of winter $PM_{2.5}$ and nitrate alone without the increase of sulfate in the same period. This phenomenon was very likely contributed by additional non-fuel combustion related N-emissions sources in the region during the period.

6) A lesson is learned that a cost-effective NH_3 management plan should have been established before the rapid growth of dairy industry in Wisconsin.

7) From the predicted frequent extreme weather events in Midwest and the discovered increasing OC composition in $PM_{2.5}$, it is recommended that an ambient OC oncentration reduction plan and human health prevention plan be established.

2.6. References:

Andrews, E., Saxena, P., Musarra, S., Hildemann, L.M., Koutrakis, P., McMurry, P.H., Olmez, I., White, W.H., 2000. Concentration and composition of atmospheric aerosols from the 1995 SEAVS experiment and a review of the closure between chemical and gravimetric measurements. Journal of the Air & Waste Management Association 50, 648-664.

Avakian, M.D., Dellinger, B., Fiedler, H., Gullet, B., Koshland, C., Marklund, S., Oberdorster, G., Safe, S., Sarofim, A., Smith, K.R., Schwartz, D., Suk, W.A., 2002. The origin, fate, and health effects of combustion by-products: A research framework. Environmental Health Perspectives 110, 1155-1162.

Baumann, K., Jayanty, R.K.M., Flanagan, J.B., 2008. Fine particulate matter source apportionment for the Chemical Speciation Trends Network site at Birmingham, Alabama, using Positive Matrix Factorization. Journal of the Air & Waste Management Association 58, 27-44.

Behera, S.N., Sharma, M., Aneja, V.P., Balasubramanian, R., 2013. Ammonia in the atmosphere: a review on emission sources, atmospheric chemistry and deposition on terrestrial bodies. Environmental Science and Pollution Research 20, 8092-8131.

Blanchard, Hidy, G.M., Tanenbaum, S., Edgerton, E., Hartsell, B., Jansen, J., 2008. Carbon in southeastern U.S. aerosol particles: Empirical estimates of secondary organic aerosol formation. Atmospheric Environment 42, 6710-6720.

Bouwman, A.F., Lee, D.S., Asman, W.A.H., Dentener, F.J., VanderHoek, K.W., Olivier, J.G.J., 1997. A global high-resolution emission inventory for ammonia. GBioC 11, 561-587.

Brook, J.R., Makar, P.A., Sills, D.M.L., Hayden, K.L., McLaren, R., 2013. Exploring the nature of air quality over southwestern Ontario: Main findings from the Border Air Quality and Meteorology Study. Atmospheric Chemistry and Physics 13, 10461-10482.

Buzcu-Guven, B., Brown, S.G., Frankel, A., Hafner, H.R., Roberts, P.T., 2007. Analysis and apportionment of organic carbon and fine particulate matter sources at multiple sites in the Midwestern United States. Journal of the Air & Waste Management Association 57, 606-619.

Dawson, J.P., Adams, P.J., Pandis, S.N., 2007. Sensitivity of PM2.5 to climate in the Eastern US: a modeling case study. Atmospheric Chemistry and Physics 7, 4295-4309.

Dawson, J.P., Bloomer, B.J., Winner, D.A., Weaver, C.P., 2014a. Understanding the meteorological drivers of U.S. particulate matter concentrations in a changing climate. Bulletin of the American Meteorological Society 95, 521-532.

Dawson, J.P., Bloomer, B.J., Winner, D.A., Weaver, C.P., 2014b. UNDERSTANDING THE METEOROLOGICAL DRIVERS OF US PARTICULATE MATTER CONCENTRATIONS IN A CHANGING CLIMATE. Bulletin of the American Meteorological Society 95, 520-532.

Duncan, B.N., Stelson, A.W., Kiang, C.S., 1995. ESTIMATED CONTRIBUTION OF POWER-PLANTS TO AMBIENT NITROGEN-OXIDES MEASURED IN ATLANTA, GEORGIA IN AUGUST 1992. Atmospheric Environment 29, 3043-3054.

Erisman, J.W., Bleeker, A., Galloway, J., Sutton, M.S., 2007. Reduced nitrogen in ecology and the environment. Environmental Pollution 150, 140-149.

Ervens, B., Carlton, A.G., Turpin, B.J., Altieri, K.E., Kreidenweis, S.M., Feingold, G., 2008. Secondary organic aerosol yields from cloud-processing of isoprene oxidation products. Geophysical Research Letters 35.

Fosco, T., Schmeling, M., 2006. Aerosol ion concentration dependence on atmospheric conditions in Chicago. Atmospheric Environment 40, 6638-6649.

Heo, J., McGinnis, J.E., de Foy, B., Schauer, J.J., 2013. Identification of potential source areas for elevated PM2.5, nitrate and sulfate concentrations. Atmospheric Environment 71, 187-197.

Hewitt, C.N.a.J., A.V., 2009. Atmospheric Science for Environmental Scientists. Wiley-Blackwell.

Jang, M.S., Czoschke, N.M., Lee, S., Kamens, R.M., 2002. Heterogeneous atmospheric aerosol production by acid-catalyzed particle-phase reactions. Science 298, 814-817.

John G. Watson, J.C.C., and L.-W. Antony Chen, 2008. ASSESSMENT OF CARBON SAMPLING ARTIFACTS IN THE IMPROVE, STN/CSN, AND SEARCH NETWORKS U.S. Environmental Protection Agency (MD-14) Office of Air Quality Planning & Standards 4201 Alexander Dr., Room 463 Research Triangle Park, North Carolina, U.S.A.

John G. Watson∗, J.C.C., and L.-W. Antony Chen, 2005. Summary of Organic and Elemental Carbon/Black Carbon Analysis Methods and Intercomparisons, Aerosol and Air Quality Research, pp. pp. 65-102.

John H. Seinfeld, S.N.P., 2006. Atmospheric Chemistry and Physics: From Air Pollution to Climate Change, 2nd Edition, p. 1332.

Katzman, T.L., Rutter, A.P., Schauer, J.J., Lough, G.C., Kolb, C.J., Van Klooster, S., 2010. PM2.5 and PM10-2.5 Compositions during Wintertime Episodes of Elevated PM Concentrations across the Midwestern USA. Aerosol and Air Quality Research 10, 140-U113.

Klemm RJ, M.R.J., Heilig CM, Neas LM, Dockery DW 2000. Is daily mortality associated specifically with fine particles? Data reconstruction and replication of analyses. Journal of the Air & Waste Management Association 1995, 1215-1222.

LADCO, 2003. PM2.5 in the Upper Midwest.

LADCO, 2004. PM2.5 in Urban Areas in the Upper Midwest.

LADCO, 2010. Episodic Air Pollution in Wisconsin (LADCO Winter Nitrate Study) and Georgia (SEARCH Network) During Jan-Mar 2009 Phase I Report.

Laurent, O., Bard, D., Filleul, L., Segala, C., 2007. Effect of socioeconomic status on the relationship between atmospheric pollution and mortality. J. Epidemiol. Community Health 61, 665-675.

Levy, J.I., Baxter, L.K., Schwartz, J., 2009. Uncertainty and Variability in Health-Related Damages from Coal-Fired Power Plants in the United States. Risk Analysis. Vol. 29 29, 1000-1014.

Lewandowski, M., Jaoui, M., Offenberg, J.H., Kleindienst, T.E., Edney, E.O., Sheesley, R.J., Schauer, J.J., 2008. Primary and secondary contributions to ambient PM in the midwestern United States. Environmental Science & Technology 42, 3303-3309.

Liao, K.-J., Tagaris, E., Napelenok, S.L., Manomaiphiboon, K., Woo, J.-H., Amar, P., He, S., Russell, A.G., 2008. Current and future linked responses of ozone and PM2.5 to emission controls. Environmental Science and Technology 42, 4670-4675.

Lim, H.-J., Turpin, B.J., 2002. Origins of primary and secondary organic aerosol in Atlanta: Results of time-resolved measurements during the Atlanta Supersite Experiment. Environmental Science and Technology 36, 4489-4496.

Lippmann, M., Frampton, M., Schwartz, J., Dockery, D., Schlesinger, R., Koutrakis, P., Froines, J., Nel, A., Finkelstein, J., Godleski, J., Kaufman, J., Koenig, J., Larson, T., Luchtel, D., Liu, L.J.S., Oberdorster, G., Peters, A., Sarnat, J., Sioutas, C., Suh, H., Sullivan, J., Utell, M., Wichmann, E., Zelikoff, J., 2003. The US Environmental Protection Agency particulate matter health effects research centers program: A midcourse report of status, progress, and plans. Environmental Health Perspectives 111, 1074-1092.

Mickley, L.J., Jacob, D.J., Field, B.D., Rind, D., 2004. Effects of future climate change on regional air pollution episodes in the United States. Geophysical Research Letters 31, 1-4.

Mishamandani, S., 2015. Global Burden of Disease Update Reveals Major Risk Factors for Death and Disability. National Institute of Environmental Health Science.

Polidori, A., Turpin, B.J., Lim, H.J., Cabada, J.C., Subramanian, R., Pandis, S.N., Robinson, A.L., 2006. Local and regional secondary organic aerosol: Insights from a year of semi-continuous carbon measurements at Pittsburgh. Aerosol Science and Technology 40, 861-872.

Robinson, A.L., Donahue, N.M., Shrivastava, M.K., Weitkamp, E.A., Sage, A.M., Grieshop, A.P., Lane, T.E., Pierce, J.R., Pandis, S.N., 2007. Rethinking organic aerosols: Semivolatile emissions and photochemical aging. Science 315, 1259-1262.

Russell, L.M., 2003. Aerosol organic-mass-to-organic-carbon ratio measurements. Abstracts of Papers of the American Chemical Society 225, U817-U818.

Seigneur, C., 2001. Current status of air quality models for particulate matter, 11 ed. Air and Waste Management Association, pp. 1508-1521.

Seinfeld, J.H.a.P., S.N., 2006. Atmospheric Chemistry and Physics - from Air Pollution to Climate Change.

Snyder, D.C., Rutter, A.P., Worley, C., Olson, M., Plourde, A., Bader, R.C., Dallmann, T., Schauer, J.J., 2010. Spatial variability of carbonaceous aerosols and associated source tracers in two cites in the Midwestern United States. Atmospheric Environment 44, 1597-1608.

Stanier, C., Singh, A., Adamski, W., Baek, J., Caughey, M., Carmichael, G., Edgerton, E., Kenski, D., Koerber, M., Oleson, J., Rohlf, T., Lee, S.R., Riemer, N., Shaw, S., Sousan, S., Spak, S.N., 2012. Overview of the LADCO winter nitrate study: Hourly ammonia, nitric acid and PM2.5 composition at an urban and rural site pair during PM2.5 episodes in the US Great Lakes region. Atmospheric Chemistry and Physics 12, 11037-11056.

Stelson, A.W., Seinfeld, J.H., 1982. Relative humidity and temperature dependence of ammonium nitrate dissociation constant. Atmospheric Environment 16, 983-992.

Stone, E.A., Zhou, J.B., Snyder, D.C., Rutter, A.P., Mieritz, M., Schauer, J.J., 2009. A Comparison of Summertime Secondary Organic Aerosol Source Contributions at Contrasting Urban Locations. Environmental Science & Technology 43, 3448-3454.

Tai, A.P.K., Mickley, L.J., Jacob, D.J., 2010. Correlations between fine particulate matter (PM2.5) and meteorological variables in the United States: Implications for the sensitivity of PM2.5 to climate change. Atmospheric Environment 44, 3976-3984.

Tang, I.N., 1980. ON THE EQUILIBRIUM PARTIAL PRESSURES OF NITRIC-ACID AND AMMONIA IN THE ATMOSPHERE. Atmospheric Environment 14, 819-828.

Tolocka, M.P., Solomon, P.A., Mitchell, W., Norris, G.A., Gemmill, D.B., Wiener, R.W., Vanderpool, R.W., Homolya, J.B., Rice, J., 2001. East versus West in the US: Chemical characteristics of PM2.5 during the winter of 1999. Aerosol Science and Technology 34, 88-96.

Tsigaridis, K., Kanakidou, M., 2007. Secondary organic aerosol importance in the future atmosphere. Atmospheric Environment 41, 4682-4692.

Tsimpidi, A.P., Karydis, V.A., Pandis, S.N., 2008. Response of fine particulate matter to emission changes of oxides of nitrogen and anthropogenic volatile organic compounds in the Eastern United States. Journal of the Air and Waste Management Association 58, 1463-1473.

Turpin, Huntzicker, J.J., 1995a. Identification of secondary organic aerosol episodes and quantitation of primary and secondary organic aerosol concentrations during SCAQS. Atmospheric Environment 29, 3527-3527.

Turpin, B., 2001. Species Contribution to PM2.5 Mass Concentrations: Revisiting Common Assumptions for Estimating Organic Mass. Science and Technology 35, 602-610.

Turpin, B.J., Huntzicker, J.J., 1995b. Identification of secondary organic aerosol episodes and quantitation of primary and secondary organic aerosol concentrations during SCAQS. Atmospheric Environment 29, 3527-3527.

U.S.EPA, 2013. Particulate Matter (PM). U.S. EPA.

White, W.H., Roberts, P.T., 1977. NATURE AND ORIGINS OF VISIBILITY-REDUCING AEROSOLS IN LOS-ANGELES AIR BASIN. Atmospheric Environment 11, 803-812.

Xing, L., Fu, T.M., Cao, J.J., Lee, S.C., Wang, G.H., Ho, K.F., Cheng, M.C., You, C.F., Wang, T.J., 2013. Seasonal and spatial variability of the OM/OC mass ratios and high regional correlation between oxalic acid and zinc in Chinese urban organic aerosols. Atmospheric Chemistry and Physics 13, 4307-4318.

CHAPTER 3. IDENTIFICATION OF POTENTIAL EMISSIONS SOURCES - PMF

3.1. Introduction

It is important to identify contributions from different source categories to ambient $PM_{2.5}$ to help in developing a sound pollution reduction policy and abatement actions. The identification can also provide useful information in epidemiological studies in examining the impact of different emissions on human health.

To derive the relationship between emission sources and monitored air pollutants, dispersion and receptor models have been widely applied in air quality management field. These two types of models have complementary strengths and limitations. When there are unknown emission sources or a lack of emission inventory, the functions of dispersion models can be impaired while the receptor models can work better at receptor sites to trace the monitored pollution to its sources through statistical and meteorological interpretation of the data. Chemical mass balance (CMB) and Positive Matrix Factorization (PMF) are the two most widely used receptor models. CMB is a deterministic model that reconstructs observed concentrations from a linear combination of emission source profiles with the assumptions that the composition of source emissions is constant and all the potential contribution sources are included in the analysis (EPA-CMB82 Manual). PMF applies advanced factor analysis technique to resolve the identities and contributions of components in an unknown mixture (Watson et al., 2008). Unlike CMB, PMF does not require prior-knowledge of the emission sources and case specific source profiles. PMF has been widely used in environmental studies, extensively in source apportionment for

$PM_{2.5}$ such as major Midwestern cities emissions and St Louis supersite PMF analysis with organic tracer (Buzcu-Guven et al., 2007; Jaeckels et al., 2007).

Due to the diverse economy in Wisconsin, this study selects PMF model to identify the potential emission sources at different regions in Wisconsin for its advantage of the ability to identify previously unknowing sources. This is the first PMF study for identifying the potential emission sources categories at different regions within one state and investigating the impact of same emissions categories to different region.

The objectives of the PMF analysis are to:

1) Identify potential major emission sources or source categories that contribute to ambient $PM_{2.5}$ at different regions (urban, rural and forests area) within Wisconsin;
2) Quantify the impacts of these sources on ambient $PM_{2.5}$ (and its component and precursors) observed in different regions;
3) Distinguish similar emission sources by applying index technique and meteorological parameters in source apportionment.

The hypotheses are as follows:

1) Regional and local emissions contribute to the atmospheric $PM_{2.5}$ at each region in different ratios.
2) Trace metals collected in CSN program for speciated $PM_{2.5}$ and meteorological parameters can help to identify the major emission sources of ambient $PM_{2.5}$.

The approach illustrated in this chapter provides an example of how to identify the major emission sources that contributed to the ambient $PM_{2.5}$ in regions within one state using the meteorological parameters and chemical and physical characteristics of speciated $PM_{2.5}$ data, including the trace metals, collected by CSN program.

3.2. Literature Review

3.2.1. PM$_{2.5}$ and Source Apportionment (SA)

The variations in concentration and composition of ambient PM$_{2.5}$ at each monitoring station have shown that the combined impact from different emission sources at each region is different. The ambient PM$_{2.5}$ is the contribution from both locally and regionally located natural and anthropogenic sources. PM$_{2.5}$ can remain in suspension much longer than its precursors; thus, it can transport a much longer distance than its precursors. Studies have revealed the monitored ambient PM$_{2.5}$ can contain as much as 2/3 long-distance transported PM$_{2.5}$. In rural areas, most of the “background” concentration of PM$_{2.5}$ is transported.

In epidemiological studies, the statistically significant associations between the mortality and the speciated PM$_{2.5}$ components, especially generated from oil burning, sulfate aerosol, and motor vehicles have been found by several studies (Laden et al., 2000; Mar et al., 2000; Tsai et al., 2000). Therefore, to have an effective PM$_{2.5}$ control strategy and health prevention planning, quantitating source contributions to ambient concentrations of PM$_{2.5}$ is very important.

Source-oriented dispersion and chemical transformation models and receptor-oriented receptor models have been used in air quality management areas. EPA has been using source-oriented dispersion and chemical transformation models to assess the efficiency of control strategies, to help states address PM$_{2.5}$ NAAQS implementation plans and forecasting future air quality conditions in planning and climate change studies (Russell, 2008).

Dispersion and chemical transformation models are based on fundamentals of chemical reaction, transport and transformation process, in which the emission inventories and meteorological data are used to predict ambient air pollutant concentrations at desired downwind locations (receptors). The biggest advantage of dispersion models is that it can estimate the formation of secondary $PM_{2.5}$ by incorporating atmospheric chemical reactions into the model. However, one big problem is that its input data is often not available or incomplete.

Receptor models, on the other hand, are mathematical or statistical procedures, which use the chemical and physical characteristics of gases and particles measured at source and receptor to identify and quantify the sources of air pollutants at a receptor location. These models are therefore often used as part of State Implementation Plans (SIPs) for identifying sources contributing to air quality problems. Receptor models are most commonly used to investigate the sources of $PM_{2.5}$, since the speciated $PM_{2.5}$ collected by CSN program provides the "chemical and physical characteristics of particles" at the receptor site. There are several different kinds of receptor models. The most commonly used in air quality management are the Chemical Mass Balance (CMB) and Positive Matrix Factorization (PMF) methods.

3.2.2. The PMF Model Used in Air Quality Management Studies

The fundamental equation of a receptor model is the mass balance. It assumes that species are conserved during transport between the source and the sampler (Henry et al., 1991). In receptor modeling, ambient air pollutant measurements collected at a monitor site (a receptor) are input to the mass conservation equation (see Eq. 3.1) to identify and quantify the major sources (factors) that contribute the air pollutants observed at that receptor (Henry et al., 1991).

$$x_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij} \qquad (3.1)$$

where i = day, i = 1 to m;

j = element, j = 1 to n;

k = number of contributors (sources), k = 1 to p;

x_{ij} = j^{th} elemental concentration measured on the i^{th} day;

g_{ik} = contribution of the k^{th} factor to the receptor on the j^{th} day;

f_{kj} = fraction of the k^{th} factor that is species j; and

e_{ij} = error between measured and calculated i^{th} elemental concentration measured in the j^{th} sample.

The chemical mass balance (CMB) is a deterministic model that reconstructs observed concentrations from a linear combination of emission source profiles (Schauer and Cass, 2000). CMB requires the knowledge of the emission sources and case specific source profiles. Sources with similar chemical and physical properties cannot be distinguished from each other by CMB. In contrast, PMF does not require source profiles and is potentially capable of identifying previously unknown emission sources or chemical and physical processes. PMF is a bilinear model, which applies advanced factor analysis to the ambient air monitoring data. The approach of PMF is to minimize the objective function Q to find the number of contributing sources (p), their composition (f_{kj}) as well as their contribution (g_{ik}) to the observed data (x_{ij}) (see Eq. 3.2). Alternative least square equations were initially used to find the minimum Q (Paatero and Tapper, 1993). A “global optimization” scheme was developed in 1997, in which G and F vary at the same time to calculate a joint solution (Paatero, 1997). In 1999, Paatero developed another least square program called Multilinear Engine (ME). ME performs the iterations via conjugate gradient algorithm until convergence to a minimum Q value (Paatero, 1999). EPA PMF 3.0 employed Multilinear engine (ME) (Gary Norris, 2008).

$$Q = \left[\frac{(X - GF)}{\delta} \right]^2_{F,G} = \sum_{i=1}^{n} \sum_{j=1}^{m} \left(\frac{e_{ij}}{s_{ij}} \right)^2 \qquad (3.2)$$

where Q = the objective function; and

s_{ij} = the error estimates for x_{ij}.

PMF uses weighted least-squires (Eq. 2.3) to fit with the known error estimates of the matrix x to derive the weights.

$$e_{ij} = x_{ij} - \sum_{k=1}^{p} g_{ik} f_{kj} \qquad (3.3)$$

3.2.3. **The Advantages and Disadvantages of PMF Modeling**

PMF is especially applicable to working with environmental data because: (1) a prior knowledge of the number of sources and source profiles is not required; (2) it incorporates user specified uncertainties associated with measurements of environmental samples. This method permits maximum use of available data and better treatment of missing and below-detection-limit values; and (3) it forces all of the values in the solution profiles and contributions to be nonnegative, which is more realistic for real world samples. However, one major problem in PMF modeling is “source contamination”, the similar sources (factors) are mixed together (Baumann et al., 2008). It has been difficult to distinguish between emissions from combustion processes, such as, on-road and non-road engine exhaust, residential wood combustion and wildfires (Watson et al., 2008).

3.2.4. **The Application of PMF**

Buzcu-Guven et al. (2007) used PMF in apportionment of OC and $PM_{2.5}$ sources at multiple major cities in the Midwest. Seven to nine factors were identified at each site. Common factors at all of the sites included mobile (gasoline)/secondary organic aerosols with high OC, diesel with a high elemental carbon/OC ratio (only at the urban sites), secondary sulfate, secondary nitrate, soil, and biomass burning. Jaeckels et al. (2007) applied both CMB and PMF to analyze the 125 $PM_{2.5}$ data collected at St. Louis Midwest Supersite. Unlike the CMB and PMF analyses done before, the particle-phase OC was used as molecular markers in these two analyses. Eight factors were attributed: two-point source factors, two winter combustion factors, a biomass-burning factor, a mobile source factor, a secondary organic aerosol factor, and a re-suspended soil factor. The modeling results by the two methods were reasonably well matched. PMF modeling has been widely used to determine the major sources of $PM_{2.5}$, NMOC and air toxics (Brown et al., 2007; Kim et al., 2005a).

The emission sources that have been identified by PMF modeling include: (1) primary sources - motor vehicles, residential and industrial fuel combustion, biomass burning, soil dust, and sea salt; (2) secondary sources – sulfate sources, nitrate sources (fuel combustion related); and (3) VOC sources: evaporative emissions, motor vehicle exhaust, industrial processes loss, natural gas and biogenic emissions (Baumann et al., 2008; Brown et al., 2007).

Despite the advance of the developed techniques, the “source contamination” still remains as a problem. Recently particle phase organic $PM_{2.5}$ has been used as index in receptor modeling. Many of these particle-phase organic $PM_{2.5}$ tracers are shared by different emission sources. These organic tracers are either not commonly available or due to the insufficient database there is a lot of uncertainty to rely on these speciated organic compounds to make quantitative determination. The final determination would still heavily rely on the physical and chemical characteristics of the monitoring data and the meteorology data.

3.3. Methods

EPA PMF 3.0 was obtained from EPA by emailing to NERL_RM_Support@epa.gov and installed on a personal computer through run3.0 Setup.exe. ME-2 is obtained as part of the EPA PMF 3.0 software download from (http://www.epa.gov/heasd/products/pmf/pmf.htm).

PMF modeling includes numerous trial and error steps. To obtain reliable results, various algorithmic parameters have been tried, such as various species involved, many factors used in the modeling and the scale of uncertainty for each species involved in the modeling. The modeling procedures are normally divided into three broad steps: (1) preparing input data, (2) PMF modeling, and (3) interpreting the modeling results.

3.3.1. **Data Preparation**

The 24-hour speciated $PM_{2.5}$ collected by the Chemical Speciation Network (CSN) program at four air monitoring stations in Wisconsin were used as the input concentration for PMF modeling. See Methods in Chapter 2 for details about the data collection, chemical analysis, and the description of the geographical locations where the monitoring stations are. The following are the PMF modeling procedures.

3.3.1.1. **Initial Data Screening**

PMF modeling requires every entry to have a valid value and requires two inputs: concentration (x_{ij}) (CON) and associated uncertainty (s_{ij}) (UNC). The initial CON are the selected species from the speciated $PM_{2.5}$ data, after removing outliers and high below detection limit (BDL) species. The data with many missing data and high BDL% will be removed, except for elements that is an index for a specific emission source, such as Se for coal combustion. The days with missing major species will be removed. Species would be further reduced during the modeling processes.

3.3.1.2. **Calculating Uncertainty**

The model allows the user to determine the uncertainty (UNC, u_{ij}) for each x_{ij}. The UNC is an estimated value, which includes the estimation of analytical uncertainty, sampling uncertainty and other adjustments during the modeling processes. There are different ways to obtain the u_{ij} for each associated x_{ij} (Baumann et al., 2008; Kim et al., 2005b; Reff et al., 2007).

The EPA posted uncertainty is calculated based on formulas that include sample concentration, minimum detection limit species, and the error estimates for each species (see Eq. (3.4).

$$UNC = \sqrt{\left(\frac{MDL}{n}\right)^2 + (P \times CONC)^2} \tag{3.4}$$

where MDL = minimum detection limit; and

P = user determined error estimate including sampling, analytical uncertainty for each species.

Eq. (3.5) is for concentration ≥ MDL. When the concentration is between half of MDL and MDL, P will be increased to ($3 \times P$) in Eq. (3.5):

$$UNC = \sqrt{\left(\frac{MDL}{n}\right)^2 + (3P \times CONC)^2} \tag{3.5}$$

Several different methods were used to calculate the uncertainty for concentration below MDL/2. Kim used 1.5 × MDL for the uncertainty of concentration below MDL/2 (Kim, 2005), while Baumann et al. used 2/3 × MDL for the uncertainty of concentration below MDL/2 (Baumann et al., 2008). The uncertainty for missing data is 4 × geometric mean of available concentration of that species.

In this study, different uncertainties were tried to find better results. A VBA program was written to calculate the different uncertainties used in the modeling.

In the above two formulas, p is user determined percentage (%) of measured concentration of speciated $PM_{2.5}$. In this study, p is modified based on the percentage (%) published in Kim (2005). For example, the % for EC, OC, Cr and NO_3 are increased to 15% to 30%, respectively. The ideal uncertainty is the one that has a correlation with its concentration shaped like a hockey stick, as showed in the following plot, when the concentration is below the detection limit, the uncertainty goes up quicker than when the concentration is above the detection limit.

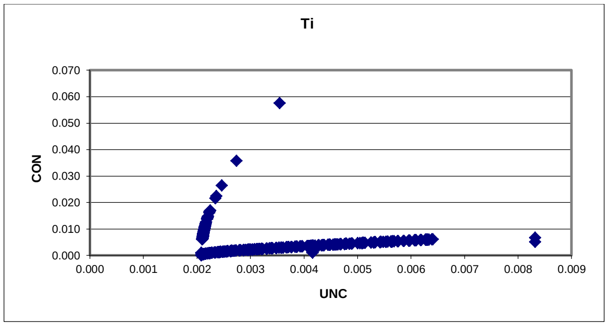


Figure 3.1. Sample Uncertainty and Concentration Correlation

The uncertainty data will be further adjusted during the modeling process based on the output of the initial run, such as signal/noise (S/N) and the scaling residuals. Another advantage of the function to let user to determine the uncertainty input is that the uncertainty can be adjusted at selected periods, for selected elements based on the knowledge about the data and the modeling outcome.

3.3.2. **PMF Modeling**

After an initial run, three groups of output are generated for further used to determine how to continue the modeling:

1. Species categorization (ratio of signal to noise - S/N)

The S/N is calculated as:

$$S/N = \left(\frac{1}{2}\right)\sqrt{\frac{\sum_{i=1}^{n} x_{ij}^2}{\sum_{i=1}^{n} s_{ij}^2}} \qquad (3.6)$$

where χ_{ij} = concentration of j^{th} species on the i^{th} day; and

S_{ij} = error (uncertainty) estimates for x_{ij}.

S/N is a very important index used in the modeling. Unless the species is an index element, only species with S/N ≥ 0.5 (check the number) will remain in subsequent modeling.

2. Three Qs (Goodness of fit)

The software generates three Qs: theoretical (Q_0), robust (Q_R) and true (Q_T). If the number of factors and uncertainty data are right, Q_R should be very close to $Q_{0,}$ and the theoretical Q_0 should be equal to the number of samples (EPA PMF 3.0 manual, 2008).

$$Q_0 = n*(m_{strong} + \frac{m_{weak}}{3} - p) \qquad (3.7)$$

where n = number of samples;

m = number of species being selected as strong (m_{strong}) or weak (m_{weak}); and

p = sources/factors.

Q_R reduces the impact of outliers by dynamically reducing the weight (S_{ij}) for points that fit poorly through an iterative process until each residual falls within the critical limit of 2 S_{ij}.

3. Modeling diagnostics

Modeling generates modeling diagnostics to show how well the modeling results fit the data. The model provides "scaled residual" for each species and requires the scaled residual for each species lie between –3 to +3. If one species has too many residuals outside the range, either the related uncertainty needs to be downgraded or the entire sample needs to be removed.

$$\text{Scaled residual} = \left| \frac{e_{ij} = x_{ij} - \sum_{k=1}^{p} g_{ik} f_{kj}}{S_{ij}} \right| \leq 3 \qquad (3.8)$$

Removing involved species, adjusting number of factors and modifying the uncertainty are the examples of many methods can be used to improve the modeling results.

3.3.3. **Interpret PMF Modeling Output**

To help identifying the potential emission sources, in addition to the available knowledge of source profile, the Emission Factor Wind Roses (EFWR) and Conditional Probability Function (CPF) analyses were used in this study to identify the directions with highest probability that the PMF estimated emission source (emission factor) would be.

3.3.3.1. **Emission Factor Wind Roses (EFWR)**

The hourly wind direction data and the PMF modeling predicted emission factors were used to make the seasonal EFWR for the Milw, Mayv and Perk stations. No EFWRs were made for the Wauk station because the wind data obtained for Wauk was not ready.

3.3.3.2. **Conditional Probability Function (CPF)**

The conditional probability function (CPF) (Kim et al., 2003a) was calculated using the source contribution estimates from PMF and with wind direction values measured at each station to determine the likely directions of the sources. The CPF is defined as:

$$\mathrm{CPF} = \frac{m_{\Delta\theta}}{n_{\Delta\theta}} \qquad (3.9)$$

where $m_{\Delta\Theta}$ = number of time source contributions are high while wind direction was from sector $\Delta\Theta$; and

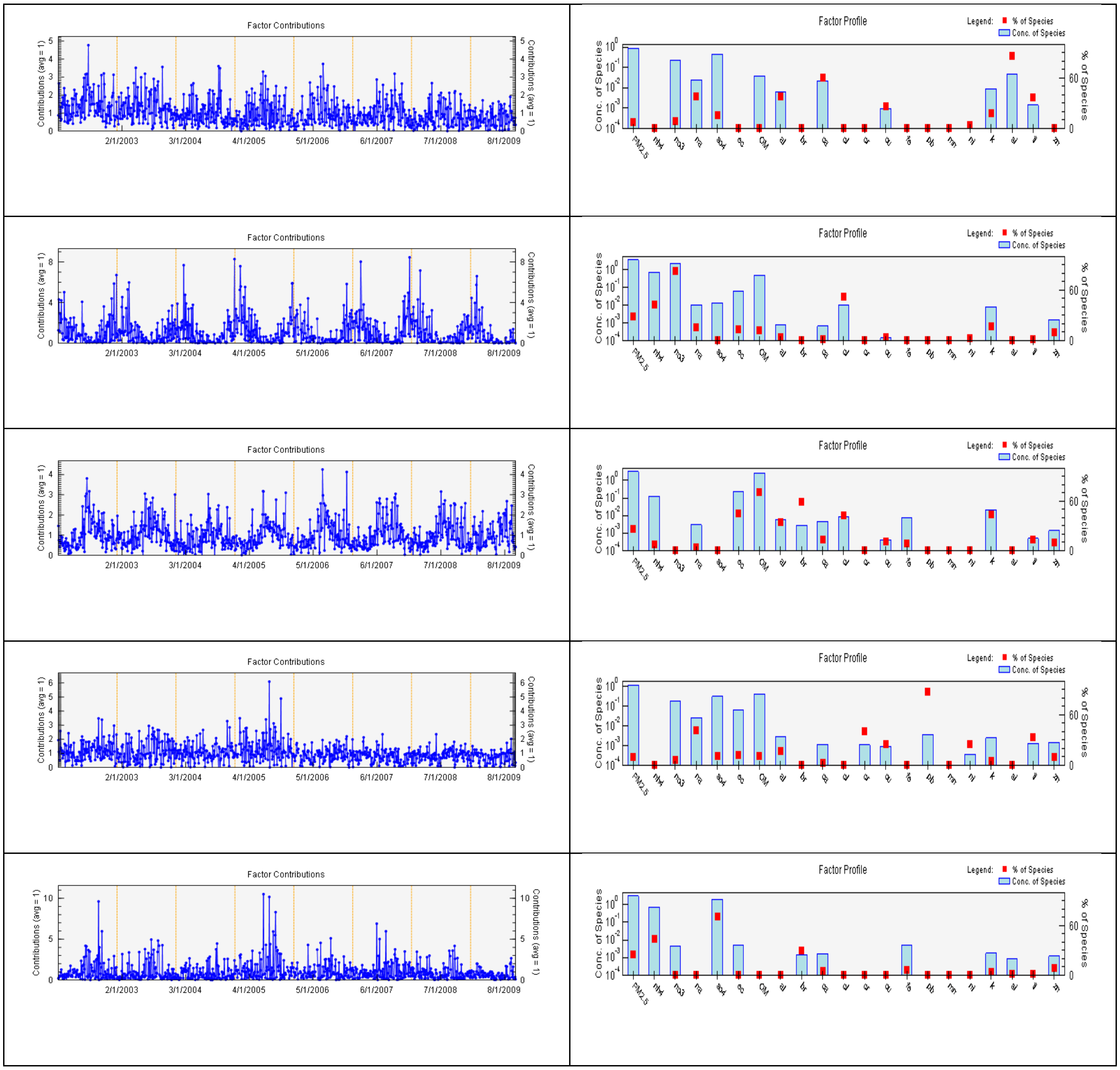
$n_{\Delta\Theta}$ = number of times wind direction is from sector $\Delta\Theta$.

CPF value close to 1.0 for a given sector ($\Delta\Theta$) indicates a high probability that a source is located in that direction.

3.4. Results and Discussion

3.4.1. Potential Emission Sources _ Milwaukee (Urban Area)

Seven potential emission sources were identified for ambient $PM_{2.5}$ monitored in Milwaukee station. Figures 3.2 to 3.9 represent the identified potential source profile and the estimated daily contribution from each source to the $PM_{2.5}$.



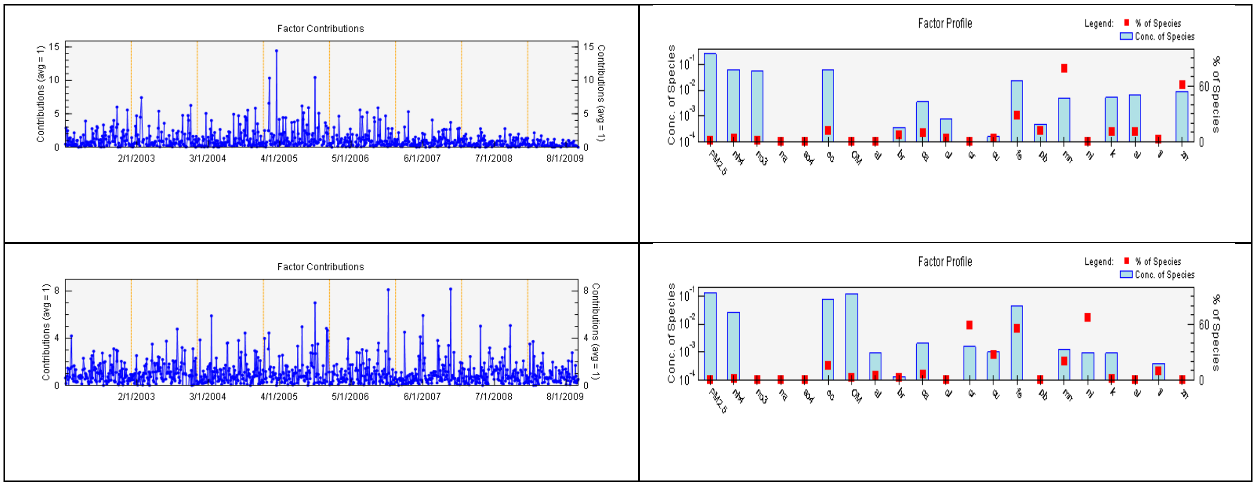


Figure 3.2. Total output of the PMF run for the Milwaukee Station

Right: The profile of the 7 potential emission sources for $PM_{2.5}$ observed at Milwaukee Station.

Left: Mass contribution of the 7 potential emission sources to the $PM_{2.5}$ at Milwaukee Station.

The left panel of Figure 3.3 is the emission factor wind roses. It shows the strength of the PMF estimated F1 at each season from each wind direction [expressed in the color from purple (low) to red (high)]. The right panel of Figure 3.3 is the CPF for Factor 1. The conditional probability function is constructed using an 80th percentile value (80% of data have lower concentrations, 20% have higher concentrations). For each spoke of the wind rose, the CPF is calculated as (number of samples in spoke > 80 percentile)/(total number of samples in that spoke). The resulting fraction is the probability that any sample from that wind direction will have a concentration higher than the 80 percentile. The line at the bottom of the plot tells the value of the 80 centile for that dataset of the factor. In this case, the value of 80 percentile of this factor is 1.5. In another words, 80% of the value for this factor is below 1.5.

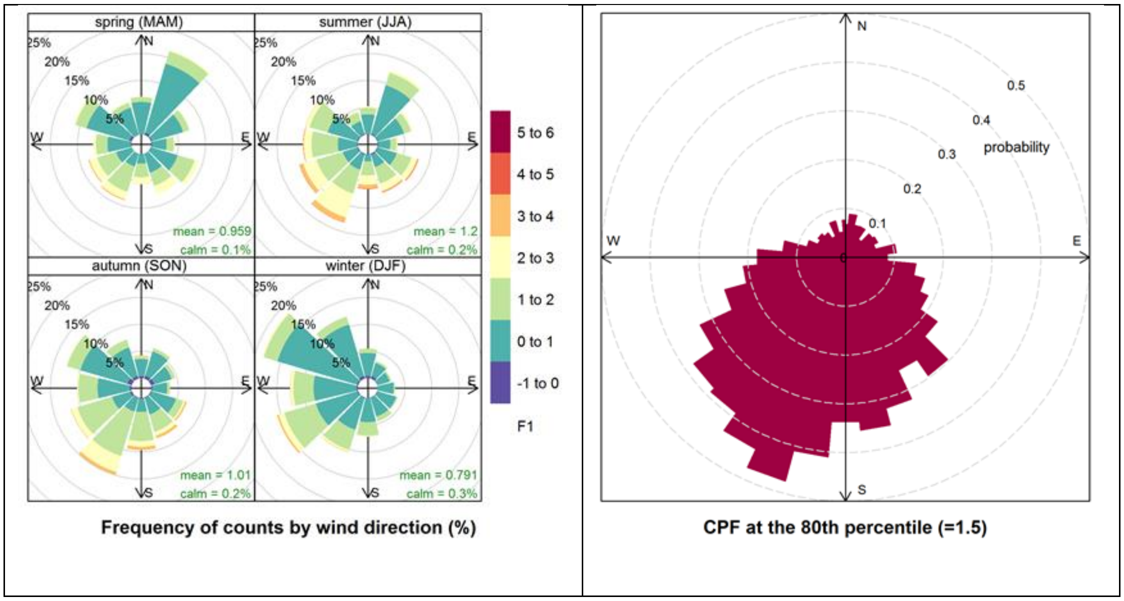


Figure 3.3. Factor 1_Milw – Soil Source

Factor 1 contains 61% of Ca, 87% of Si, 38% of Al and 37% of Ti. Ca, Si, Al and Ti are the major crustal elements and soil contains a large fraction of crustal elements. The 26 % of Cu might be from the traffic. This factor shows relatively high concentration during warm seasons and lower concentration in winter. Snow covered land in winter and more activities during warm seasons may have contributed these variations. Therefore, this factor represents soils. The soil source contributed about 7.3% of the $PM_{2.5}$ mass.

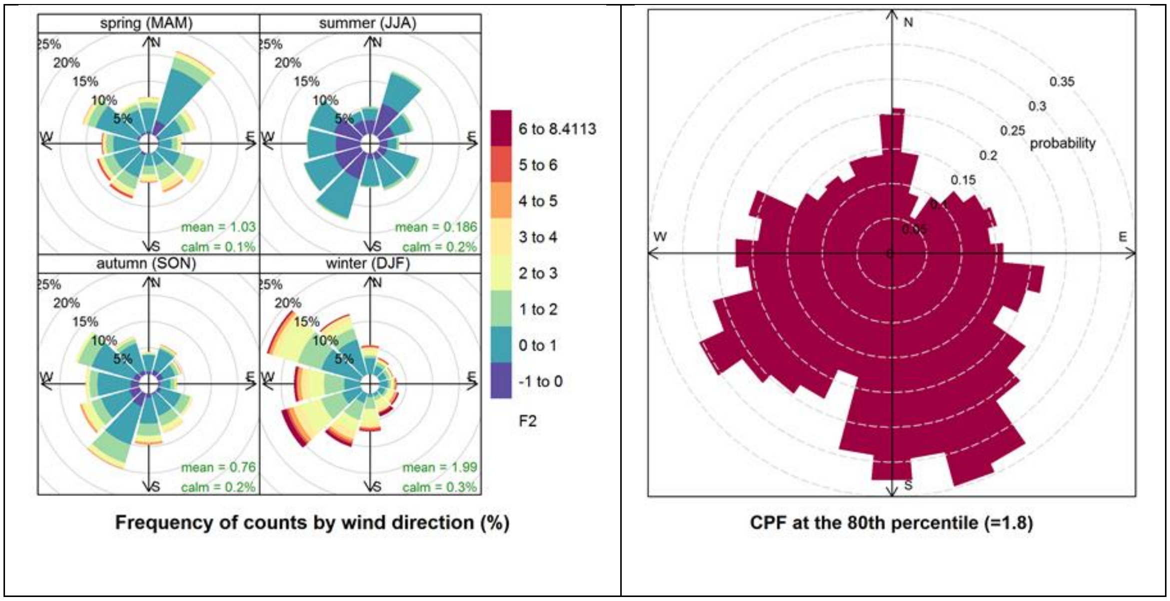


Figure 3.4. Factor 2_Milw – Secondary nitrate

Factor 2 contains high percentage of NO_3^- (83%) and NH_4^+ (42%). Factor 2 represents secondary nitrate emissions, a major winter factor. This factor has clear seasonality: winter high and summer low (see Figure 3.4). The CPF pointed the probability (30% to 35%) of concentration of nitrate will be higher than 1.8 when wind comes from south to southeast. Major coal fired power plant are located at that direction from Milwaukee station. The Menomonee valley industrial park is located southwest of the Milwaukee station. Southwest wind can bring the nitrate emitted from the industrial processes in that industrial park.

If high concentrations were evenly distributed around the whole wind rose, then the CPF plot would look like a perfect circle at the 0.2 line (because the criterion of 80 percentile of F). Meaning all days would have a 20% chance of high concentration from around area.

In addition to the fuel combustion, Automobile and agricultural activities are the other two major emission sources for the secondary nitrate. Milwaukee station sits in a busy intersection of two major local commercial streets. Nitrate emitted from the traffic and commercial boilers surround the station and constantly affect the monitoring station. The nearly circle CPF plot reflects this kind of emissions.

There is another point need to present when exploring the potential emission sources for secondary nitrate. Since the relatively long residence lifetime of the nitrate and its precursor, CPF can also pointed to wind direction where the air parcel containing higher nitrate is from. The real physical emissions facility could be at different directions.

The factor 3 also includes winter salt application (53% of Cl) and wood burning (17% of K).

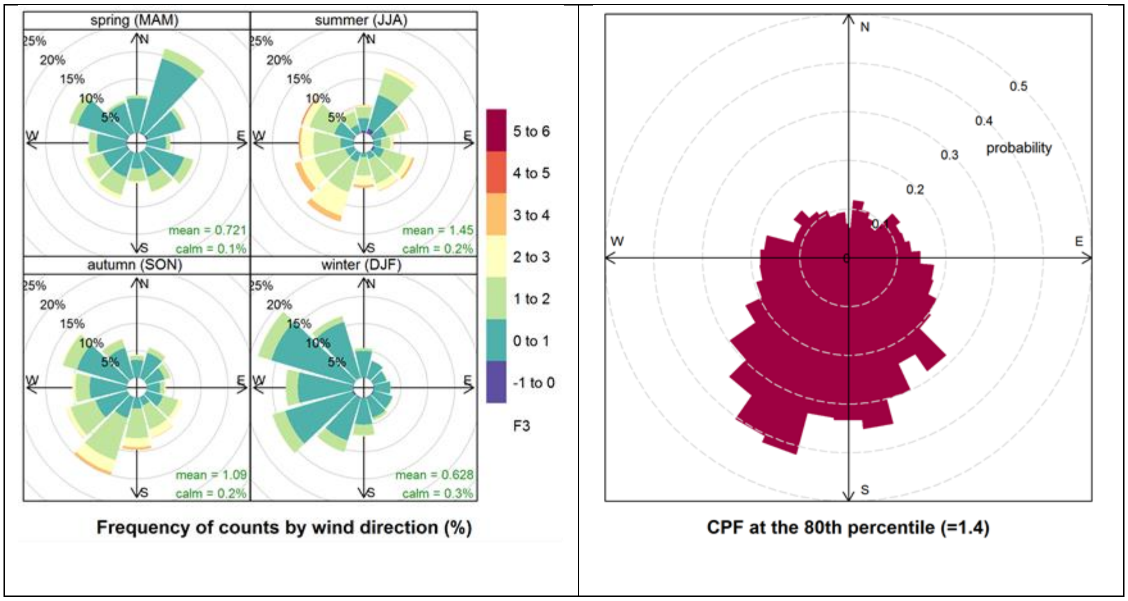


Figure 3.5. Factor 3_Milw – Organic Carbon

Factor 3 contains OM (71%), EC (46%), Br (61%), K (44%), --- Cl (43%) and Al (34%). Factor 3 represents combined organic carbon emission sources, which covers the OC from industrial operations and diesel combustion (the high OC/EC ratio), biomass burning, biogenic

VOC emission and summer activity that caused OC increase (the seasonality and the high K content).

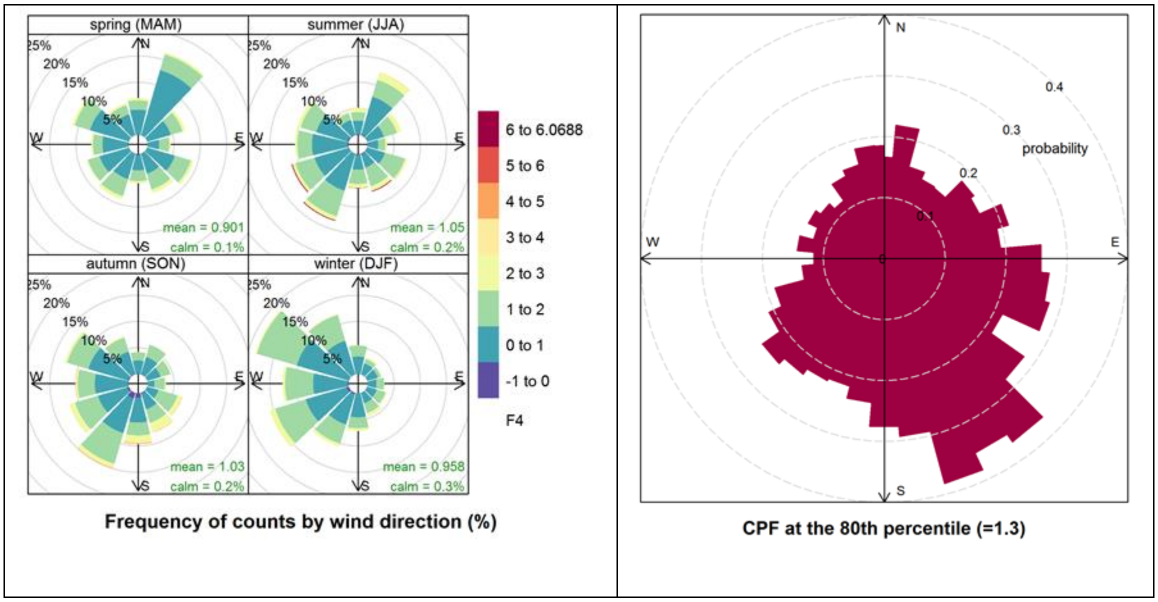


Figure 3.6. Factor 4_Milw – Lead factor

Factor 4 contains lead (88%), Cr (40%) and Cu (26%). At the national level, major sources of lead in the air are ore and metals processing and piston-engine aircraft operations using leaded aviation fuel. Other sources are waste incinerators, utilities, and lead-acid battery manufacturers. The highest air concentrations of lead are usually found near lead smelters (www.epa.gov). Except for aircraft operations, none of these sources are likely nearby Milwaukee. Since the Milwaukee Mitchell AirPort is about 13 km south of Milwaukee station, it is assumed that the Pb is from the burning high Pb contained fuel for aircraft. CPF clearly pointed to the southeast as the location of the sources.

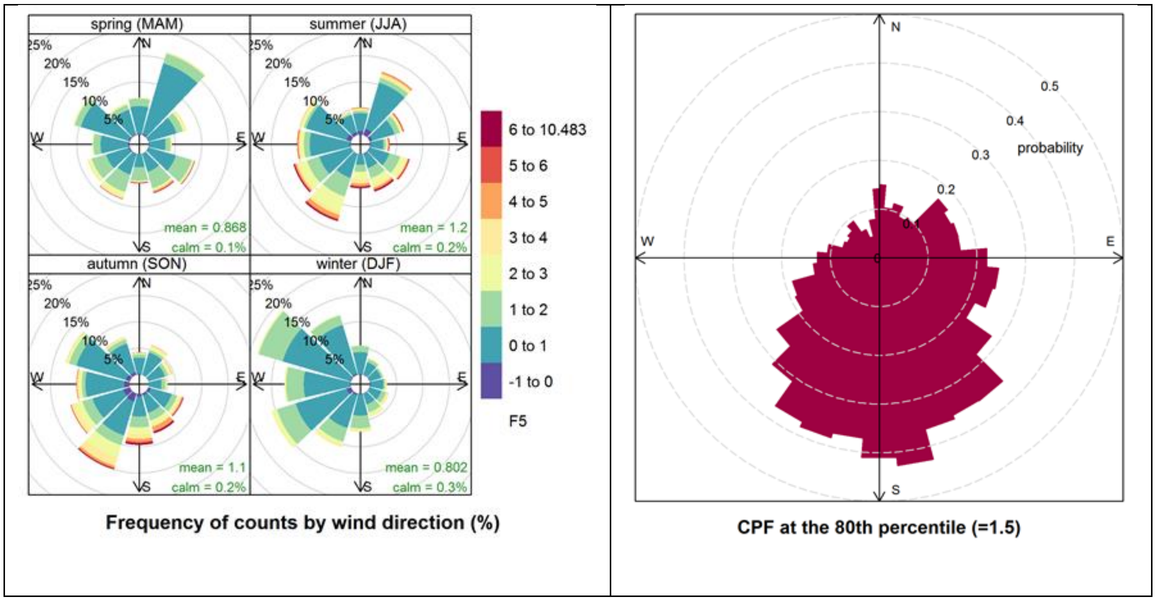


Figure 3.7. Factor 5_Milw – Sulfate

Factor 5 contains high sulfate (72%) and NH_4^+ (45%) and Br (30%). Based on CPF plot, the sources are likely to be located at the location south of Milw Station. Sulfate does not have clear seasonality like nitrate does.

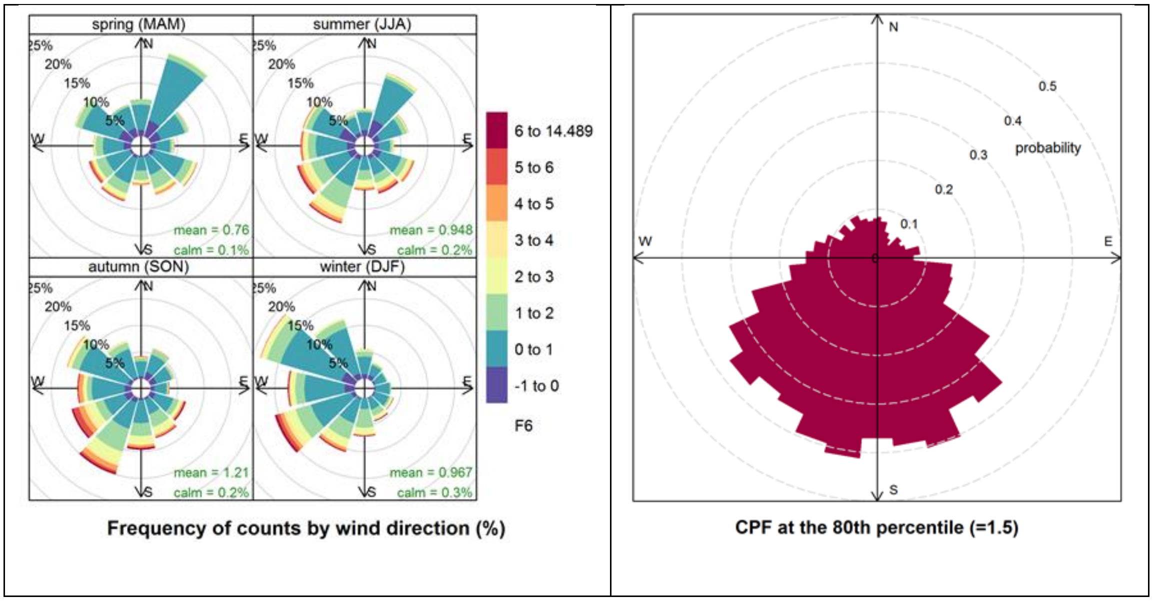


Figure 3.8. Factor 6_Milw – Mn and Zn sources

Factor 6 contains Mn (78%) and Zn (61%). Mn and Zn are widely used in different industries. This factor has apparent weekday and weekend difference (see Figure 3.9), which is a good indicator that Factor 6 represents industrial processes where Mn and Zn are used. CPF indicated that the emission sources for Factor 6 are located south of the station.

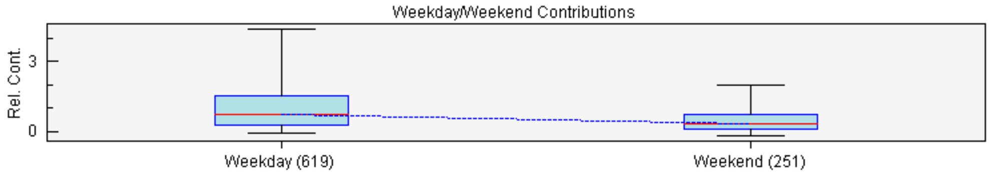


Figure 3.9. Weekday and Weekend Variation for Factor 6

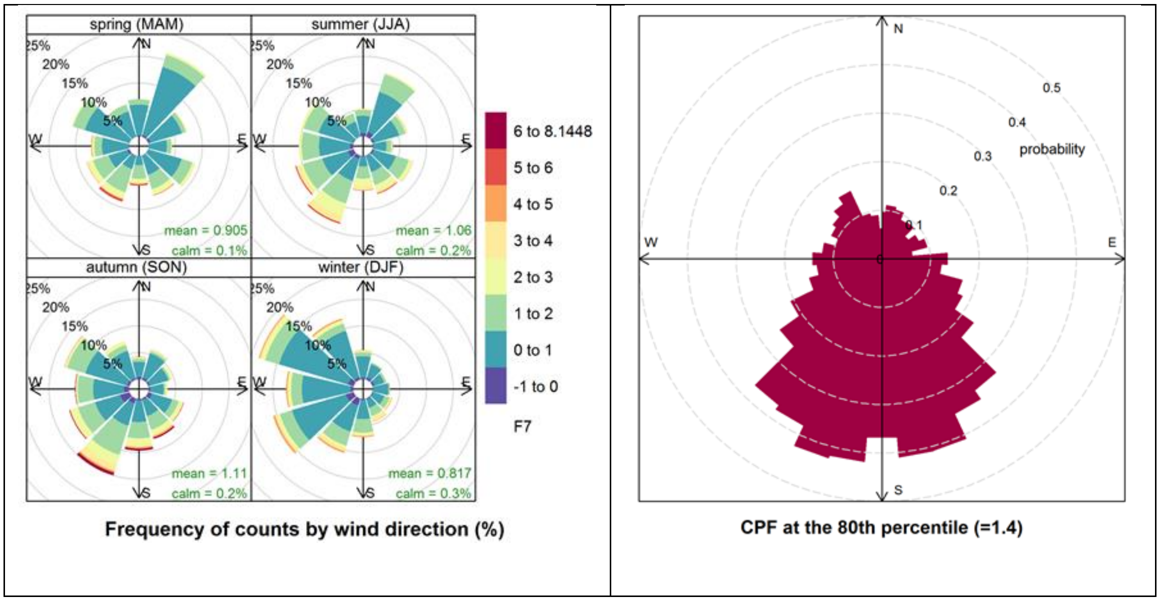


Figure 3.10. Factor 7_Milw – Metal emission source

Factor 7 contains Ni (67%), Cr (60%), Fe (56%) and Cu (28%). Similar to Factor 6, this factor has weekday and weekend variations. Ni, Cr, Fe and Cu are the widely used industrial materials. Ni also comes from coal and diesel combustion. Cu could come from the wear and tear of tires and brakes. Different from Factor 6, Factor 7 has clear seasonal variations. This is one sign that Factor 7 represents activities that are affected by temperature, such as summer recreation related-automobile activities. Therefore, Factor 7 represents emission sources of industries and traffic.

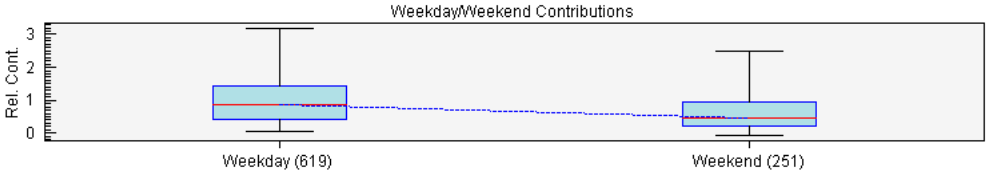


Figure 3.11. Weekday and Weekend Variation for Factor 7

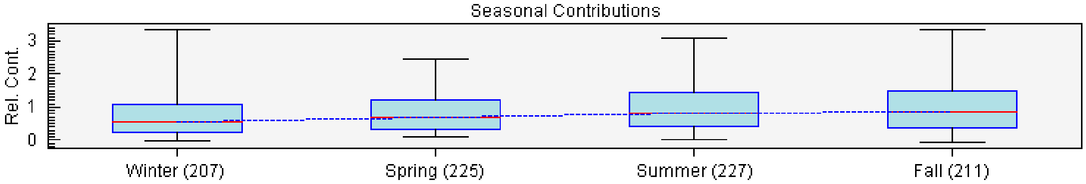
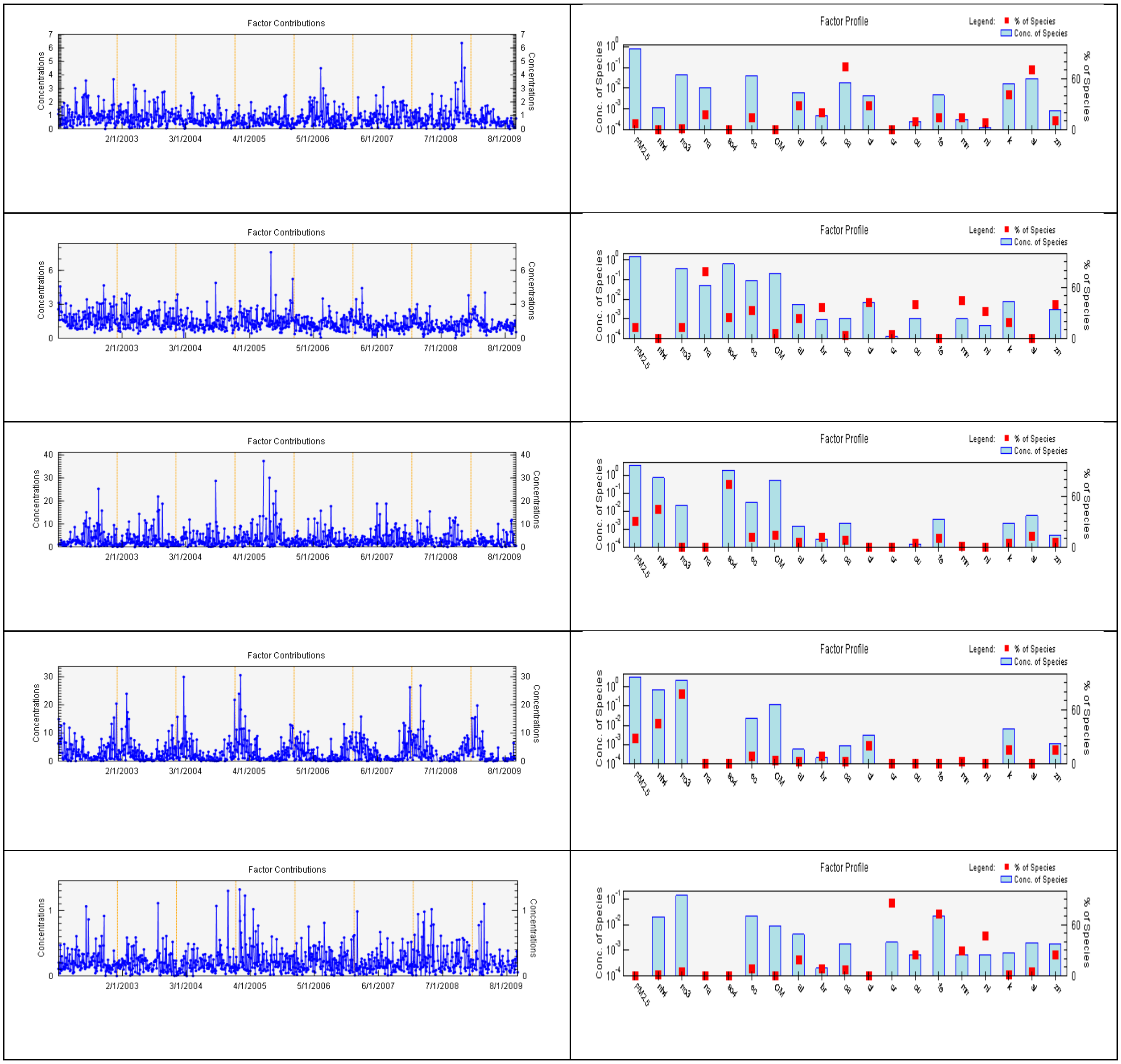


Figure 3.12. Seasonal Variation for Factor 7

3.4.2. **Potential Emission Sources _ Mayville (Agriculture Area)**

Six potential emission sources were identified for $PM_{2.5}$ monitored at Mayville station. Figure 3.13 to Figure 3.19 represent the identified potential source profile and the estimated daily contribution from each source to the $PM_{2.5}$.



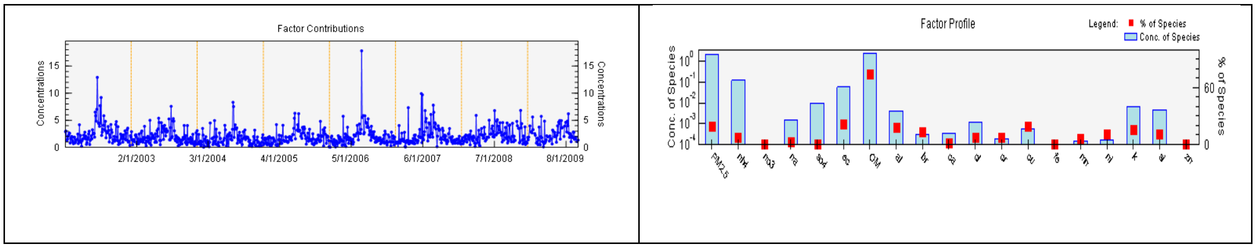


Figure 3.13. Total output of the PMF run for the Mayville Station

Right: The profile of the 6 potential emission sources for $PM_{2.5}$ observed at Mayville Station. Left: Mass contribution of the 6 potential emission sources to the $PM_{2.5}$ at Mayville Station

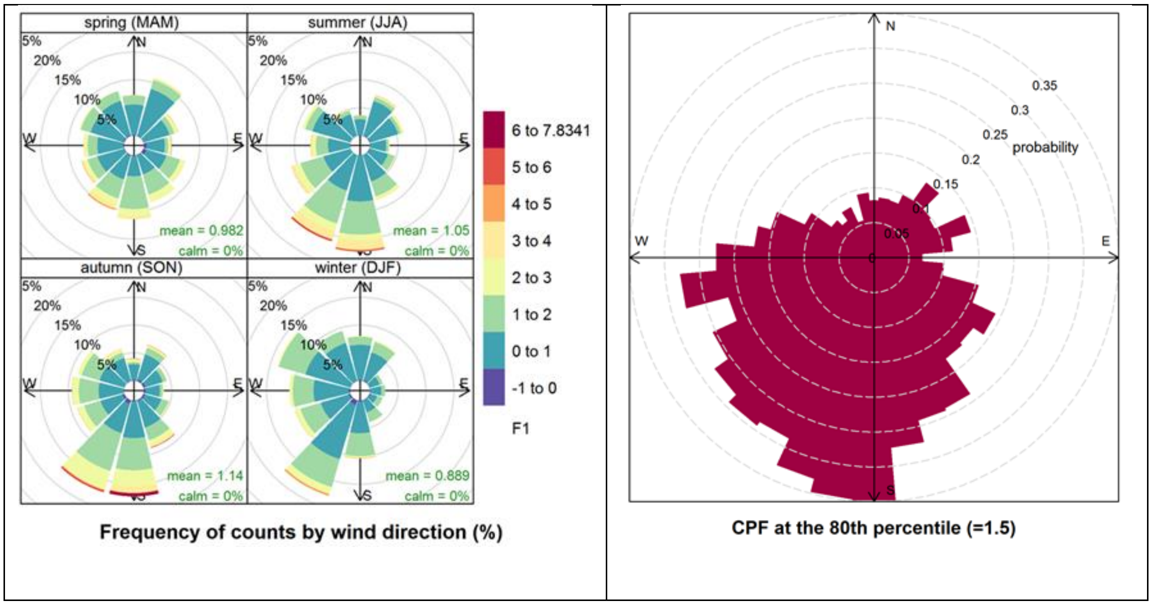


Figure 3.14. Factor 1_Mayv - Soil

The Factor 1 contains high Ca (75%) and Si (71%), as well as Al (28%), K(42%) and Cl (28%), represents soil. The CPF indicated that 80 percentile of the probability the emission sources are located at the southwest of Mayv Station.

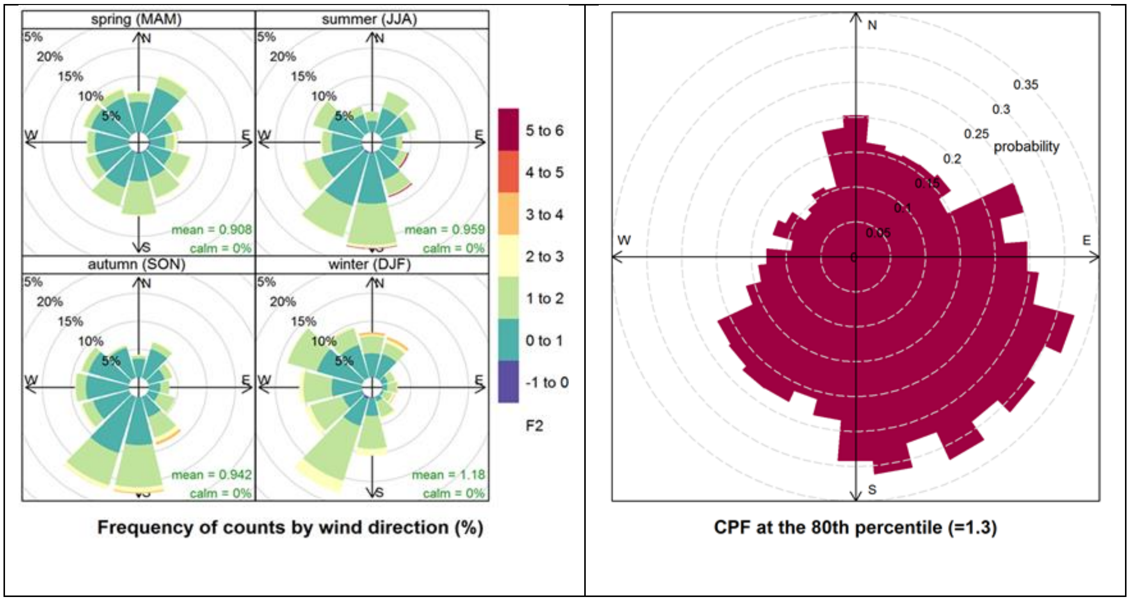


Figure 3.15. Factor 2_Mayv – Miscellaneous emission sources

The Factor 2 contains higher Na (80%), Cl(43%), Mn(45%), Cu(40%), Zn(40%), Ni(32%), Br(38%) and EC(34%), Al(25%) and K(19%)

This factor is higher in winter with no weekday and weekend variation. From CPF indication, the southeast has the highest probability where the emission sources are located. The sources are located at northeast and southwest as well. Factor 2 represents miscellaneous emissions and perhaps the high sodium is the result of road salting in the winter.

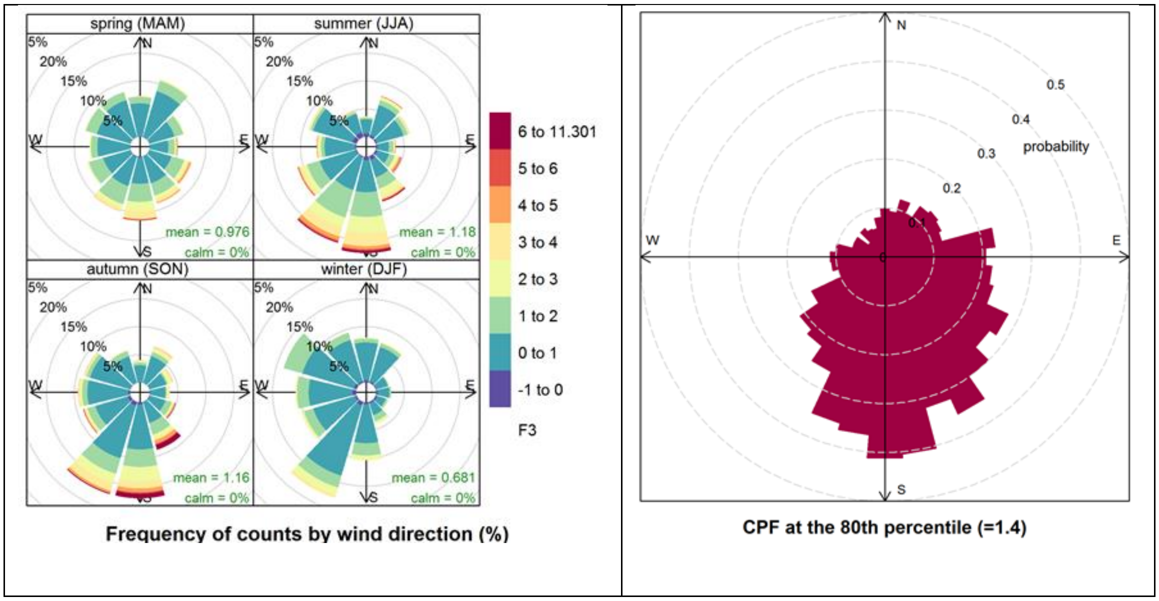


Figure 3.16. Factor 3_Mayv – Secondary Sulfate

Factor 3 contains higher sulfate (74%) and NH_4^+ (45%), OM (15%) and EC (12%) and Br (12%), Si (13%) and Fe (11%). This factor represents sulfate. The emission sources are mainly located at the south of the station.

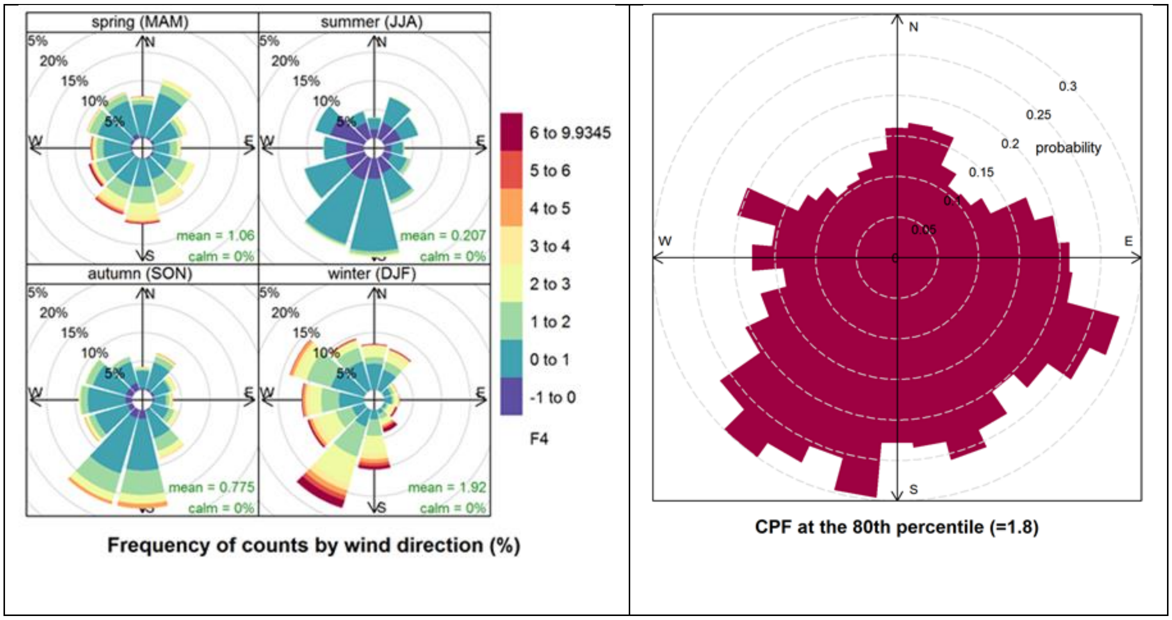


Figure 3.17. Factor 4_Mayv – Secondary Nitrate

Factor 4 contains high NO_3^- (79%) and NH_4^+ (45%). The winter salt application may be associated with Cl (20%) and wood burning may be associated with K (17%). This factor primarily represents nitrates. The major nitrate sources are located from south of the station, east and southwest of the station. The high probability source locations for nitrates are wider than the high probability source location for sulfate. This is consistent with an additional nitrate source, in addition to power plant emissions.

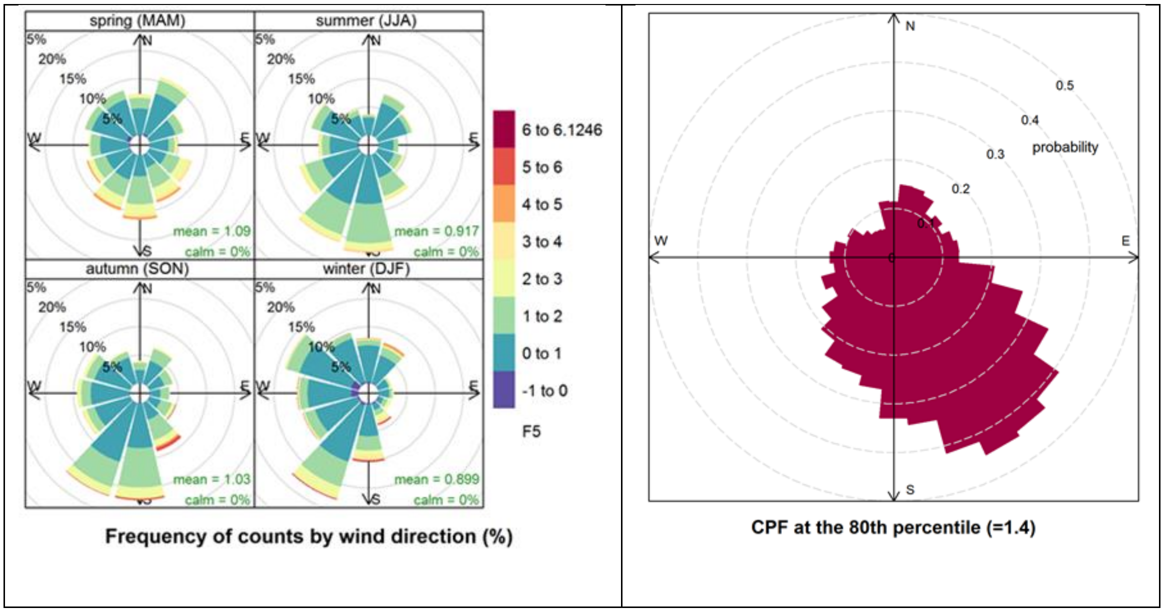


Figure 3.18. Factor 5_Mayv – Industrial processing and Agricultural activities

The Factor 5 contains Cr (87%), Fe (74%), Ni (47%), Zn (26%), Mn (30%), and Cu (24%). This factor represents emissions from industrial processing, agricultural activities, and traffic related emissions. It is higher in spring and high during weekdays, which support the suggestion that this factor is related to the agricultural and industrial activities. CPF indicates that the emission sources are most likely located southeast of the Mayv station.

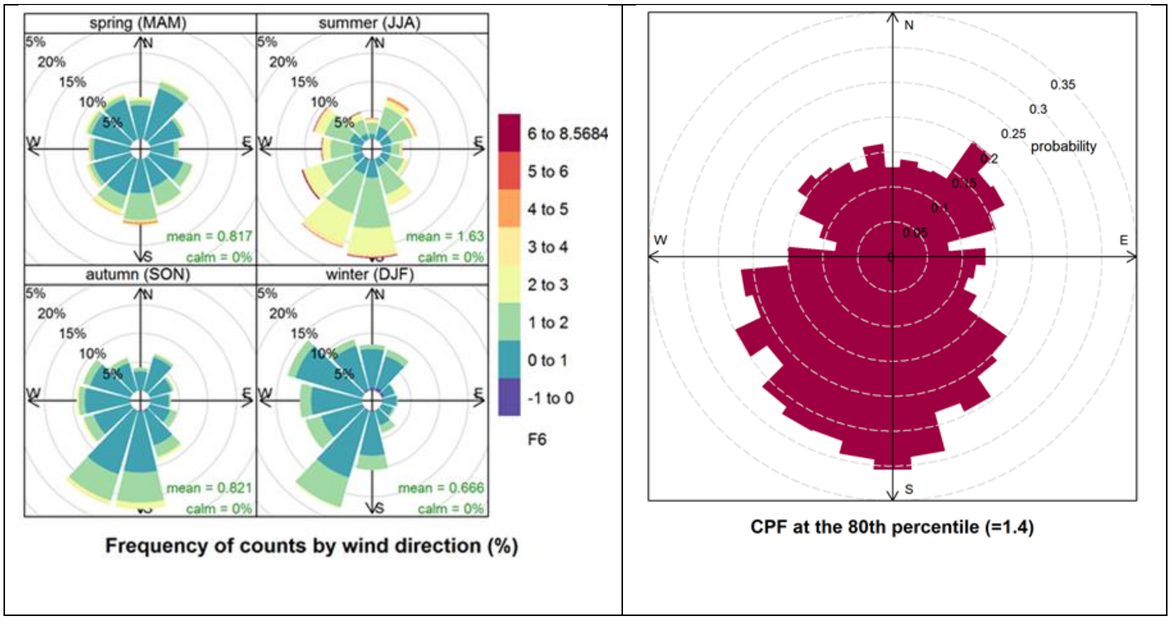
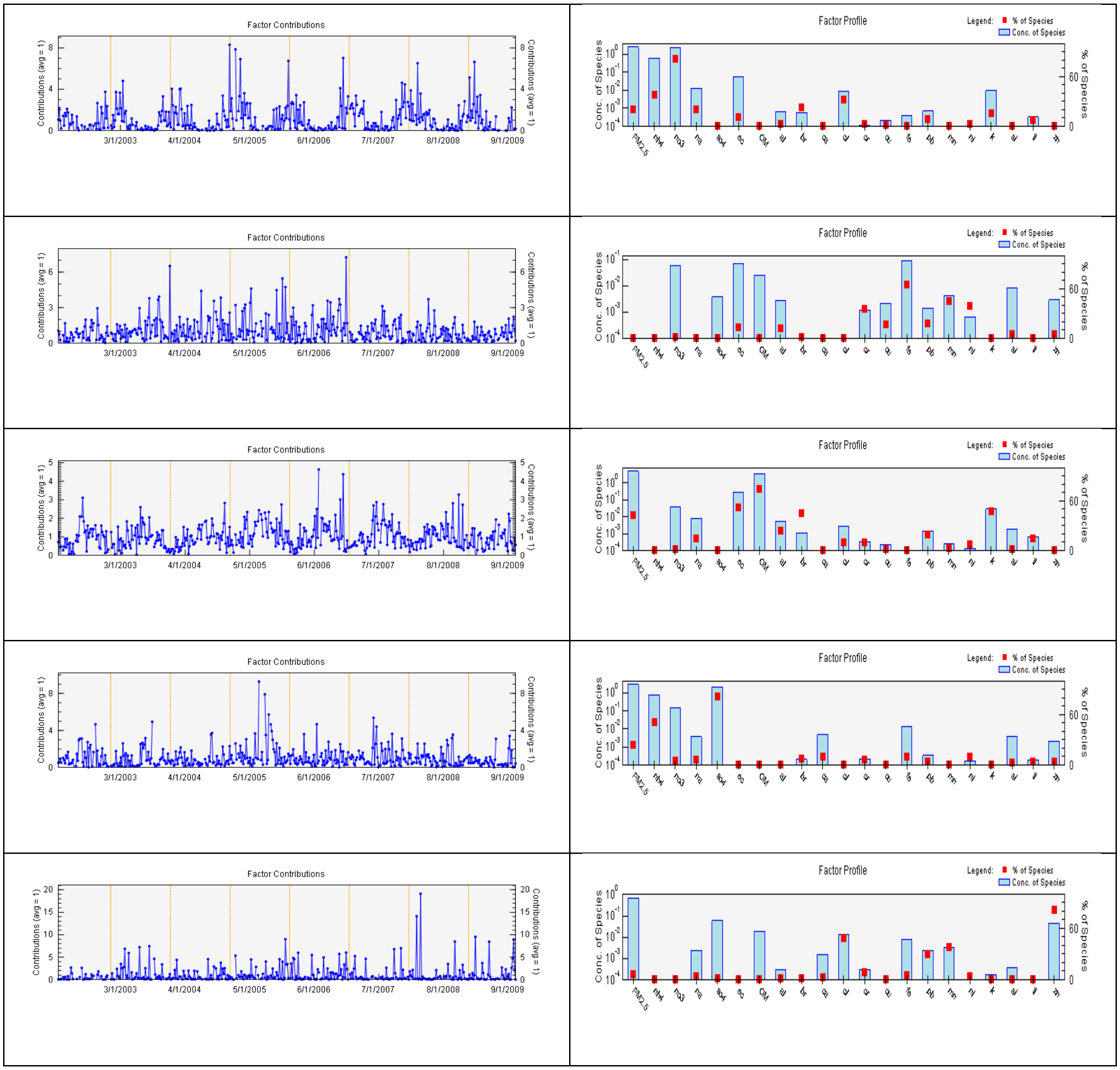


Figure 3.19. Factor 6_Mayv – OC sources

Factor 6 contains OM (75%), EC (22%), Br (13%), K (16%), Cu (20%) and Al (18%). This is an OC emissions dominated factor. The higher probability direction where the emission sources are located is south of the station.

3.4.3. **Potential Emission Sources _ Waukesha (Industrial area)**

Eight potential emission sources were identified for $PM_{2.5}$ monitored at Waukesha station with $Q_0/Q_R = 1.1$. Figure 3.20 represent the identified source profile and the estimated daily contribution from each source to the $PM_{2.5}$.



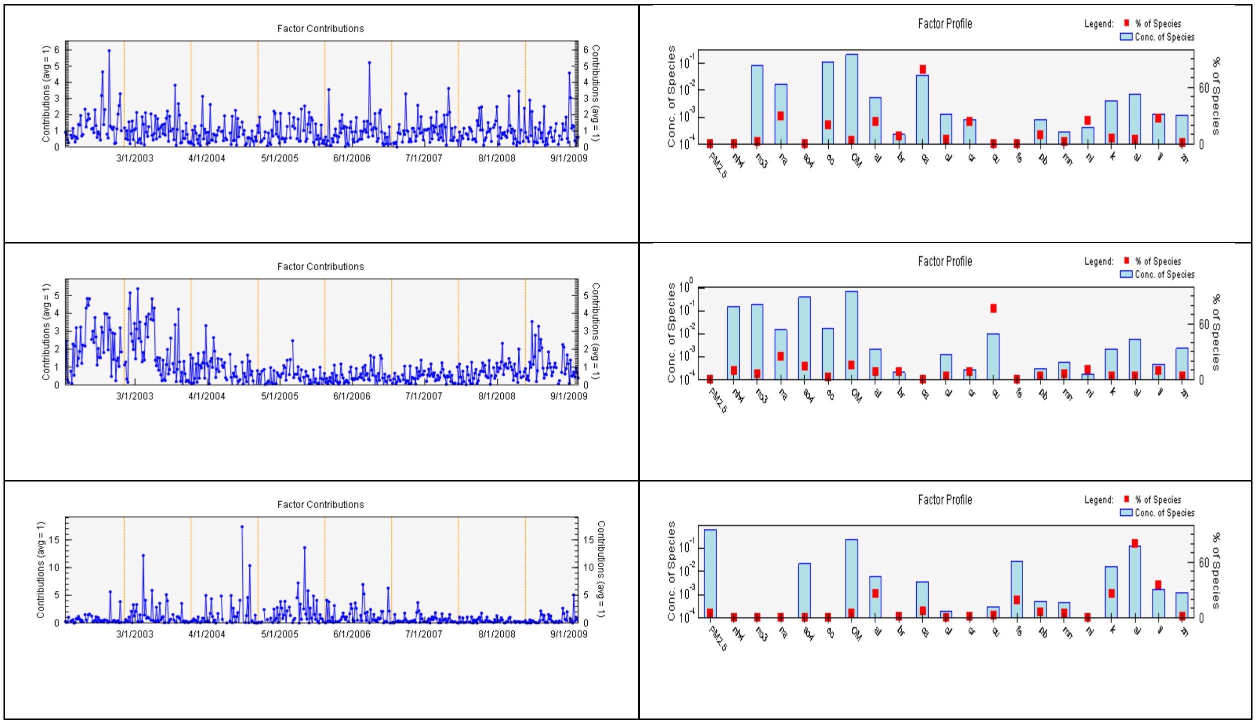


Figure 3.20. Total output of the PMF run for the Waukesha Station

Right: The profile of the 8 potential emission sources for $PM_{2.5}$ observed at Waukesha Station. Left: Mass contribution of the 8 potential emission sources to the $PM_{2.5}$ at Waukesha Station

Factor 1 contains high NO_3^- (82%) and NH_4^+ (39%). The winter salt application may be associated with Cl (32%) and Na (21), and wood burning may be associated with K (16%) and Br (24%). This factor has a very strong seasonal signal, winter is the highest and summer is the lowest. No significant weekday and weekend variation. This factor represents secondary nitrate.

The Factor 2 contains higher Fe (64%), Mn (44%), Cr (36%) and Ni (38%). About 10% each for EC (12%), Al (12%), Cu (17%) and Pb (17%). Slightly seasonal difference, fall and summer emissions are higher than that for winter and spring. Weekdays are higher than weekend, which indicates this is very likely an industrial source. From the scatter plots for Ni vs. Cr and Fe vs. Mn, the R^2 values are less than 0.48. Therefore, these metals are likely from different industrial processes and mobile sources. Factor 2 represents a metal emission dominated source.

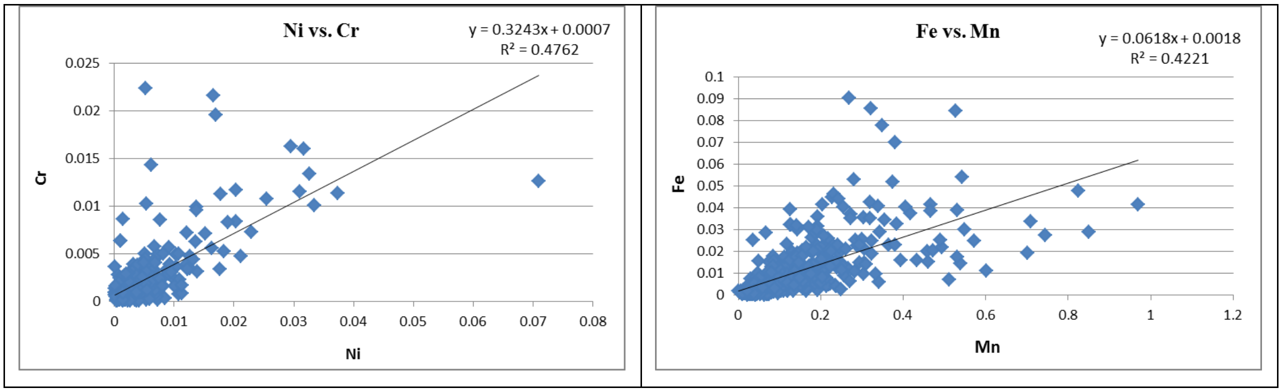


Figure 3.21. Scatter plot for Ni ~ Cr and Fe ~ Mn

Factor 3 contains higher OM (74%), high EC (52%), Br (45%), K (47%), Ti (14%) and Al (23%). It has a very strong seasonal signal. Summer is the highest, followed by fall and spring, and winter is the lowest. There was no significant weekday and weekend difference. Organic $PM_{2.5}$ sources, includes OC emissions from biomass burning, biogenic OC emission and traffic emissions. OC emissions from burning diesel has higher OC/EC ratio. K represents the biomass burning. This factor represents OC emissions from biogenic and anthropogenic sources, including fuel combustions. The source for Br may be due to the application of pesticides in agricultural fields during the summer (Ashworth, 2013).

Factor 4 contains higher sulfate (82%) and NH_4^+(52%). There are no significant seasonal variations, but summer and fall have wider sulfate emission ranges. No weekday and weekend differences were observed. This factor represents secondary sulfate from industrial and traffic emission sources.

Factor 5 contains higher Zn (79%), and Cl (47%), Mn (36%) and Pb (29%). There are not significant seasonal variations among these metals. Winter and fall have higher emission days. There was a very strong weekday and weekend difference. This factor represents an industrial emission source.

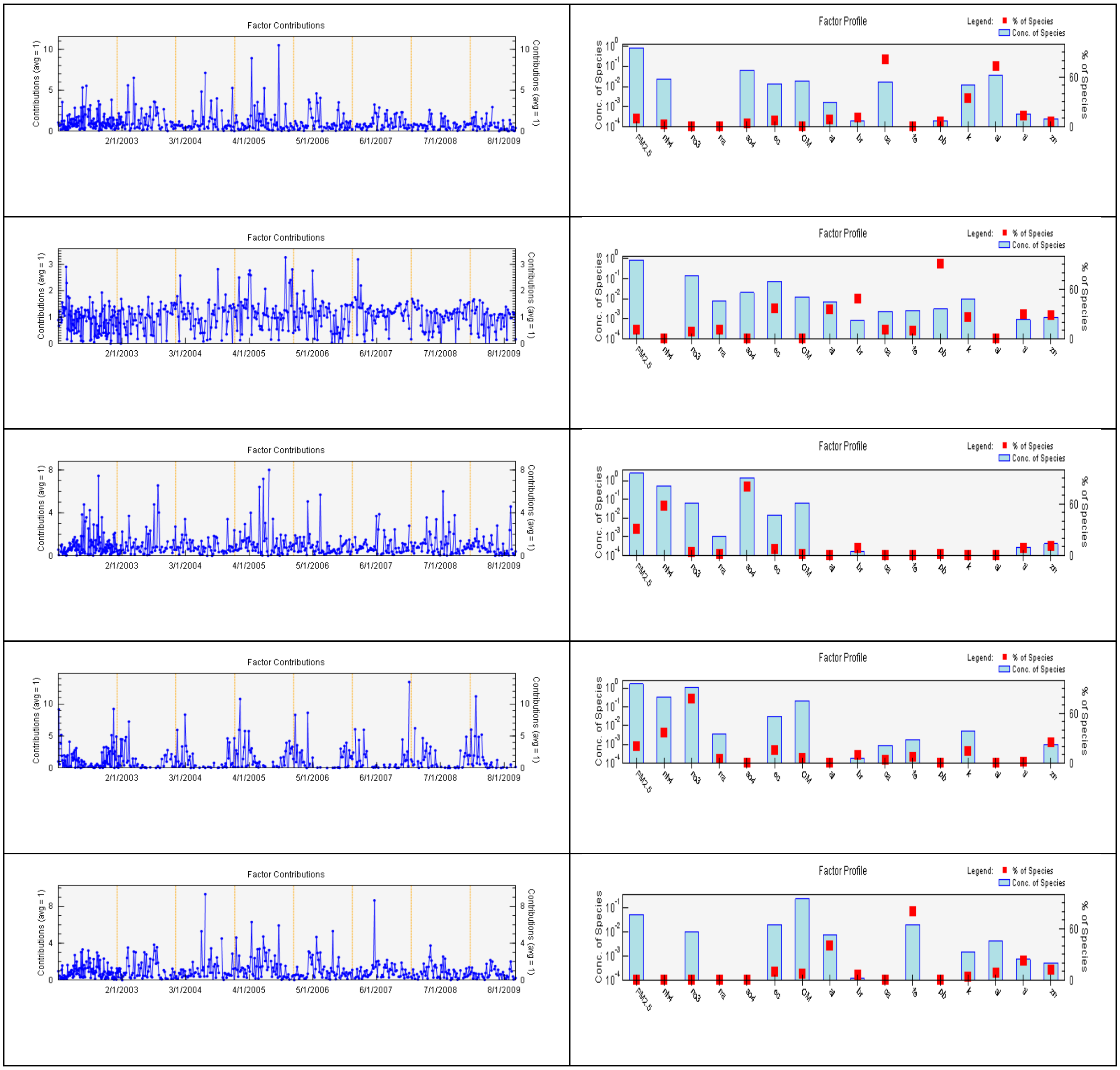
The Factor 6 contains high Ca (78%), Na (21%), EC (21%), OM (5%), Si (4%), Al (24%), Cr (25%), Ni (25%) and Ti (28%). Fall is the highest, followed by summer, spring and winter (fall > summer > spring > winter) and with strong weekday and weekend difference. This factor may represent emissions from quarrying operations mixed with soil.

The Factor 7 contains Cu (75%), Na (25%) and OM (15%). Winter is lower than spring and summer. There was no weekday and weekend difference. This factor represents Cu emissions related to stationary source(s) and/or traffic emissions.

The Factor 8 contains Si (82%), Ti (37%), Al (27%) and Fe (19%). Winter is lower due to the snow coverage and frozen grounds. There was no significant variations among spring, summer and fall for Factor 8, except for several higher concentration days in summer and fall. There is significant weekday and weekend difference. This factor likely represents wind-blow and traffic-mobilized soil.

3.4.4. **Potential Emission Sources _ Perkingstown (Rural/Forest area)**

Seven potential emission sources were identified for $PM_{2.5}$ monitored at Perkingstown station. Figure 3.22 represents the identified source profile and the estimated daily contribution.



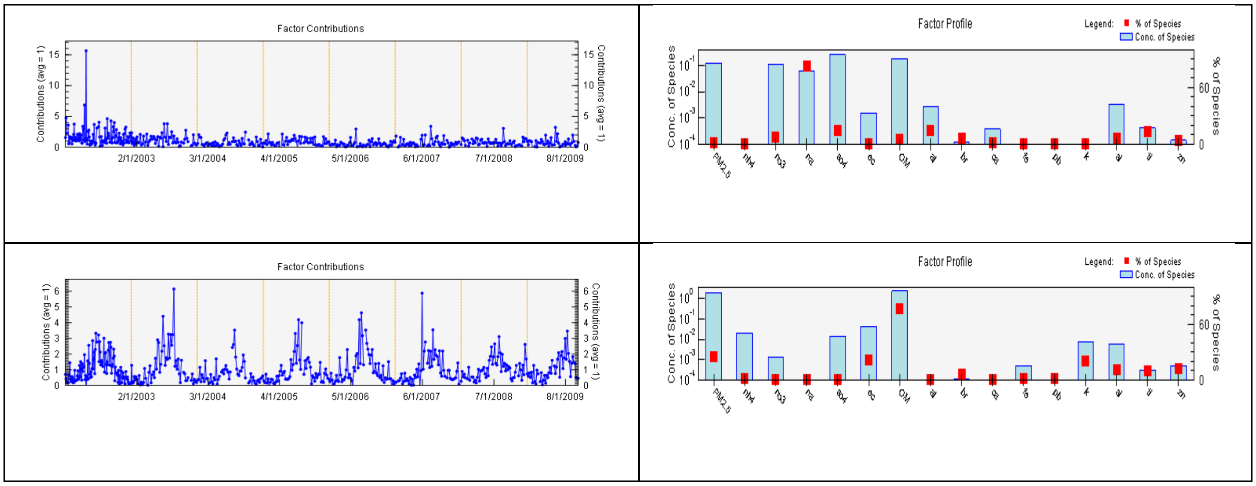
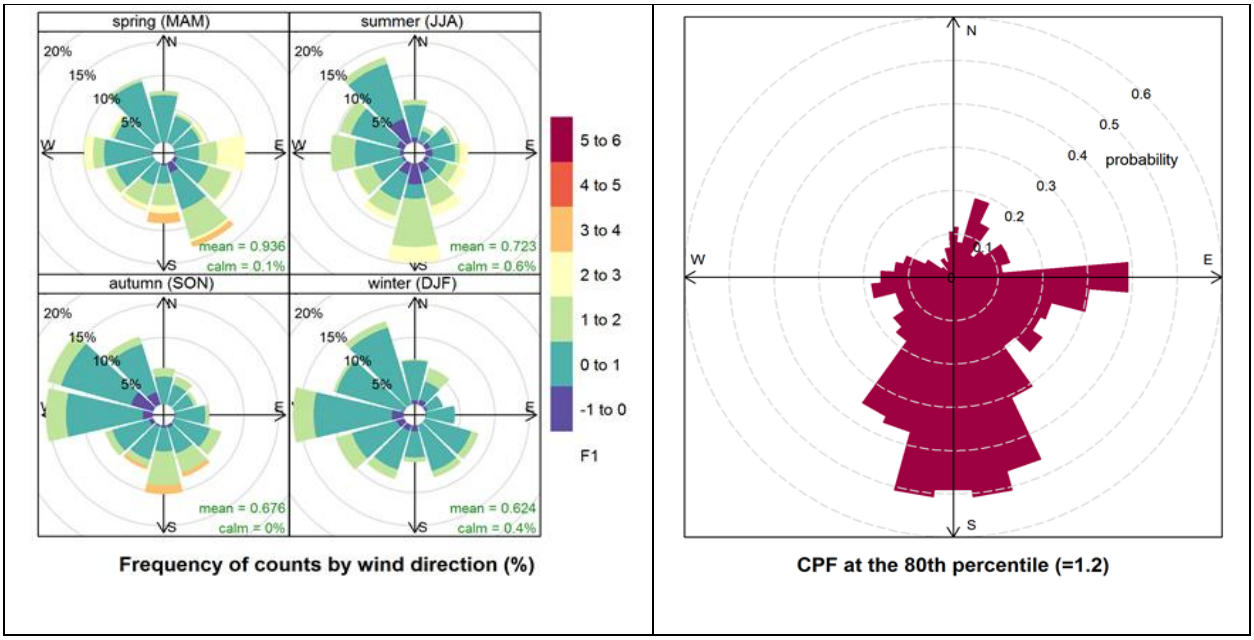


Figure 3.22. Total output of the PMF run for the Perkinstown Station

Right: The profile of the 7 potential emission sources for $PM_{2.5}$ observed at Perk Station.

Left: Mass contribution of the 7 potential emission sources to the $PM_{2.5}$ at Perk Station.



Frequency of counts by wind direction (%)

CPF at the 80th percentile (=1.2)

Figure 3.23. Factor 1_Perk - Soil

Factor 1 contains Si (48%), Na (47%), Ca (33%), Al (25%), SO_4^{2-} (23%) and Ti (14%). Winter is the lowest season. There were no significant seasonal variations for spring, summer and fall, but daily variations were wider. This factor represents soil emissions and the major emission sources are located to the south of the station.

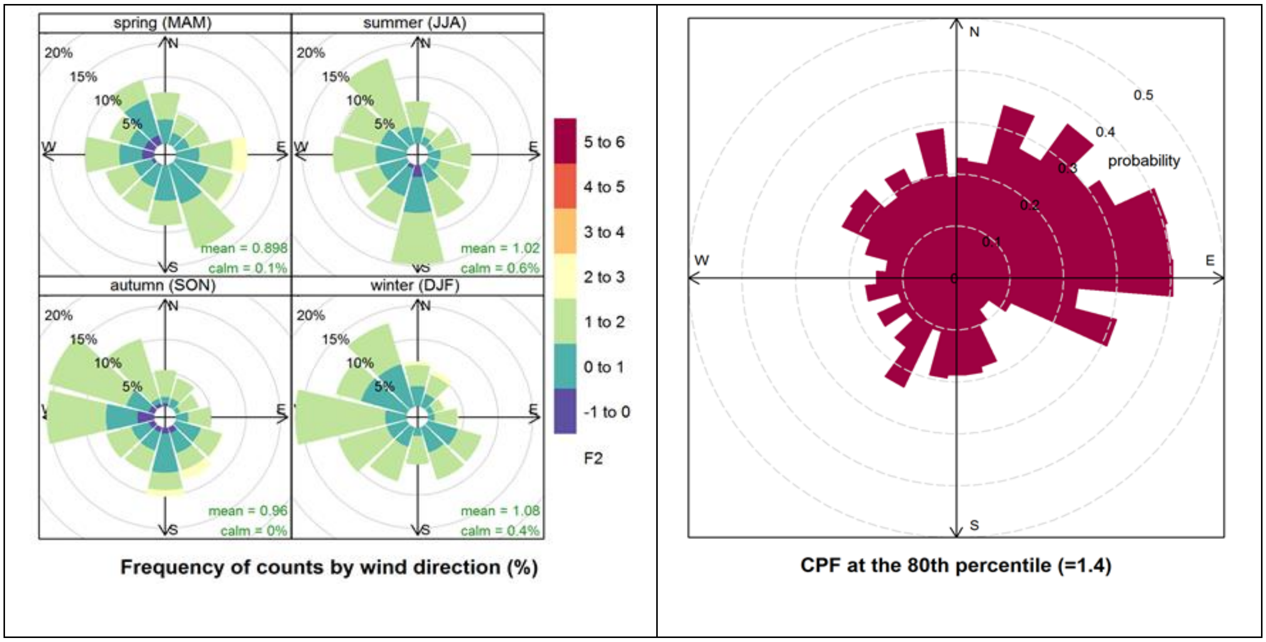


Figure 3.24. Factor 2_Perk – Lead Factor

Factor 2 contains higher Pb (87%), Br (42%), Na (36%), EC (30%), Al (37%), Ti (30%) and Zn (20%). Winter emission is slightly higher than that in other three seasons. The major emission sources are located at the northeast and northwest.

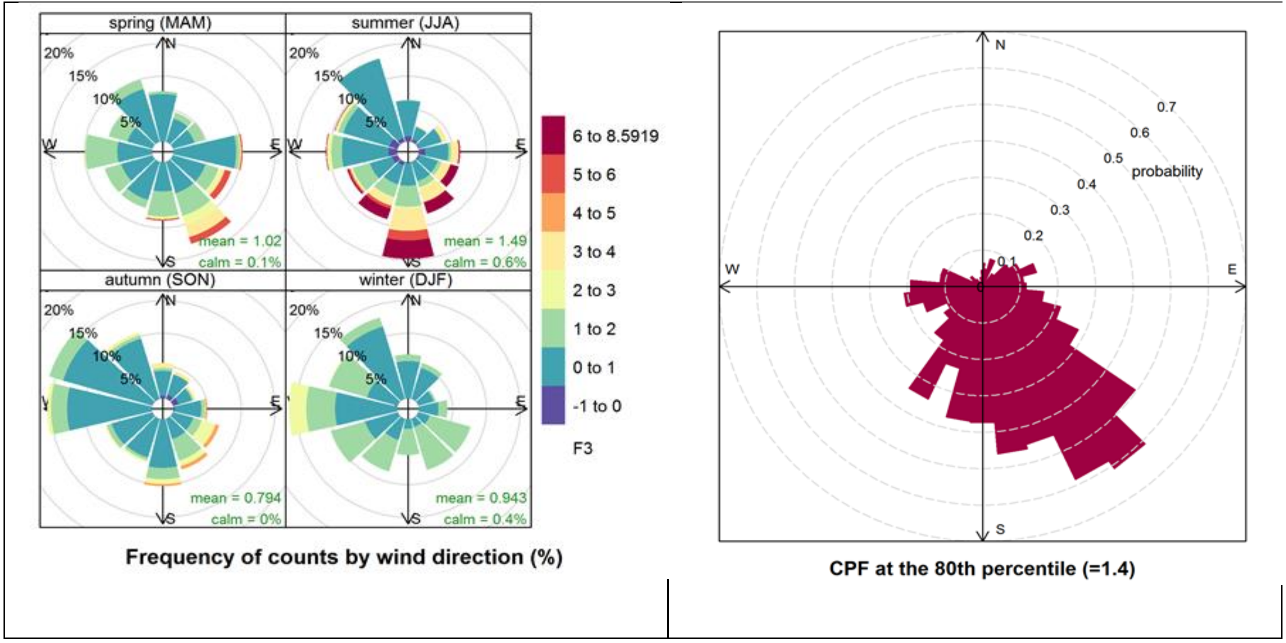


Figure 3.25. Factor 3_Perk – Secondary sulfate

Factor 3 contains higher sulfate (74%) and NH_4^+ (54%) and represents secondary sulfate. Summer emission is higher than that for other three seasons. Weekend emission is slightly higher than that for weekdays. Summer is higher, but no significant seasonal variation. CPF clearly indicated there is the highest probability of 60% the sulfate emission sources are located in the southeast direction of the station.

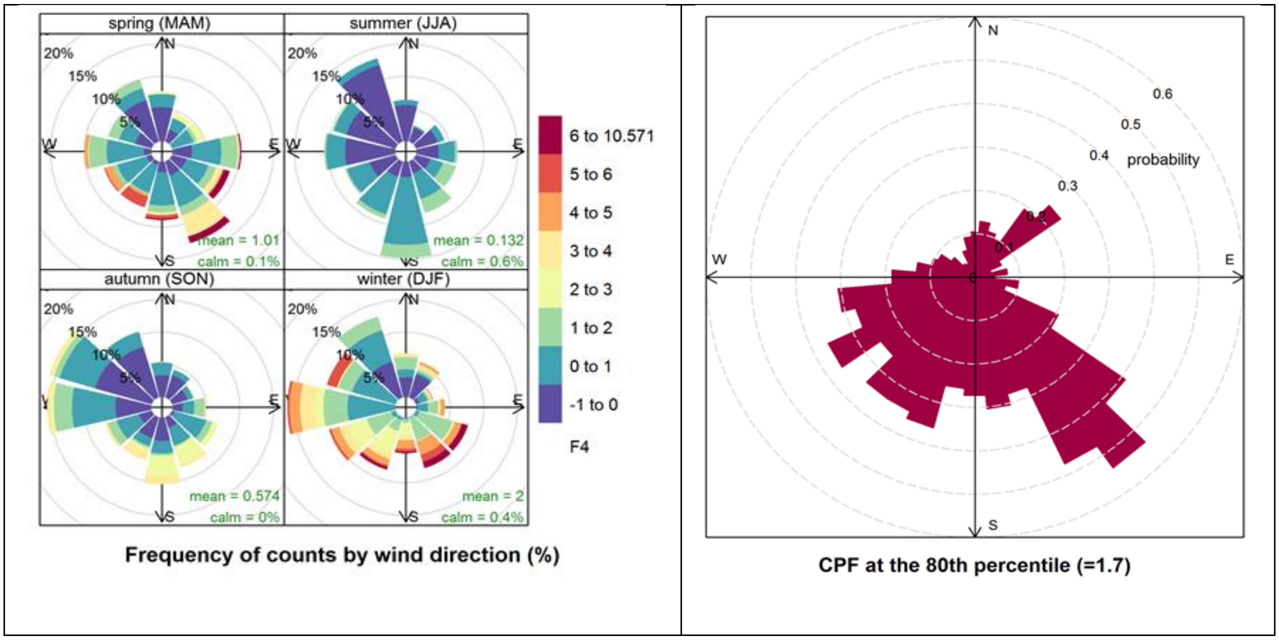
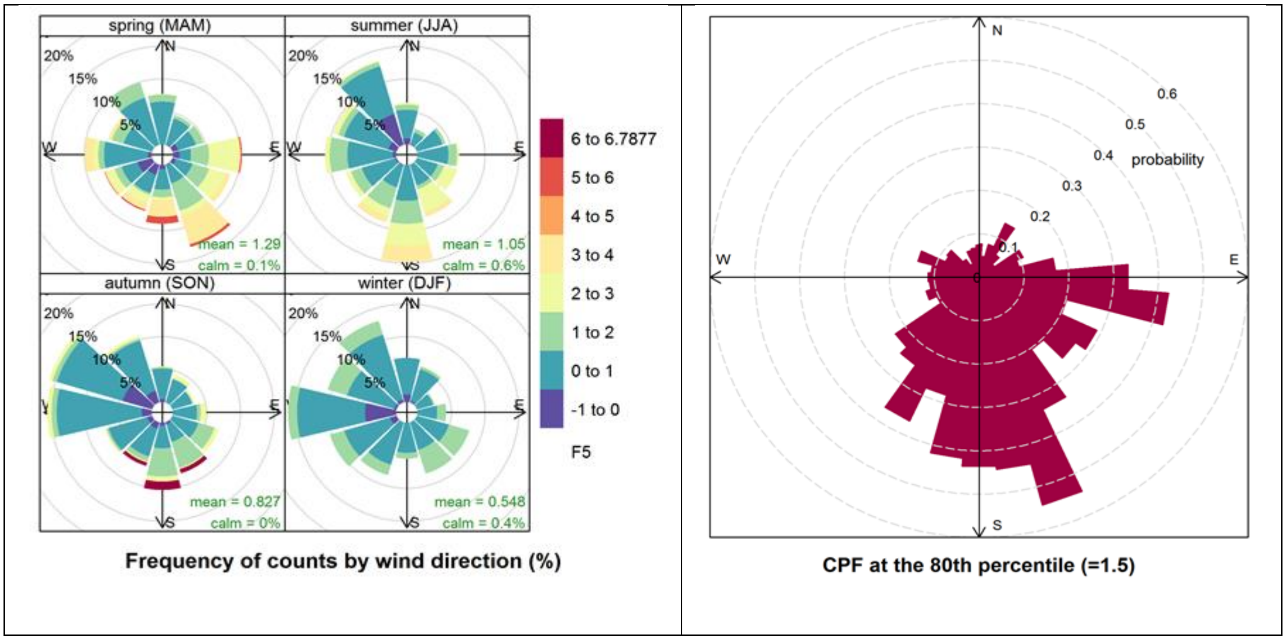


Figure 3.26. Factor 4_Perk – Secondary nitrate

Factor 4 contains higher nitrate (81%) and NH_4^+ (38%) and represents a secondary nitrate emission source. There are significant seasonal changes with the highest in winter and lowest emissions in summer. CPF indicated southeast of the station has the highest percentile of probability for the emission source location and southwest of the station is another probable direction for the emission source.



Frequency of counts by wind direction (%)

CPF at the 80th percentile (=1.5)

Figure 3.27. Factor 5_Perk – Iron mixed soil factor

Factor 5 has higher Fe (74%), Si (45%), Ca (38%), Al (37%) and Ti (29%). Winter has low emissions, while spring and summer has the higher emission. Weekend emission is slightly higher than that for weekdays. This factor represents soil factor with rich Fe and has more than 80 percentile of the probability located at the south of the station and east of the station. This factor is similar to Factor 1 and has a similar emission source location profile.

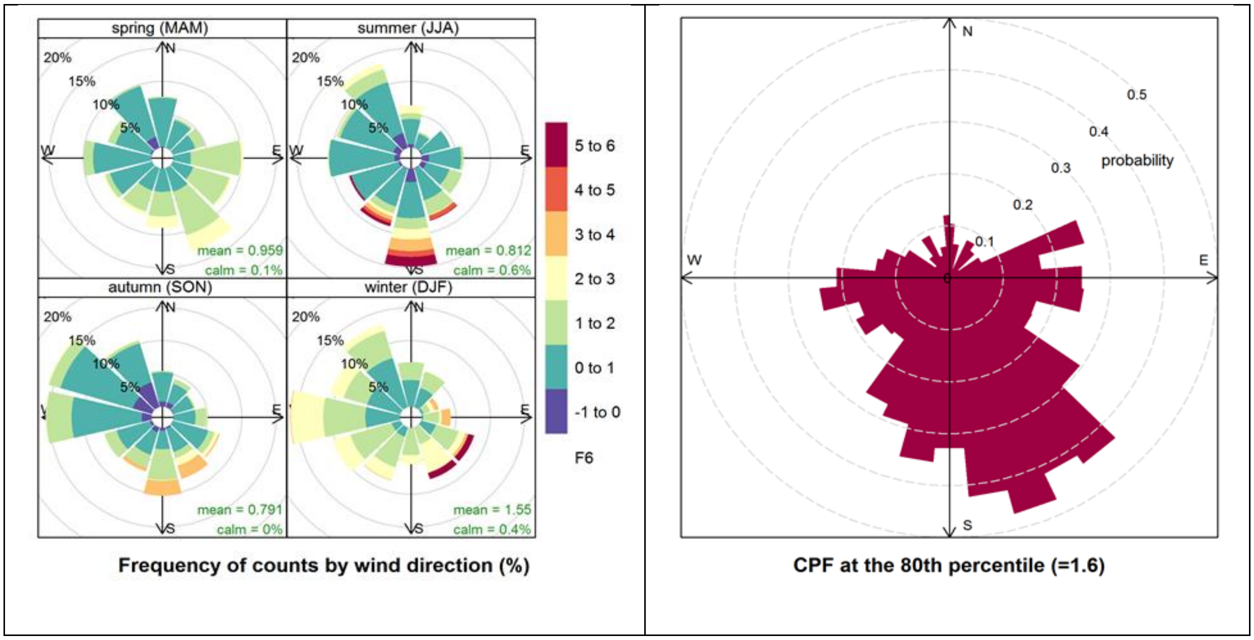


Figure 3.28. Factor 6_Perk – High K source

Factor 6 contains higher K (78%), Zn (26%), Ca (29%), EC (23%) and Br (19%). There were no significant seasonal changes, except the higher emission rage in summer. Weekday emissions were higher than that in weekend.

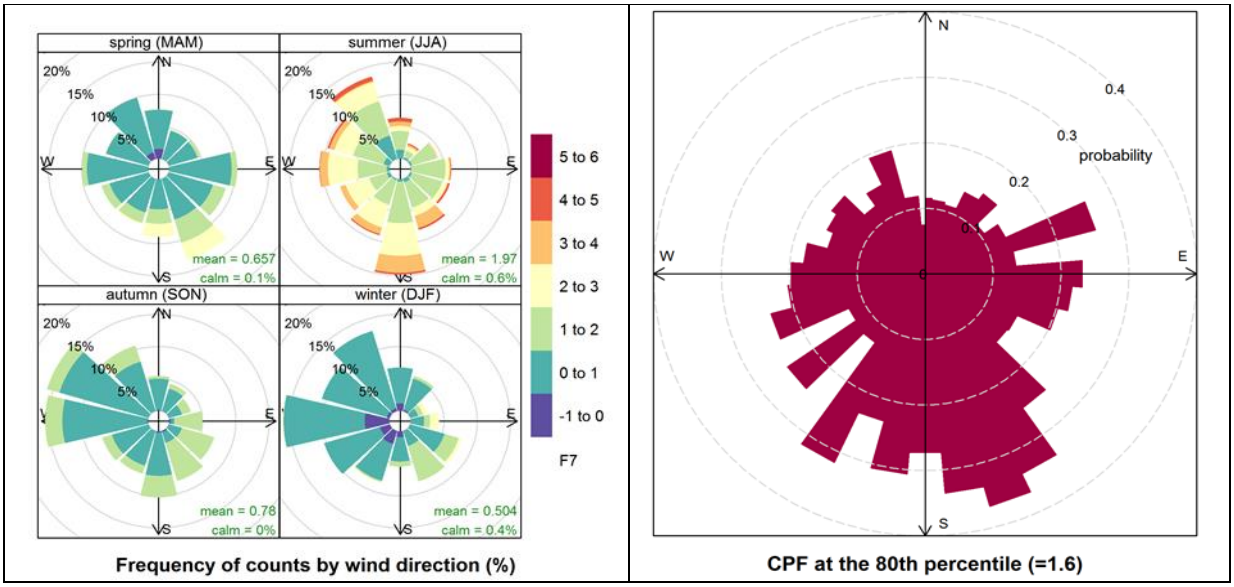


Figure 3.29. Factor 7_Perk – OC emission factor

Factor 7 contains higher OM (70%), EC (18%) and K (19%). This factor has very strong seasonal variation: summer is the highest, following fall and spring, winter is the lowest. There was no significant weekday and weekend difference. Since Perk is in the forest area, biogenic VOC emissions are the main sources for the observed OC. K represents the open burning.

3.4.5. **Summary**

The OM/EC ratio in the PMF estimated summer OC factor at each station clearly distinguished diesel emission from gasoline emission and other OC emissions. The diesel emissions contain a large amount of the elemental carbon fractions, represented ty lower OM/EC ratio. Table 3.1 lists the OM/EC, potassium (K) and Bromine (Br) concentration of the PMF estimated OC emissions factor.

Table 3.1. Composition of PMF-estimated OC emission factors

	OM	**EC**	**OM/EC**	**K**	**Br**
Milwaukee	71%	46%	1.54	44%	61%
Waukesha	74%	52%	1.42	47%	45%
Mayville	75%	22%	3.41	16%	13%
Perkinstown	70%	18%	3.89	19%	na

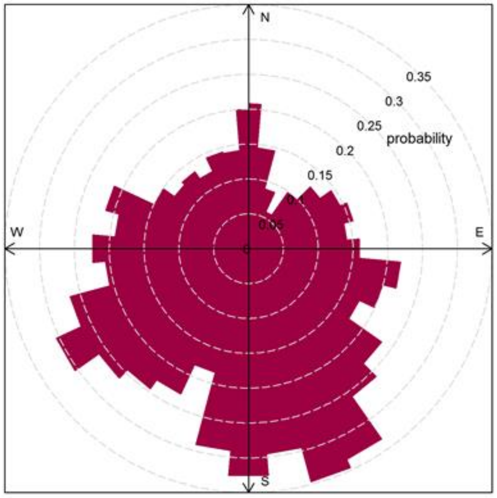
Milwaukee and Waukesha are sitting along busy highway I-94 and I-43. Due to the higher EC emission from diesel combustion, Milwaukee and Waukesha have the OM/EC ratio of 1.54 and 1.42, respectively, while Mayville and Perkinstown have ratios larger than 3.4.

In this summer OC emissions factor, there are another two distinguishing elements, potassium (K) and bromine (Br). Milwaukee and Waukesha have 40^{+}% of K and 45% to 61% of Br. K represents wood burning in winter and open burning in summer. K would be strongly influenced by firework too. Br mainly appeared in warm seasons. This Br content is very likely associated with the pesticides applications in summer to control insects. As contrast, the content of K and Br are lower in Mayville and Perkinstown.

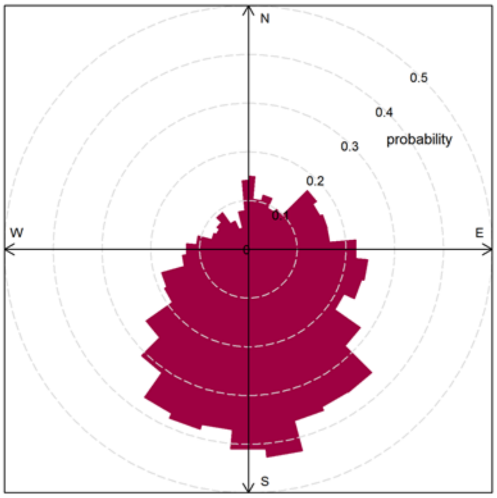
Soil source has very strong local characteristics, from the composition and the concentration of the major soil ingredients, like Ca, Si, Al, Ti, etc. There were soil sources which are "contaminated" by other metals, such as soil + quarry emissions, soil + traffic emissions.

The CPF plots of secondary nitrate and sulfate sources point to different pictures (see Figure 3.30). If the emission sources of nitrate are same as that for sulfate, mainly from fuel combustion, CPF plot for nitrate should be similar. The CPF plot for nitrates clearly indicated there are other emission source category for nitrate. Mayville station sits in an agriculture field. The circle shaped CPF plot indicated the station received constant emissions sources impact and from all directions. In addition to the non-fuel combustion related N source in that region, the nitrate formed from the N released from fertilizer application may have contributed to the uniform distribution of nitrates around the station (see Figure 3.29/Mayv).

The CPF indicated high probability emission source location for NO^{3-} (left) and SO_4^{2-} (right).

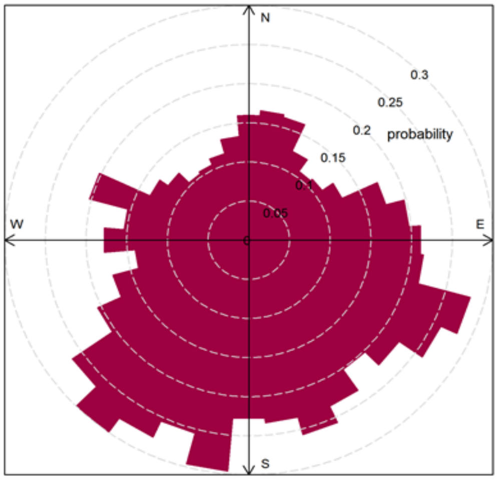


CPF at the 80th percentile (=1.8)

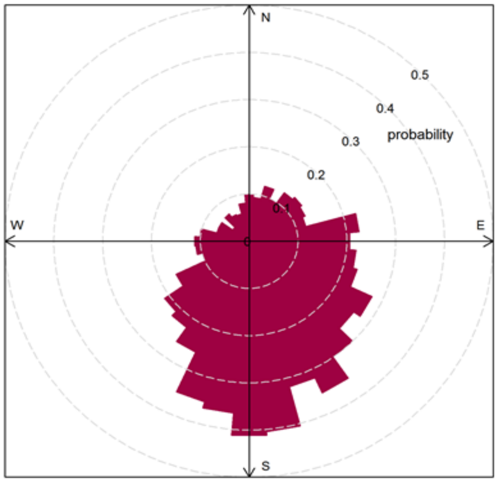


CPF at the 80th percentile (=1.5)

Milw



CPF at the 80th percentile (=1.8)



CPF at the 80th percentile (=1.4)

Mayv

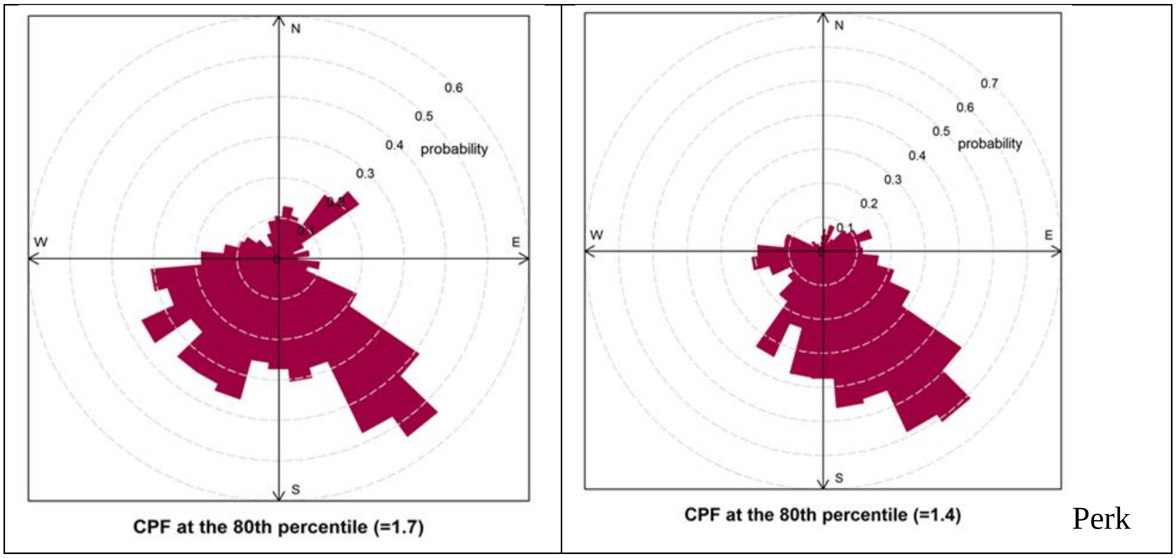


Figure 3.30. CPF plot for nitrate (left) and sulfate (right)

3.5. Conclusions and Recommendations

3.5.1. The Emission Sources at the Four Stations

Different number of emission factors and many sets of different uncertainty have been tried on the data from the four stations to improve the PMF modeling results. Meteorology parameters are employed to help interpret the PMF modeling results, such as emission factor wind roses and CPF analysis. The methods used in this study worked very well. For the pollutants that have long lifetime, incorporating meteorology parameter into the analysis might be the better way to improve the results.

Speciated $PM_{2.5}$ data from monitoring stations of Milwaukee, Waukesha, Mayville and Perkinstown were analyzed through PMF for potential emission sources that contributed to the ambient $PM_{2.5}$ on site. Milwaukee, Waukesha, Mayville and Perkinstown represent urban, industrial, agricultural and rural areas, respectively. PMF effectively resolved 6 to 8 sources of the $PM_{2.5}$ for each station area. The common emission sources identified by PMF at the four stations are:

1) Secondary nitrate sources (mobile and stationary sources; fossil fuel combustion emissions such as power plants and paper mills; foundries and non-fuel combustion related N emissions);
2) Secondary sulfate sources (mobile and stationary sources);
3) Soil sources;
4) Organic carbon (OC) sources.

PMF has its limits in separating the emission source categories for the secondary pollutants, especially when both the precursors and the secondary pollutants have long residence lifetimes and the regions to be compared are closely located.

3.5.2. **Recommendations for Future PMF Analysis**

Analyze the ambient air quality monitoring data used in the PMF analysis. These data contain very useful information. Develop the updated and localized source profile for the study, such as, particulate Fe/Mg ratio can provide signature of oil-derived combustion aerosol, the particulate V/Se ratio can provide signature of coal vs. oil derived aerosol on the regional scale and the particulate As/Se ratio can provide signature of western vs. eastern coal derived aerosols (Rubin, 1999).

Trace metals are good tracers of local industrial emissions (Moreno et al., 2006). Improving the quality of the collected trace metal data and incorporating the metals in urban areas that are influenced by local industrial activities can help separating local and regional emission impact.

$PM_{2.5}$ concentration is very sensitive to temperature, wind speed, absolute humidity, mixing height and precipitation (Dawson et al., 2007). Meteorological parameter based techniques, such as HYSPLIT can support improved source apportionment of $PM_{2.5}$.

3.6. Reference

Ashworth, D.J., Luo, L., Yates, S.R, 2013. Pesticide emissions from soil - fate and predictability. Outlooks on Pest management 24, 4-7.

Baumann, K., Jayanty, R.K.M., Flanagan, J.B., 2008. Fine particulate matter source apportionment for the Chemical Speciation Trends Network site at Birmingham, Alabama, using Positive Matrix Factorization. Journal of the Air & Waste Management Association 58, 27-44.

Brown, S.G., Frankel, A., Hafner, H.R., 2007. Source apportionment of VOCs in the Los Angeles area using positive matrix factorization. Atmospheric Environment 41, 227-237.

Buzcu-Guven, B., Brown, S.G., Frankel, A., Hafner, H.R., Roberts, P.T., 2007. Analysis and apportionment of organic carbon and fine particulate matter sources at multiple sites in the Midwestern United States. Journal of the Air & Waste Management Association 57, 606-619.

Dawson, J.P., Adams, P.J., Pandis, S.N., 2007. Sensitivity of ozone to summertime climate in the eastern USA: A modeling case study. Atmospheric Environment 41, 1494-1511.

Gary Norris, R.V., 2008. EPA Positive Matrix Factorization (PMF) 3.0 - Fundamentals & User Guide, p. 81.

Henry, R.C., Wang, Y.J., Gebhart, K.A., 1991. The relationship between Empirical Orthogonal Functions and sources of air pollution. Atmospheric Environment - Part A General Topics 25 A, 503-509.

Jaeckels, J.M., Bae, M.S., Schauer, J.J., 2007. Positive matrix factorization (PMF) analysis of molecular marker measurements to quantify the sources of organic aerosols. Environmental Science & Technology 41, 5763-5769.

Kim, E., Brown, S.G., Hafner, H.R., Hopke, P.K., 2005a. Characterization of non-methane volatile organic compounds sources in Houston during 2001 using positive matrix factorization. Atmospheric Environment 39, 5934-5946.

Kim, E., Hopke, P.K., Pinto, J.P., Wilson, W.E., 2005b. Spatial variability of fine particle mass, components, and source contributions during the regional air pollution study in St. Louis. Environmental Science & Technology 39, 4172-4179.

Kim, E., Hopke, P.K. and Qin, Youjun 2005. Estimation of Organic Carbon Black Value and Error Structure of the Speciation Trend Network Data for Source Apportionment. Journal of Air & Waste Management Association9 55, 1190-1119.

Laden, F., Neas, L.M., Dockery, D.W., Schwartz, J., 2000. Association of fine particulate matter from different sources with daily mortality in six US cities. Environmental Health Perspectives 108, 941-947.

Mar, T.F., Norris, G.A., Koenig, J.Q., Larson, T.V., 2000. Associations between air pollution and mortality in Phoenix, 1995-1997. Environmental Health Perspectives 108, 347-353.

Moreno, T., Querol, X., Alastuey, A., Viana, M., Salvador, P., de la Campa, A.S., Artinano, B., de la Rosa, J., Gibbons, W., 2006. Variations in atmospheric PM trace metal content in Spanish towns: Illustrating the chemical complexity of the inorganic urban aerosol cocktail. Atmospheric Environment 40, 6791-6803.

Paatero, P., 1997. A weighted non-negative least squares algorithm for three-way 'PARAFAC' factor analysis. Chemometrics and Intelligent Laboratory Systems 38, 223-242.

Paatero, P., 1999. The multilinear engine - A table-driven, least squares program for solving multilinear problems, including the n-way parallel factor analysis model. Journal of Computational and Graphical Statistics 8, 854-888.

Paatero, P., Tapper, U., 1993. ANALYSIS OF DIFFERENT MODES OF FACTOR-ANALYSIS AS LEAST-SQUARES FIT PROBLEMS. Chemometrics and Intelligent Laboratory Systems 18, 183-194.

Reff, A., Eberly, S.I., Bhave, P.V., 2007. Receptor modeling of ambient particulate matter data using positive matrix factorization: Review of existing methods. Journal of the Air & Waste

Management Association 57, 146-154.

Rubin, E.S., 1999. Toxic releases from power plants. Environmental Science & Technology 33, 3062-3067.

Russell, A.G., 2008. EPA supersites program-related emissions-based particulate matter modeling: Initial applications and advances. Journal of the Air and Waste Management Association 58, 289-302.

Schauer, J.J., Cass, G.R., 2000. Source apportionment of wintertime gas-phase and particle-phase air pollutants using organic compounds as tracers. Environmental Science & Technology 34, 1821-1832.

Tsai, F.C., Apte, M.G., Daisey, J.M., 2000. An exploratory analysis of the relationship between mortality and the chemical composition of airborne particulate matter. Inhalation Toxicology 12, 121-135.

Watson, J.G., Chen, L.W.A., Chow, J.C., Doraiswamy, P., Lowenthal, D.H., 2008. Source apportionment: Findings from the U.S. supersites program. Journal of the Air and Waste Management Association 58, 265-288.

CHAPTER 4. ATMOSPHERIC AEROSOL ACIDITY IN WISCONSIN

4.1. Introduction

Acidic aerosols are ubiquitous in the atmosphere, which have a significant implication for increasing the risk of human health, leading to severe degradation of ecosystem and increasing climate forcing changes (Jickells et al., 2005; Likens et al., 1996; Nenes et al., 2011; Speizer, 1989). The relative potency of toxics is likely related to the degree of acidic environment. Atmospheric acidic aerosols are more hygroscopic than their neutralized forms, and thus, more effective in reducing atmospheric visibility and disturbing radioactive balance (Khlystov et al., 2005; Zhang et al., 2007). Aerosol acidity is one of the most important parameters that influence atmospheric chemistry and physics. The acidity level of atmospheric aerosols is linked to secondary aerosol formation through its influence to the phases of the precursors, the heterogeneous reactions as well as the functions of the reactants and oxidants of photochemical reactions (Jang et al., 2002; Seinfeld, 2006; Ziemba et al., 2007).

Acidic aerosols are converted from SO_2 and NOx and exist in gaseous (HNO_3) and liquid or solid phase [H_2SO_4, $(NH_4)_2SO_4$, $(NH_4)HSO_4$, $(NH_4)_3H(SO_4)_2$, NH_4NO_3, etc.] (Schlesinger and Graham, 1992). The level of atmospheric aerosol acidity is dynamic, varying by the composition of the aerosols, the season, time of a day and meteorology. Elevated winter $PM_{2.5}$ and summer haze events have been frequently occurred at many regions in Wisconsin recently. From air quality data collected from 2002 to 2013 at Milw, Wauk, Mayv and Perk stations in Wisconsin, the winter's high $PM_{2.5}$ events were dominated by high nitrate and above-normal sulfate and OC, while the summertime high $PM_{2.5}$ events were accompanied by both high sulfate and OC. At one summer episode, the strong acid of one day PM2.5 was as high as 0.0998 μg/m3 (08/02/2005, Milw), even though the seasonal average was only 0.0137 μg/m3. Studies from the U.S. suggested that daily mortality were associated with aerosol acidity and the city-specific-chronic respiratory illnesses were correlated with the annual mean sulfate, rather than the concentration of $PM_{2.5}$ (Schlesinger and Graham, 1992).

Research issues for acid aerosols are quite challenging, as they are a complex mixture and constantly changing. The goals of this study are:

1) Investigate the characteristics of aerosol acidity distribution in the Great Lake region;
2) Discuss the major factors that determine the spatial and temporal aerosol acidity distribution;
3) Investigate the correlation of organic carbon growth and aerosol acidity in the region.

The methods that have been widely used to estimate atmospheric aerosol acidity are: (1) ion balance based strong acid (H_{AER}); (2) ion ratio based neutralization degree (NH_4mn) and 3). The thermodynamic modeling based in-situ aerosol acidity: $[H^+]_{In\text{-}Situ}$. The Aerosol acidity cannot be directly measured due to its low water content, one common method is measuring the inorganic ions in the water extracts of the aerosols collected on the filter. The problem of this method is the dilution of the sample can promote the dissociation of bisulfate ions and increase the hydrogen ion concentration (Saxena et al., 1993). In this study, the inorganic $PM_{2.5}$ components collected by Chemical Speciation Network (CSN) program at the stations of Milwaukee, Mayville, Waukesha and Perkinstown, Wisconsin from 2002 to 2009 are used to estimate the strong acid (H_{AER}) and neutralization degree (NH_4mn). The estimated H_{AER} are then used as input in EAIM II modeling to calculate the $[H^+]_{In\text{-}Situ}$. The seasonal deliquescent relative humidity (DRH) for the mixture of major inorganic ions are used as criteria for selecting data in further analyses. Only the estimated aerosol acidity at the days when RH is above the estimated seasonal DRH is used in the analysis of the aerosol acidity with the NH_4^+/SO_4^{2-} condition and the temperature also taking into consideration.

The hypotheses of this study are:

1) The in-situ aerosol acidity of $[H^+]_{In\text{-}situ}$, strong acidity of $[H^+]_{AER}$ and neutralization degree (NH_4mn) have spatial and temporal variations, which vary according to the spatial and temporal changes of concentration and composition of $PM_{2.5}$ and the local meteorological conditions;
2) There are correlations between aerosol acidity and ambient concentration of OC. The significance of the correlation varies depending on the change in meteorological conditions and the composition of $PM_{2.5}$ in the region.

Spatiotemporal variations of atmospheric aerosol acidity were observed in four regions with different patterns. The cause of the variations was complex and unique for each region. The levels of acidity are influenced by emission of SO_2 and NOx, available ambient ammonia, the degree of neutralization and local meteorology. The atmospheric aerosol is more acidic at industrial areas. In general, summer has more acidic days while winter has more days when atmospheric aerosols are fully neutralized. Significant and positive correlations between organic carbon (OC) and sulfate are observed at all regions.

Implication: This study has explored how to use speciated $PM_{2.5}$ data to estimate aerosol acidity in a region. The knowledge about the concentration and the spatial and temporal variation of the atmospheric acidity in different regions provides insights on the causes of the elevated air pollution events and on how to establish a better air quality management plan. The above knowledge also provides information on the true toxicity and duration that a human being may be exposed to, which helps human health study to achieve a more comprehensive interpretation of health risk assessment.

4.2. Literature Review

4.2.1. The Formation of Atmospheric Acidic Aerosol

Acidic aerosols are formed from oxidation of acidic gases, mainly SO_2 and NOx. These acidic gases, emitted from either natural or anthropogenic sources, are rapidly oxidized into more acidic forms, H_2SO_4 (sulfuric acid) and HNO_3 (nitric acid) in the air (Chang, 1987; Seinfeld, 2006; Tanner et al., 1981; US EPA). H_2SO_4 and HNO_3 are formed predominately from the reaction of OH with SO_2 and NO_2 via the homogeneous gas-phase reaction under sunlight, respectively. HNO_3 can also be formed via heterogeneous chemical reactions (John H. Seinfeld, 2006; Pathak et al., 2004). When ammonia (NH_3) and basic cations such as Ca^{2+}, Mg^{2+} exist, H_2SO_4 and HNO_3 will be fully or partially neutralize to form sulfates [eg., $(NH_4)_2SO_4$ and $(NH_4)HSO_4$], nitrate (NH_4NO_3) and other secondary aerosols. Under acidic conditions, hydrolysis of dinitrogen-pentaoxide (N_2O_5) can happen on surface of preexisting sulfate and form nitrate (Pathak et al., 2009). Aerosols become acidic when the acidic sulfates and nitrates become dominant components of the ambient aerosols (Putaud et al., 2010; Ziemba et al., 2007).

The release of NH_3 from agricultural activities and its conversion to NH_4^+ are controlled by thermodynamics and kinetic equilibrium, which are in turn controlled by atmospheric pH and temperature. Under acidic conditions, more NH_3 will be released and converted to NH_4^+ format.

4.2.2. **Factors Affecting Aerosol Acidity**

Aerosol acidity varies with the changes in atmospheric aerosol composition and meteorological conditions. In a humid atmosphere, the inorganic ions can exist in different phases either as solid crystals or as aqueous droplets, or present as gases, like the nitric acid and ammonia (Seinfeld, 2006). The partitioning of these compounds between the solid, aqueous, and vapor phases is a complex function of temperature, relative humidity, and the degree of atmospheric aerosol acidity. NH4NO3 dissociation constant depends on the temperature and RH. (Stelson and Seinfeld, 1982a) found that the greatest NH_4NO_3 losses occurred at the RH < 60%, while RH = 100%, no NH_4NO_3 loss. At a condensed phase, the heterogeneous reactions are pH dependent (Hewitt, 2009). The gas-aerosol partitioning of HNO_3/NO_3^- and NH_3/NH_4^+ is also pH dependent (Van Oss et al., 1998; Nemitz et al., 2004).

4.2.3. **Aerosol Acidity and Formation of $PM_{2.5}$ and OC**

Laboratory chamber tests have shown that the formation of SOA was significantly enhanced when acidic aerosols were present. Filed sampling also found the positive correlations between the aerosol acidity and the mass of measured ambient organic carbon (OC) (Chu, 2004).

The conventional theory about SOA formation is, in the atmosphere the gas-phase oxidation of these precursors leads to multifunctional, higher polarity but low-volatility products (eg, aldehydes) that can continue partitioning themselves between the gas and aerosol phase (Gao et al., 2004). Jang et al. evaluated the particle growth by the heterogeneous reaction of different VOC precursors (like aldehydes) in chamber tests under darkness in the presence of acid catalysts with different composition and observed that the produced organic particle was increased by factors of 4 to 6 compared with neutral aerosol systems and the product organic particles were more stable as particles aged (Jang et al., 2003; Jang et al., 2002; Jang and Kamens, 2001). Chu (2004) found a clear link between the elevated concentration of organic aerosols (OC) and elevated concentration of sulfate in many regions during the summer episode in the Eastern US, when he studied urban speciated $PM_{2.5}$ data from 2000 to 2002. Chu (2004) suggested that the sulfate catalyzed heterogeneous reactions might have played a role in enhancing the SOA production.

4.2.4. **Application of Aerosol Acidity in Air Quality Management**

Different indicators, such as, in-situ acidity, strong acidity, neutralization index, etc., have been used to describe the aerosol acidity in related studies. Among all the indicators only the in-situ aerosol acidity, which provides the deliquescent acidic characteristics of the atmospheric aerosols, can best reflect the acidities that influence the chemical behavior of atmospheric aerosols (Pathak et al., 2009). The in-situ aerosol acidity more relevant in controlling the activities of the oxidants in the atmosphere. However, due to the low water content of the deliquesced atmospheric aerosols, the in-situ aerosol acidity cannot be directly measured and in most cases, the in-situ aerosol acidity is estimated by thermodynamic models. The strong acidity and neutralization index are calculated using the measurable inorganic cations (NH_4^+,

Ca^{2+}, Mg^{2+}, etc.) and the inorganic anions (SO_4^{2-} , NO_3^-, Cl^-, etc.) obtained from different techniques.

Based on the difference in required data input, the thermodynamic models used for estimating in-situ aerosol acidity can be categorized into two groups (Yao et al., 2006). The second group of thermodynamic models are represented by SCAPE2, ISORROPIA and EQUISOLV-II, are full thermodynamic gas–aerosol equilibrium models. In these models, $[H^+]$ was estimated from gas–particle partitioning, both gas and aerosol compositions are required as inputs. These models estimate the equilibrium concentration of all species as well as in-situ aerosol acidity in the gas and particulate phases under the minima Gibbs free energy for a multicomponent system. The first group of thermodynamic models is represented by Extended AIM Aerosol Thermodynamic Model (EAIM) (Clegg et al., 1998). This model only requires inputs of $[H^+]$, $[NH_4^+]$, $[NO_3^-]$ and $[SO_4^{2}]$. The $[H^+]$ value can be either calculated, or measured. The inputs required by first group model were easier to obtain. One of the models of the first group frequently used to calculate the in-situ atmospheric acidity is Extended AIM Aerosol Thermodynamic Model (EAIM) (http://www.aim.env.uea.ac.uk/aim/aim.php). EAIM is a state-of-the-art aerosol thermodynamic model developed by Simon Clegg and Anthony Wexler to predict the water content of atmospheric aerosols, phase state (solid, liquid, or gas) and partitioning of the inorganic components of aerosol systems containing inorganic and organic component and water (Clegg et al., 1998). Model EAIM-II is an equilibrium thermodynamic model of a H^+-NH_4^+-SO_4^{2-}-NO_3--H_2O system. EAIM-II carries out calculations ranging from water, ion, and organic solute activities in aqueous solutions and liquid mixture, to aerosol/vapor partitioning calculation, and the formation of solids. These calculations can be done for one or more individual cases and/or for a range of values of a selected parameter such as temperature or relative humidity (RH). The system contains species in liquid phase (H^+, NH_4^+, HSO_4^-, SO_4^{2-}, NO_3^- and NH_3); gases (water vapor, HNO_3, NH_3 and H_2SO_4) and solids. The chemical system modelled by EAIM-II consists of a gas phase, inorganic and organic solids, and up to two liquid phases.

He's group and Pathak's group studied aerosol acidity distribution in different regions and different period in China (He et al., 2012; Pathak et al., 2004; Pathak et al., 2009). He et al. (2012) analyzed data collected from January 2005 to March 2006 in Chongqing and Beijing, China; Pathak et al. (2009) studied the data collected from four mega cities in China at different periods - Beijing (June 29 to August 2, 2005), Shanghai (May 5 to June 15, 2005), Lanzhou (June 18 to July17, 2006) and Guangzhou (May 15 to May 27, 2004); and in 2004 from seven monitoring stations in Hong Kong (HK) (Pathak et al., 2004).

4.3. Methodology

4.3.1. **Sampling Location and Source of Data**

The speciated $PM_{2.5}$ (SO_4^{2-} , NO_3^-, NH_4^+, OC, EC and trace metals) collected by Chemical Speciation Network (CSN) at monitoring stations at Milwaukee, Mayville, Waukesha and Perkinstown are used in this study. See Chapter 2 for details of sampling location and the surrounding areas. The $PM_{2.5}$ mass, speciated $PM_{2.5}$ (SO_4^{2-}, NO_3^-, NH_4^+, OC, EC and trace metals) and other available gaseous data at the four selected stations were downloaded from AQS website (http://www.epa.gov/ttn/airs/airsaqs/). In brief, the $PM_{2.5}$ samples were collected on a set of three different filters over a 24-hour sampling period at an interval of every third day at Milwaukee and Mayville stations and every sixth day at Waukesha and Perkinstown. A Teflon filter was used to collect $PM_{2.5}$ for measuring the total mass by gravimetry, elements by X-ray fluorescence (XRF), and in some cases, anions and cations by ion chromatography (IP). A nylon filter was used to collect $PM_{2.5}$ for measuring the anions and cations by ion chromatography (IP), and a quartz filter was used to collect $PM_{2.5}$ measuring the organic, elemental, carbonate, and total carbon. In addition to above-mentioned inorganic ions, CSN also collects ions of Na^+ and K^+ (only at Milwaukee station), and mass of selected metals, like, Ca, Al, K, etc. See Chapter 2 for details about the sampling and analysis procedures for those inorganic $PM_{2.5}$ components used in obtain aerosol acidity in this study.

Meteorological data for the four station sites were obtained from Midwest Regional Climate Center (MRCC).

Meteorology data for Milwaukee station is obtained from Milwaukee Mitchell Airport Station (WBAN: 14839; NWS Coop: 475479; WMO: 72640; ICAO ID: KMKE; GHCN ID: USW00014839; NWSLI: MKE). This station started collecting the meteorology data since 1927.

Meteorology data for Mayville Station is obtained from Horicon Station (NWS Coop: 473756; GHCN ID: USC00473756; NWSLI: HORW3). This station started collecting meteorology data since 1970.

Meteorology data for Perkinstown Station is obtained from Medford Station (NWS Coop: 475255; GHCN ID: USC00475255; NWSLI: MEDW3). This station started collecting meteorology data since 1889 (or, 1893).

Meteorology data for Waukesha Station is obtained from Oconomowoc Station (NWS Coop: 476200; GHCN ID: USC00476200; NWSLI: OCOW3). This station started collecting meteorology data since 1893.

4.3.2. **Indicators of Aerosol Acidity**

The followings three aerosol acidity indexes are used in this study:

4.3.2.1. **Ratio Based Aerosol Acidity**

The $[NH_4^+]_{meas}/[NH_4^+]_{neu}$ ($[NH_4^+]_{M/N}$) ratio is used to identify the "fully neutralized particle period" and "partially neutralized (or acidic) particle period" at each region in this study. This index is a normalized ratio of measured $[NH_4^+]$ to the $[NH_4^+]$ needed for full neutralization of the anion ($[SO_4^{2-}]$x2+$[NO_3^-]$) (see Eq. 1) (Zhang et al., 2007). The square brackets indicate the molar concentration of the species inside, in unit of nmol/m^3. In this index, the inorganic ions of SO_4^{2-}, NO_3^- and NH_4^+ are obtained from measurements. The assumption applied to this indicator is that the cations of $[Ca^{2+}]$, $[Mg^{2+}]$ and $[K^+]$ are negligible due to their small concentrations in the air compare with the concentration of $[NH_4^+]$. The $[Cl^-]$ is negligible for the same reason that its concentration is very low compare with the sum of concentration of $[SO_4^{2-}]$ and $[NO_3^-]$ in the air.

$$\frac{[NH_4^+]_{measured}}{[NH_4^+]_{neutralized}} = \frac{[NH_4^+]}{2[SO_4^{2-}] + [NO_3^-]}$$

4.3.2.2. **Ionic Mass Balance Based Aerosol Acidity**

The $[H^+]_{Aerosol}$ index is the molar concentration of H^+ in $PM_{2.5}$ in unit of nmol/m^3. The $[H^+]_{Aerosol}$ is calculated based on ion balance:

$[H^+]_{Aerosol} + [NH4^+] + [Ca^{2+}] = [SO_4^{2-}]\times 2 + [NO_3^-] + [Cl^-]$.

Since $[Ca^{2+}]$ and $[Cl^-]$ are negligible, above equation becomes:

$$[H^+]_{Aerosol} = 2[SO_4^{2-}] + [NO_3^-] - [NH_4^+]$$

The $[H^+]_{Aerosol}$ at the ammonia-rich condition ($[H^+]_{AR}$, when $[NH_4^+]/[NO_3^-]\geq 1.5$), and at the ammonia-poor condition ($[H^+]_{AP}$, when $[NH_4^+]/[NO_3^-]<1.5$) can be written as (Koutrakis et al., 1992; Pathak et al., 2004; Saxena et al., 1993):

i. $[H^+]_{AP} = [H^+]_{Strong} = 2 \text{ x } [SO_4^{2-}] - [NH4^+]$
ii. $[H^+]_{AR} = [H^+]_{Strong} = 2 \text{ x } [SO_4^{2-}] + [SO_4^{2-}] \times ([NH4^+]/[SO_4^{2-}] – 1.5) - [NH4^+]$

4.3.2.3. **In Situ Aerosol Acidity**

Model EAIM-II provides the calculations in a NH_4^+, SO_4^{2-} and NO_3^- system, which is the system on which this study is based. In addition, Model EAIM-II only requires the input of inorganic ions of the aerosols and ambient temperature and RH.

4.3.3. **Method Development**

4.3.3.1. **EAIM-II Model**

EAIM-II model is an equilibrium thermodynamic model that works in an H^+-NH_4^+-SO_4^{2-} -NO_3^--H2O system and only requires the input of aqueous inorganic ions of the aerosols and the ambient temperature and relative humidity**.** This model determines the equilibrium composition of the system by specifying an initial ionic composition, a fixed relative humidity (RH) or total amount of water, and temperature. EAIM-II model is selected to estimate the in-situ atmospheric aerosol acidity in the study region for its simplified input requirements and ability to provide what we needed in the study.

4.3.3.2. **Development of Criteria for Data Selection**

EAIM-II modeling requires input of concentration of aqueous phase inorganic ions, such as [H^+], [NH_4^+], [NO_3^-] and [SO_4^{2-}], etc. Due to the low water content of the deliquescent aerosols, the aqueous phase concentrations of inorganic ions are very difficult to measure. Several different sampling and analyzing procedures have been used by researchers to obtain the aqueous phase concentrations of inorganic ions required by the thermodynamic models. The most common method is 1). Water extracts the inorganic ions from the collected $PM_{2.5}$ filter; 2). Measuring the concentrations of [NH_4^+], [NO_3^-] and [SO_4^{2-}] of the water extracts from the $PM_{2.5}$ filter using the same analytical method as used in CSN program for these inorganic ions; 3). Using the results as the inputs in EAIM-II modeling (Chu, 2004; He et al., 2012; Pathak et al., 2004; Pathak et al., 2009). Studies found the dilution of the samples during water extraction can promote the dissociation of bisulfate ions (NH_4HSO_4) resulting in increased hydrogen ion concentration. The ion concentration of the water extracted represents the total extractable acidity, but not the acidity of the aerosol (Saxena et al., 1993).

In this study, with deliquescent relative humidity (DRH) for inorganic ions is used as the criteria to determine which data are "the aqueous phase inorganic ion concentration", the inorganic ions of $PM_{2.5}$ collected by CSN program are used as input in EAIM-II modeling. The rationale for this method is that all compounds of alkali metals, all NH_4^+ and NO_3^- salts are water soluble. All sulfates, except for sulfate of Ca^{2+}, Sr^{2+}, Ba^{2+} and Hg^{2+} and Pb^{2+}, are water soluble. Mg and Na are mainly from sea-water and in the percentages about 2% (Newberg et al., 2005). $NaNO_3$

and $NaNO_3$ are usually in coarse modes and therefore are not the components of $PM_{2.5}$. In the Great Lakes Regions, the concentrations of Ca^+, Mg^{2+}, Na^+ and K^+ are usually very low, so the concentrations of their sulfates can be negligible. As a result, the inorganic ions of $PM_{2.5}$ will be in liquid phase when the atmospheric relative humidity is above their deliquescence relative humidity.

At very low relative humidity (RH), inorganic salt contained in atmospheric aerosol particle is solid until the RH reaches the DRH of the salt, then a phase transition occurs. At DRH, the solid inorganic salts spontaneously absorb water from air and produce a saturated aqueous solution. The highly hygroscopic aerosols do not exhibit the deliquescent behavior. For example, water content changes smoothly in H_2SO_4 (Seinfeld, 2006). DRH is a function of temperature, especially the dew point temperature (Ephrath et al., 1996). Table 4.1 shows the DRHs of single $(NH_4)_2SO_4$, NH_4NO_3 and $NaNO_3$ at 0°C, 15°C, 25°C and 30°C, as well as the DRHs of other electrolyte solution at 25°C only (Seinfeld, 2006; Tang and Munkelwitz, 1993).

From Table 4.1, when at 25°C (298.15K), the DRH values for the most common inorganic ions, $(NH_4)_2SO_4$, $(NH_4)_3H(SO_4)_2$, $(NH_4)H(SO_4)$ and NH_4NO_3 are 79.9±0.5%, 69.0%, 40.0% and 61.8%, respectively. $(NH_4)_2SO_4$ and $(NH_4)_3H(SO_4)_2$ have higher DRH compared with NH_4NO_3 at the same temperature. For $(NH_4)_2SO_4$, DRH at the 0°C (273.15°K), 15°C (288.15°K), 25°C (298.15K) and 30°C (303.15K) are 81.8%, 80.6%, 79.9 + 0.5% and 79.5%, respectively. For NH_4NO_3, $(NH_4)_2SO_4$ and $(NH_4)_3H(SO_4)_2$ the DRH are lower when the temperature is higher (John H. Seinfeld, 2006; Tang and Munkelwitz, 1993) .

Table 4.1 The DRHs of $(NH_4)_2SO_4$, NH_4NO_3 and $NaNO_3$ etc. at different Temperatures

Salt	0°C (273.15°K)	15°C (288.15°K)	25°C (298.15°K)	30°C (303.15°K)
$(NH_4)_2SO_4$	81.8	80.6	79.9 + 0.5	79.5
NH_4NO_3	76.6	68.1	61.8	58.5
$NaNO_3$	80.9	76.9	74.3 ± 0.4	73.0
$(NH_4)_3H(SO_4)_2$			69.0	
$NaHSO_4$			52.0	
NH_4HSO_4			40.0	
Na_2SO_4			84.2 ± 0.4	

In a multi-component atmosphere, when the ambient RH is below the DRH of the multi-component atmospheric aerosol mixtures, the mixtures are solid. When the RH increases and reaches the deliquescence point of the mixture, the aerosols start to absorb atmospheric moisture and become a saturated solution. The DRH of the multicomponent atmospheric aerosol particles depends on the temperature, atmospheric RH and the composition of the atmospheric aerosol system (Seinfeld, 2006). Table 4.2 shows the DRH of the mixtures of common salts at 303 °K. The DRH of a mixture is lower than the lowest DRH of its ingredients. For example, the DRH for the mixture of $(NH_4)_2SO_4$ and NH_4NO_3 is 52.3%, at 30°C (303.15 °K).

Table 4.2 Deliquescent RH (DRH*) at Mutual solubility Point at 30°C

Compound 1	Compound 2	DRH*	DRH_1	DRH_2
NH_4NO_3	NaCl	42.2	59.4	75.2
NH_4NO_3	$NaNO_3$	46.3	59.4	72.4
NH_4NO_3	NH_4Cl	51.4	59.4	77.2
$NaNO_3$	NH_4Cl	51.9	72.4	77.2
NH_4NO_3	$(NH_4)_2SO_4$	52.3	59.4	79.2
$NaNO_3$	NaCl	67.6	72.4	75.2
NaCl	NH_4Cl	68.8	75.2	77.2
NH_4Cl	$(NH_4)_2SO_4$	71.3	77.2	79.2

Note: DRH* is for the mixture of compound 1 and compound 2,

Sources: Wexler and Seinfeld (1991) (John H. Seinfeld, 2006)

Since the temperature dependence of a DRH can be expressed as (Seinfeld, 2006):

$$\ln\frac{\mathrm{DRH}(T)}{\mathrm{DRH}(T_0)} = \frac{\Delta H_s}{R}\left[A\left(\frac{1}{T}-\frac{1}{T_0}\right) - B\ln\frac{T}{T_0} - C(T-T_0)\right]$$

The DRH for each region is determined by the temperature distribution at the station region. A representative temperature at each station is calculated based on the probability density function (pdf) of the daily temperature at each station for the designated period. The pdf at each station was obtained through the available daily temperature records at each of the four regions. Table 4.3 lists the calculated temperature (pdf temperature) for the whole period when the data is available at each station region and the maximum, minimum and mean provided by Midwestern Region Climate Center (MRCC).

Table 4.3. The historical and the calculated representative annual temperature:

Temp	Milw	Wauk	Mayv	Perk
Max (°F)_MRCC	55.6	56.5	55.7	52.5
Min (°F) _MRCC	40.1	37.1	35.8	31.6
Mean (°F) _MRCC	47.9	46.8	45.8	42.1
pdf (°F) Temp (°C) Temp (°K)	54.2 12.33 285.44	50.4 10.22 283.33	52.3 11.28 284.39	49.6 9.78 282.89

The pdf temperatures at the four stations are: 12.33 °C for Milwaukee, 10.22°C for Waukesha, 11.28°C for Mayville and 9.78°C for Perkinstown, respectively. They fall between 0°C and 15°C. At the 0°C, the DRH for $(NH_4)_2SO_4$, NH_4NO_3 and $(NH_4)_3H(SO_4)_2$ are 80.6%, 68.1% and 76.9%, respectively. Since the DRH of multi-component atmospheric aerosol would be lower than the DRH for single salt, it is assumed that the major inorganic ions would be in an aqueous phase if only selecting the data collected at the days when the RH is higher than 80%.

The DRH is not only influenced by temperature, but also by the composition and the pressure of the system of interest. The composition of the system constantly changes with the changes in meteorological conditions. The RH collected at each station is used as a surrogate of the results of the combined influences.

A representative RH at each station is calculated based on the probability density function (pdf) of the daily RH at each station for the designated period. The pdf at each station was obtained from the available daily RH records at each of the four station regions. Table 4.4 listed the calculated pdf RH at the four regions.

Table 4.4. Seasonal RH at the different regions

	Winter	Spring	Summer	Fall
Milw	80.10	70.92	76.84	76.90
Mayv	74.03	66.70	70.82	72.24
Wauk	80.10	70.92	76.84	76.90
Perk	78.61	62.95	74.70	77.07
Average	78.21	67.87	74.80	75.78

Since

1) the DRHs for the NH4NO3 are 76.6%, 68.1%, 61.8 and 58.5%, at the temperatures of 0, 15, 25 and 30°C, respectively;

2) from Table 4.1, the DRHs for NH_4NO_3 are the lowest compared with those for $(NH_4)_2SO_4$ and $(NH_4)_3H(SO_4)_2$; and

3) the DRH for the mixture of $(NH_4)_2SO_4$ and NH_4NO_3 at 30°C (303.15K) is 52.3%, which is lower than the lowest DRH of the individual ingredients in the mixture (in this case, it is the DRH of 59.4% for NH_4NO_3) at that temperature (see Table 4.2), the seasonal DRHs can be selected referencing the DRHs for NH_4NO_3 at different temperature.

Assume the representative temperature for winter, (spring and fall), and summer are 0, 15, (25 and 30)°C, representatively. Thus, the seasonal DRHs are: 75% for winter (0°C), 65% for spring and fall (15°C) and 60% for summer (25 and 30°C), respectively.

4.3.3.3. **Calculations of $[H^+]_{In\text{-}Situ}$, $[H^+]_{AER}$ and NH_4mn**

The aerosol acidities (NH4mn, $[H^+]_{In\text{-}situ}$ and $[H^+]_{AER}$) calculated with the data from the days when RH was above the seasonal DRH are used in further analyses. Following is the summary of the procedures involved in calculating $[H^+]_{In\text{-}situ}$, $[H^+]_{AER}$ and NH4mn:

1) $[H^+]_{In\text{-}situ}$ calculation

a. Prepare input for EAIM modeling

i. $[H^+]_{AER} = [SO_4^{2-}]\times2 + [NO_3^-]-[NH_4^+]$.

- The $[H^+]_{AER}$ is used as the input of atmospheric acidity. The days associated with $[H^+]_{AER} < 0$ are removed;

ii. Collecting 24-hour average ambient temperature (K); Pressure (atmosphere); Volume; relative humidity (RH), standard air pressure

b. Output from EAIM modeling (only listed the ones that will be used in this study)

i. $[H^+]_{In\text{-}situ}$

- The days associated with $[H^+]_{In\text{-}situ} = 0$ are removed

ii. $\mathrm{pH} = -\log(f[H^+]_{In-situ} \times x[H^+]_{In-situ})$

where, $[H^+]_{\text{In-situ}}$, $f[H^+]_{\text{In-situ}}$, and $x[H^+]_{\text{In-situ}}$ are the modeling output. $f[H^+]_{\text{In-Situ}}$ is the activity coefficient on mole fraction basis and $x[H^+]_{\text{In-Situ}}$ is mole fraction of aqueous particle phase H^+.

2) Calculation of $[H^+]_{\text{AER}}$ and NH4mn

- a. $[NH4^+]/[SO_4^{2-}] < 1.5$ is defined as ammonium poor (AP) period and $[NH4^+]/[SO_4^{2-}] \geq 1.5$ is defined as ammonium rich (AR) period in this study. Based on the value of $[NH4^+]/[SO_4^{2-}]$, the calculation of strong acid $[H^+]_{\text{AER}}$ are split into two group:
  - a) $NH_4^+/SO_4^{2-} \geq 1.5$ (AR)

    $[H^+]_{\text{AER}}$ and NH4mn when RH ≥ seasonal DRH;
  - b) $NH_4^+/SO_4^{2-} < 1.5$ (AP)

    $[H^+]_{\text{AER}}$ and NH4mn when RH ≥ seasonal DRH;
- b. Degree of Neutralization
  - a) The $NH4_{mn}$ range = $NH4_{mn\_AP} \sim NH4_{mn\_AR}$
  - b) The "more acidic" aerosol = The $NH4_{mn} < (NH4_{mn\_AP} - \sigma)$;
  - c) The "partially neutralized" aerosol = The $NH4_{mn} > (NH4_{mn\_AR} + \sigma)$
  - d) The "The fully neutralized period" = $NH4_{mn} = (1 \pm \sigma)$

where σ is the standard deviation of NH_{4mn}, calculated for each station at different season, under AP or AR conditions.

4.4. Results and Discussion

4.4.1. Spatiotemporal Variations of Atmospheric Aerosol Acidities

The seasonal DRHs for each season are: 70% for winter, 65 % for spring and fall and 60% for summer. The data from days with the RH below the seasonal DRH are not included in the discussion.

Descriptive statistical analysis was done for in-situ aerosol acidity ($H^+]_{In\text{-}Situ}$), strong acidity ($[H^+]_{AER}$), neutralization degree (NH4mn), mass and stoichiometric ratios of inorganic $PM_{2.5}$ components (see Table 4.6). Only the data used in EAIM modeling are included in this analysis. Data of Several higher $PM_{2.5}$ days were removed from the dataset due to the calculated $[H^+]_{AER}$ ($[SO_4^{2-}]\times2 + [NO_3^-] - [NH4^+]$) is negative. Tables 4.5 summarize the acidity study data for Milwaukee Station. See Appendix B for the tables of statistical analysis results and summary of the acidity study data for other three stations.

Table 4.5. A Summary of Acidity Parameters_Milwaukee

Parameters	Winter	Spring	Summer	Fall	Whole year
SO_4^{2-}(mol m^{-3})	0.0244±0.0125	0.0206±0.0143	0.0222±0.0307	0.0223±0.0275	0.0223±0.025
NO_3^- (mol m^{-3})	0.0709±0.0523	0.0316±0.0371	0.0105±0.0141	0.0235±0.0347	0.0207±0.0383
NH_4^+(mol m^{-3})	0.1158±0.0712	0.0659±0.059	0.0449±0.0662	0.0698±0.0747	0.0665±0.0694
Sum of anions (μg m^{-3})	0.1247±0.0701	0.0742±0.0601	0.0569±0.071	0.0802±0.0764	0.0781±0.0715
$PM_{2.5}$(μg m^{-3})	14.6±7.1407	9.3±5.8515	10.1±6.9313	10.5±7.5829	10.25±7.0015
$(NH_4^+)_{mea}/(NH_4^+)_{neu}$	0.9067±0.1004	0.8693±0.1137	0.8182±0.1452	0.8634±0.1157	0.853±0.1301
$(NO_3^-)/(SO_4^{2-})$	1.4096±0.7999	0.7039±0.5064	0.25±0.1865	0.546±0.5667	0.4503±0.6251
$(NH_4^+)/(SO_4^{2-})$	2.2171±0.8398	1.4737±0.5305	0.982±0.2473	1.3284±0.5889	1.2009±0.6572
$[H^+]_{AR,}$ (mol m^{-3})	0.0122±0.0062	0.0103±0.0071	0.0111±0.0153	0.0111±0.0137	0.0111±0.0125
$[H^+]_{AER,}$ (mol m^{-3})	0.0076±0.0063	0.0079±0.007	0.009±0.0093	0.0084±0.0061	0.0083±0.0077
$[H^+]_{in\text{-}situ}$, (mol m^{-3})	0.0021±0.0034	0.0015±0.0034	0.0015±0.003	0.0015±0.002	0.0015±0.0029
Aerosol H_2O (mol m^{-3})	0.6742±1.3962	0.388±1.1323	0.1706±0.4571	0.2705±0.7389	0.2939±0.9191

pH	2.8009±0.5199	2.6272±0.5808	2.7187±0.4884	2.7568±0.4491	2.7312±0.5052

Note: $(NH_4^+)_{mea}/(NH_4^+)_{neu}$, $(NO_3^-)/(SO_4^{2-})$ and $(NH_4^+)/(SO_4^{2-})$ are molar ratio

Table 4.6. A Summary of Acidity Parameters_Milwaukee

	Winter	Spring	Summer	Fall	Whole year
1). $[H^+]_{In\text{-}Situ,}$ (mol m^{-3})					
Mean	0.0021±0.0034	0.0015±0.0034	0.0015±0.003	0.0015±0.002	0.0015±0.0029
median	0.0032	0.0029	0.0024	0.0021	0.0026
90th	0.0066	0.0070	0.0046	0.0043	0.0057
75th	0.0042	0.0039	0.0028	0.0028	0.0032
25th	0.0010	0.0008	0.0007	0.0008	0.0008
10th	0.0006	0.0003	0.0004	0.0006	0.0004
2). $[H^+]_{AER,}$ (mol m^{-3})					
Mean	0.0076±0.0063	0.0079±0.007	0.009±0.0093	0.0084±0.0061	0.0083±0.0077
median	0.0093	0.0101	0.0122	0.0098	0.0107
90th	0.0169	0.0209	0.0219	0.0175	0.0201
75th	0.0124	0.0128	0.0159	0.0114	0.0139
25th	0.0054	0.0053	0.0058	0.0060	0.0057
10th	0.0024	0.0024	0.0043	0.0041	0.0036
3). $[H^+]_{AR,}$ (mol m^{-3})					
Mean	0.0122±0.0062	0.0103±0.0071	0.0111±0.0153	0.0111±0.0137	0.0111±0.0125
median	0.0128	0.0117	0.0163	0.0156	0.0146
90th	0.0183	0.0218	0.0344	0.0347	0.0314
75th	0.0163	0.0148	0.0216	0.0207	0.0181
25th	0.0089	0.0065	0.0064	0.0057	0.0063
10th	0.0054	0.0045	0.0030	0.0048	0.0041
4). NH_4^+ meas / NH_4^+ neu					
Mean	0.9067±0.1004	0.8693±0.1137	0.8182±0.1452	0.8634±0.1157	0.853±0.1301
median	0.8899	0.8400	0.7818	0.8422	0.8263
90th	0.9874	0.9711	0.9339	0.9625	0.9657
75th	0.9682	0.9266	0.8774	0.9388	0.9243
25th	0.8379	0.7706	0.7154	0.7689	0.7585
10th	0.7769	0.6704	0.5759	0.6769	0.6466
5). NH_4^+/SO_4^{2-}					
Mean	2.21±0.8398	1.47±0.5305	0.982±0.2473	1.32±0.5889	1.2±0.6572
median	2.2246	1.5482	1.0049	1.4613	1.4211
90th	3.1526	2.2964	1.2992	2.1839	2.3108
75th	2.7805	1.8428	1.1328	1.8063	1.7109

25th	1.5334	1.1474	0.8676	1.0497	0.9686
10th	1.2274	0.9207	0.7162	0.8995	0.8398

The following discussion is based on the data from Milwaukee Station only. Table 4.7 shows that the seasonal means of sulfate, nitrate and ammonium used in EAIM modeling is close to the seasonal means of those inorganic components in the whole data sets. Comparing the means of H_{AR}, H_{AER} and $H_{IN\text{-}SITU}$, H_{AR} (0.0163 mol/m^3) has the highest value among the three parameters used for estimate the atmospheric aerosol acidity. Next is H_{AER} (0.0122 mol/m^3), $H_{IN\text{-}SITU}$ (0.0032 mol/m^3) has the smallest value. H_{AR} and H_{AER} are higher in summer and lower in other seasons. $H_{IN\text{-}SITU}$ is higher in winter and lower in spring (see Table 4.5). From Table 4.6, the 90^{th} percentile of summer H_{AR} is 0.0344 (mol/m^3), of H_{AER} is 0.0219 (mol/m^3), and of $H_{IN\text{-}SITU}$ is 0.0046 (mol/m^3).

Table 4.7. The Seasonal Means of Inorganic ions in Aerosol Acidity $PM_{2.5}$ Data _ Milw

	Whole PM2.5 data set			Aerosol Acidity PM2.5 data set		
Component	SO4	NO3	NH4	SO4	NO3	NH4
Winter	0.0243	0.0795	0.1224	0.0257	0.0764	0.1185
Spring	0.0247	0.0434	0.0856	0.0235	0.0411	0.0780
Summer	0.0339	0.0160	0.0720	0.0327	0.0157	0.0689
Fall	0.0300	0.0370	0.0887	0.0311	0.0373	0.0897

The ammonium level (NH_4^+/SO_4^{2-}) is in the order of winter > (spring and fall) > summer. The neutralization degree and $[H^+]_{In\text{-}Situ}$ have positive relationships with the ratio of NH_4^+/SO_4^{2}. The higher the ratio of NH_4^+/SO_4^{2-}, the higher the neutralization degree and $[H^+]_{In\text{-}Situ}$. However, $[H^+]_{AER}$ has a negative correlation with the ratio of NH_4^+/SO_4^{2-}, when the ratio of NH_4^+/SO_4^{2-} is higher, the $[H^+]_{AER}$ is lower.

4.4.1.1. **Spatiotemporal Variations of Aerosol Acidities at AP or AR Condition**

Tables 4.8 to 4.10 list seasonal $[H^+]_{In\text{-}Situ}$, $[H^+]_{AER}$ and NH4mn at the four stations under ammonium-poor (AP) and ammonium-rich conditions (AR) respectively. Only the data that has higher than minimum seasonal DRH is used in the calculation. Figures 4.1 to 4.3 show the plots for $[H^+]_{In\text{-}Situ}$, $[H^+]_{AER}$ and NH4mn under AR conditions.

Table 4.8 Seasonal $[H^+]_{In\text{-}Situ}$ at the four stations

	NH4/SO4 < 1.5				**NH4/SO4 > 1.5**			
	Winter	Spring	Summer	Fall	Winter	Spring	Summer	Fall
Milw	0.0035	0.0020	0.0028	0.0025	0.0032	0.0035	0.0018	0.0020
Wauk	0.0075	0.0053	0.0044	0.0046	0.0046	0.0057	0.0031	0.0045
Mayv	0.0045	0.0023	0.0019	0.0028	0.0037	0.0021	0.0013	0.0023
Perk	0.0047	0.0029	0.0031	0.0027	0.0044	0.0029	0.0021	0.0023

Table 4.9 Seasonal $[H^+]_{AER}$ at the four stations

	NH4/SO4 < 1.5				**NH4/SO4 > 1.5**			
	Winter	Spring	Summer	Fall	Winter	Spring	Summer	Fall
Milw	0.0097	0.0088	0.0132	0.0108	0.0093	0.0110	0.0107	0.0094
Wauk	0.0133	0.0140	0.0144	0.0125	0.0109	0.0128	0.0098	0.0142
Mayv	0.0113	0.0099	0.0095	0.0103	0.0106	0.0083	0.0073	0.0087
Perk	0.0103	0.0081	0.0096	0.0076	0.0096	0.0108	0.0084	0.0076

Table 4.10 Seasonal NH_4mn at the four stations

	NH4/SO4 < 1.5				**NH4/SO4 > 1.5**			
	Winter	Spring	Summer	Fall	Winter	Spring	Summer	Fall
Milw	0.7385	0.7935	0.7318	0.7698	0.9160	0.8636	0.8711	0.8852
Wauk	0.6642	0.6518	0.6942	0.7017	0.8811	0.8270	0.8283	0.8422
Mayv	0.7529	0.8411	0.7851	0.7884	0.8947	0.8867	0.8866	0.8757
Perk	0.6573	0.6452	0.5854	0.6004	0.8508	0.8325	0.8968	0.8908

From Tables 4.8 & 4.9 and Figures 4.1 & 4.2, the $[H^+]_{In\text{-}Situ}$ and $[H^+]_{AER}$ values under AP conditions are more acidic than those under AR conditions. The value of $[H^+]_{AER}$ is higher than that of $[H^+]_{In\text{-}Situ}$. Under AP conditions, winter $[H^+]_{In\text{-}Situ}$ is highest among all seasons. Under AR conditions, the highest is at winter (Mayv and Perk) and spring (Milw and Mayv). For $[H^+]_{AER}$, under AP conditions, the summer $[H^+]_{AER}$ at Milw and Wauk is the highest. Another interesting phenomenon is that $[H^+]_{AER}$ from Waukesha is the highest at all season compare with $[H^+]_{AER}$ from other stations, under both AP and AR conditions. Waukesha is an industrial town. Local emissions of SO_4^{2-}, or NO_3^- might be the contributor of the higher $[H^+]_{AER}$.

From Table 4.10 and Figure 4.3, the neutralization degree of NH_4mn under AR conditions is higher than that under AP conditions. NH4mn under AR conditions also has higher spatial and temporal variations than those under AP conditions. For Mayv data, there is no big seasonal difference in NH_4mn under both conditions. Under AR conditions, Milw, Wauk and Mayv have the highest NH_4mn in winter, while Perk has the highest NH4mn in summer. The degree of neutralization in winter at Milw and Wauk is much higher than those in other seasons. Perk has the higher values of NH4mn in summer and fall.

Under AP conditions, NH_4mn is controlled by the available NH_4^+ in the air. While under AR conditions, the NH_4^+ reacts with SO_4^{2-} first, then the excess NH_4^+ reacts with NO_3^-. NH4mn controlled by not only NH_4^+, but also the available SO_4^{2-} and NO_3^-.

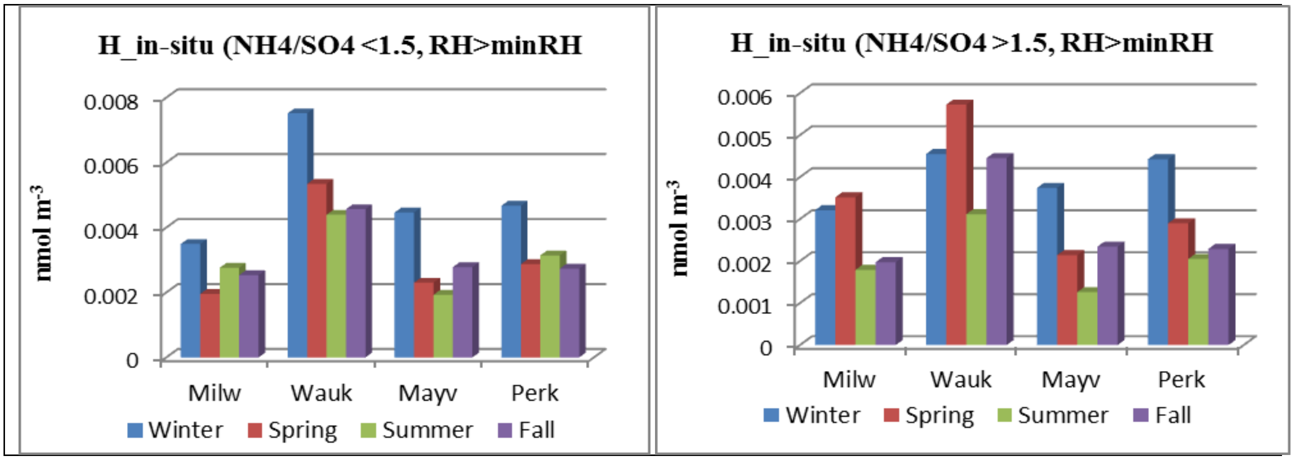


Figure 4.1 The seasonal H_in-situ at the four stations

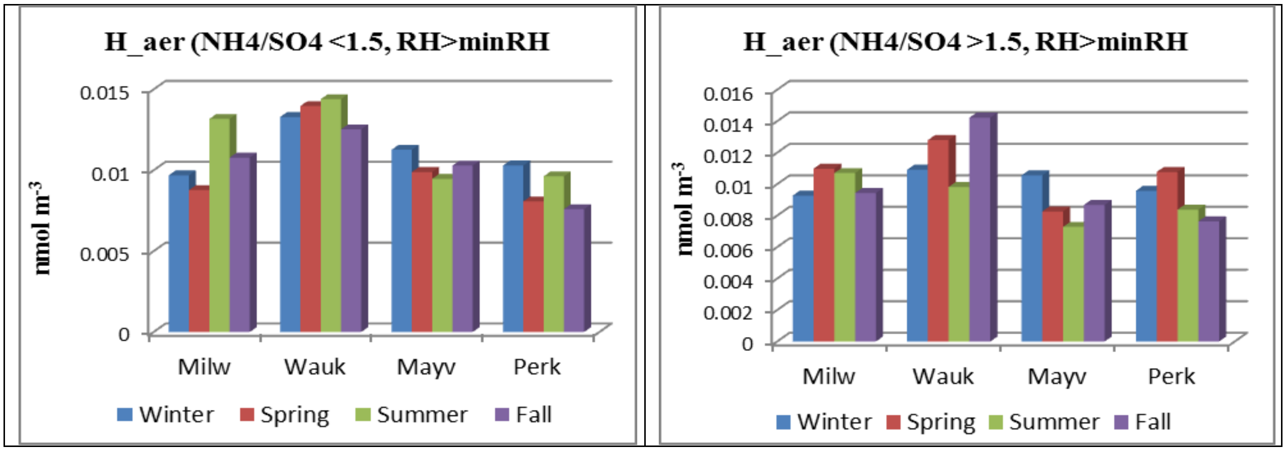


Figure 4.2 The seasonal Strong Acid H_aer at the four stations

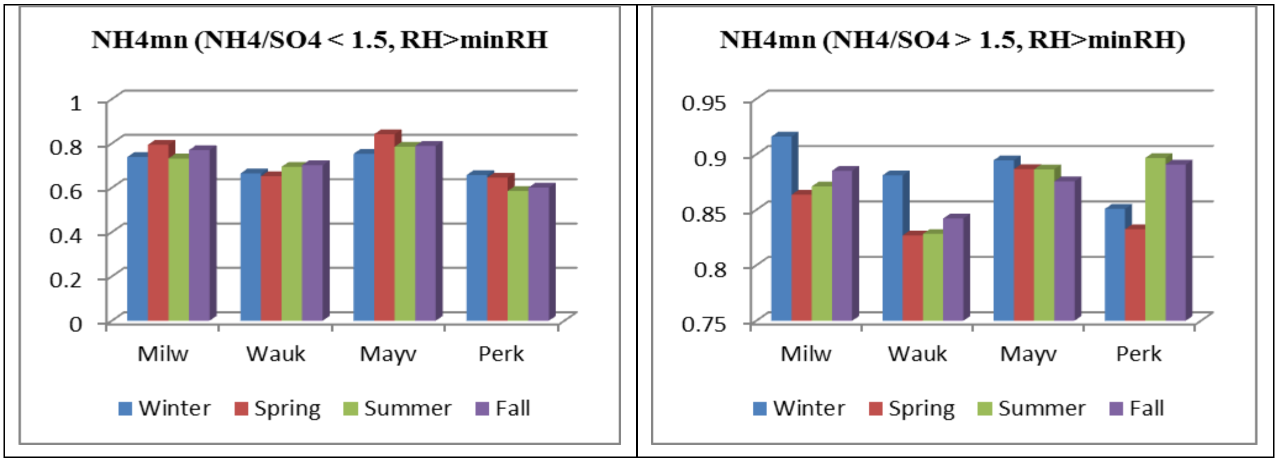


Figure 4.3. The seasonal neutralization ratio (NH4m/n) at the four stations

Summary:

Spatiotemporal variations of atmospheric aerosol acidity were observed at each station. The cause of the variations were complex and unique for each station. The H_{AER} value was found to be higher under AP conditions and higher in urban and industrial areas. NH_4mn has higher temporal variations under AR condition, compared with the NH_4mn under AP conditions. Under AR conditions, the winter NH_4mn at Milw and Mayv, the urban and industrial region, are the highest compared with the other three seasons. Based on the neutralization degree, under AP conditions, summer has more days under more acidic conditions at all regions.

4.4.1.2. **Spatiotemporal Variation of Neutralization Degree**

The acidic aerosols are defined as the ones whose NH_4mn is less than (NH4mn (AP) – σ). Table 4.11 lists the thresholds for "acidic aerosol" and the number of days when the NH4mn below the thresholds.

Table 4.11. The neutralization degree at more acidic conditions

Acidic condition (NH4/SO4 < 1.5)					**More acidic days at each season**				
	Winter	Spring	Summer	Fall	Winter	Spring	Summer	Fall	Total
Milw	0.6154	0.6899	0.5893	0.6490	10	38	111 (53.6%)	48	207
Mayv	0.5618	0.5526	0.5625	0.5816	14	25	71 (45.5%)	46	156
Wauk	0.6149	0.687	0.6414	0.6061	5	9	31 (51.6%)	15	60
Perk	0.5702	0.5118	0.3325	0.4089	9	12	50 (45.0%)	40	111

Table 4.11 listed the standard deviation (σ) for seasonal NH4mn at AP and AR conditions, respectively.

Table 4.12. The σ of NH4mn for each station at four seasons

	NH4/SO4 < 1.5				NH4/SO4 > 1.5			
	Winter	Spring	Summer	Fall	Winter	Spring	Summer	Fall
Milw	0.1231	0.1036	0.1425	0.1208	0.0743	0.0679	0.0667	0.0754
Mayv	0.1024	0.0992	0.1317	0.1201	0.0738	0.0662	0.0650	0.0751
Wauk	0.1380	0.1541	0.1437	0.1823	0.0850	0.0826	0.0535	0.0795
Perk	0.0871	0.1334	0.2529	0.1915	0.0802	0.0851	0.0803	0.0472

On Table 4.11, the data inside the parenthesis is the percentage of the more acidic days over the days with $NH_4/SO_4 < 1.5$ at each station. It can be seen from Table 4.11 that more than 45% days are acidic and summer has more days below the acidic thresholds. The urban and industrial regions (Milw and Wauk) have higher percentage of more acidic days compared with those in agricultural and rural areas.

Table 4.13 listed the minimum NH_4mn at four stations where the full neutralization occurs and the percentages of "neutralized" aerosols. The percentage of fully neutralized was calculated based on the data with RH ≥ 80% only (the days with NH4mn ≥ Minimum fully neutralization degree divided by the days with RH ≥ 80%). Due to the incomplete meteorological data and the different sampling interval, the percentage of neutralized for Wauk and Perk stations are not calculated.

Table 4.13. Minimum fully neutralization degree and the percentage of fully neutralized

Season	**Milwaukee**		**Mayville**		**Waukesha**		**Perkingstown**	
	NH4mn	Neutralized	NH4mn	Neutralized	NH4mn	Neutralized	NH4mn	Neutralized
Winter	0.8995	63.4%	0.8873	63.9%	0.8662	NA	0.8384	NA
Spring	0.8863	47.9%	0.9020	50.0%	0.8177	NA	0.7617	NA
Summer	0.8547	29.2%	0.8704	51.0%	0.8117	NA	0.7229	NA
Fall	0.8842	51.4%	0.8874	44.6%	0.7633	NA	0.7243	NA

From Table 4.13, one can see that the minimum fully neutralization degree (NH4mn) at Mayville station is higher than those in Milwaukee station. The $PM_{2.5}$ is more acidic in summer, in Milwaukee and Perkinstown. Another common characteristic is that the minimum NH_4mn in winter is the highest among the four seasons.

Table 4.14 lists the comparison of summer $[H^+]_{AER}$ and NH4mn from Milwaukee station (2002 to 2009) and the $[H^+]_{AER}$ and NH4mn for data collected at the Pittsburgh EPA Supersite from September 7 to 22, 2002 (Zhang et al., 2007). The two sets data are reasonably compatible.

Table 4.14. The aerosol acidity at Pittsburgh vs at Milwaukee

	Pittsburgh (2002)				**Milwaukee (2002~2009)**			
	NH4mn			$[H^+]_{AER}$	NH4mn			$[H^+]_{AER}$
	whole	acidic	neutralized		whole	acidic	neutralized	
Mean	0.89	0.69	0.99	28	0.82	0.59	0.85	13
Median	0.88	0.71	0.99	15	0.93	na	na	9

The $[H^+]_{AER}$ value from Pittsburgh is higher than that from Milwaukee. Pittsburgh is a larger urban and industrial city. The worse air pollution in Pittsburgh and the short sampling interval may have contributed to the higher $[H^+]_{AER}$ in Pittsburgh. The NH_4mn from Milwaukee is compatible to NH_4mn observed in Pittsburgh.

4.4.2. **The Trend of Atmospheric Aerosol Acidity**

Figure 4.4 shows the trends of atmospheric aerosol acidity at Milwaukee station from 2002 to 2013 (see Appendix B for the trends of atmospheric aerosol acidity at the other stations). Figure 4.5 shows the trends of atmospheric aerosol acidity from Mayville station from 2002 to 2009. From Mayville data, the downward trend was observed for sulfate, $H^+]_{IN-SITU}$ and

$[H^+]_{AER}$, and a slightly upward trend for neutralization degree. The data collection was terminated at the end of 2009 at Mayville station.

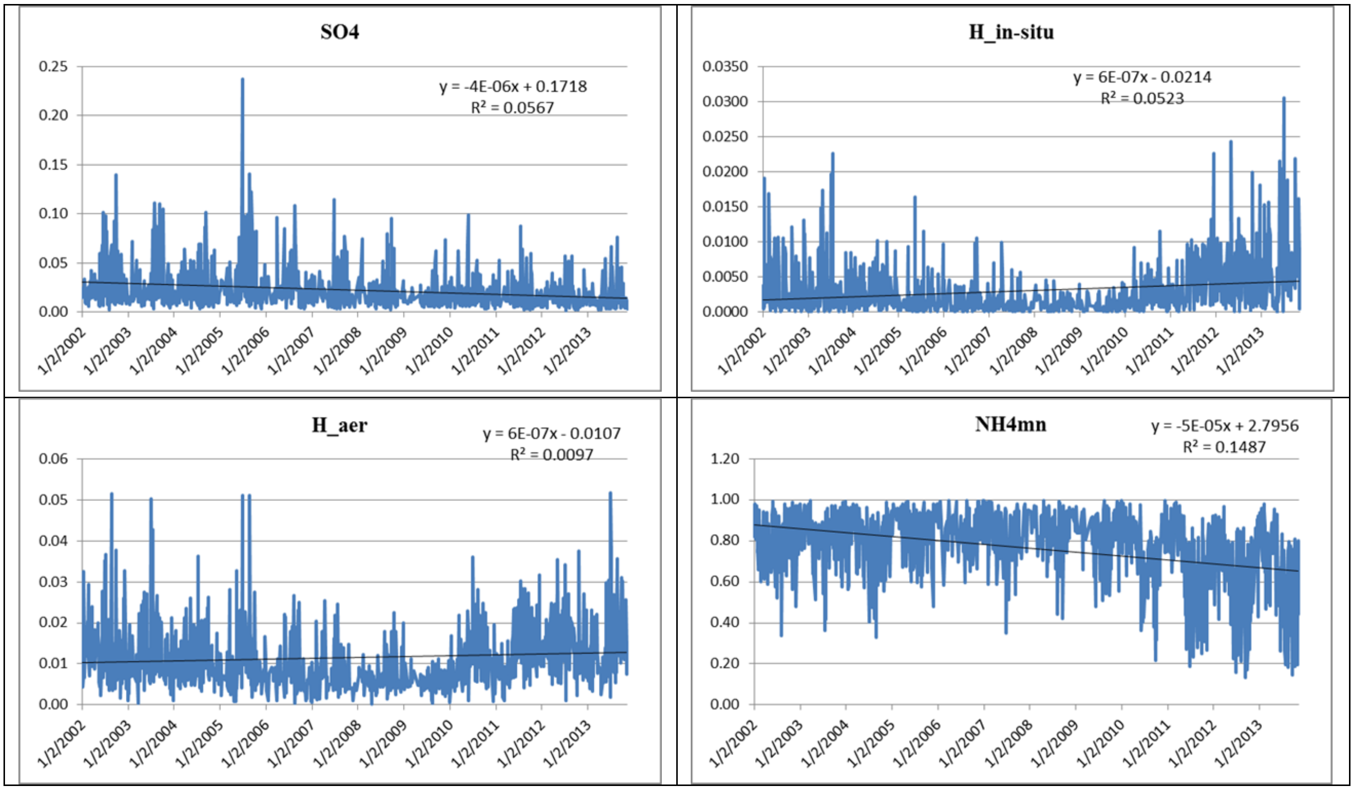
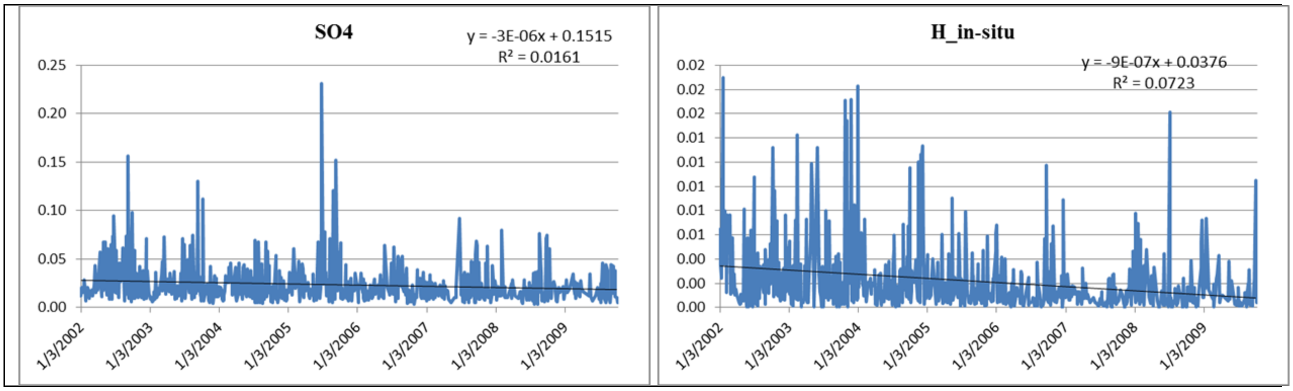


Figure 4.4 The Trend of Increasing Atmospheric Aerosol Acidity in Milwaukee

However, the time series for station Milwaukee, Waukesha and Perkinstown showed a downward then an upward curve between 2009 to 2010.



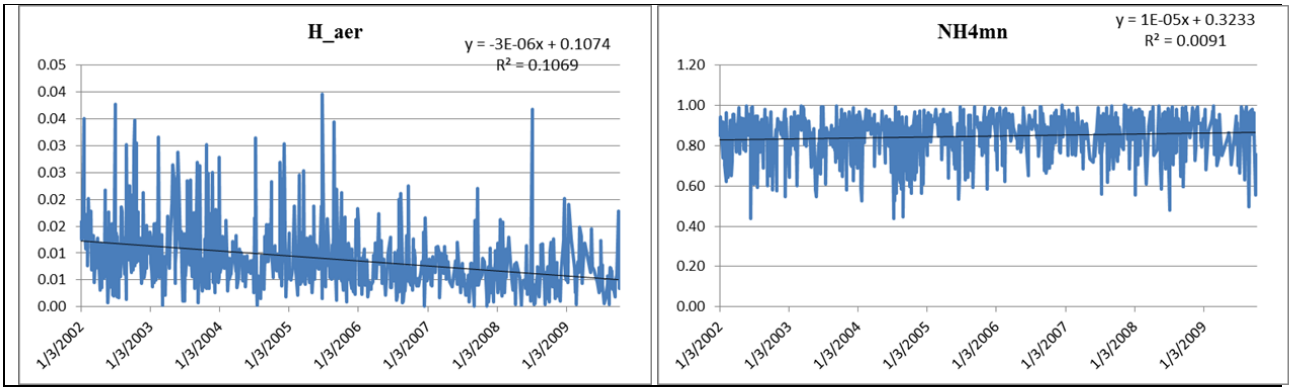


Figure 4.5 The Trend of decreasing Atmospheric Aerosol Acidity in Mayville

Figure 4.6 showed the timeseries of H_in-situ and NH4mn from Milwaukee at the periods from 2002 to 2009 and from 2010 to 2013. There are clearly two different trends at the two periods.

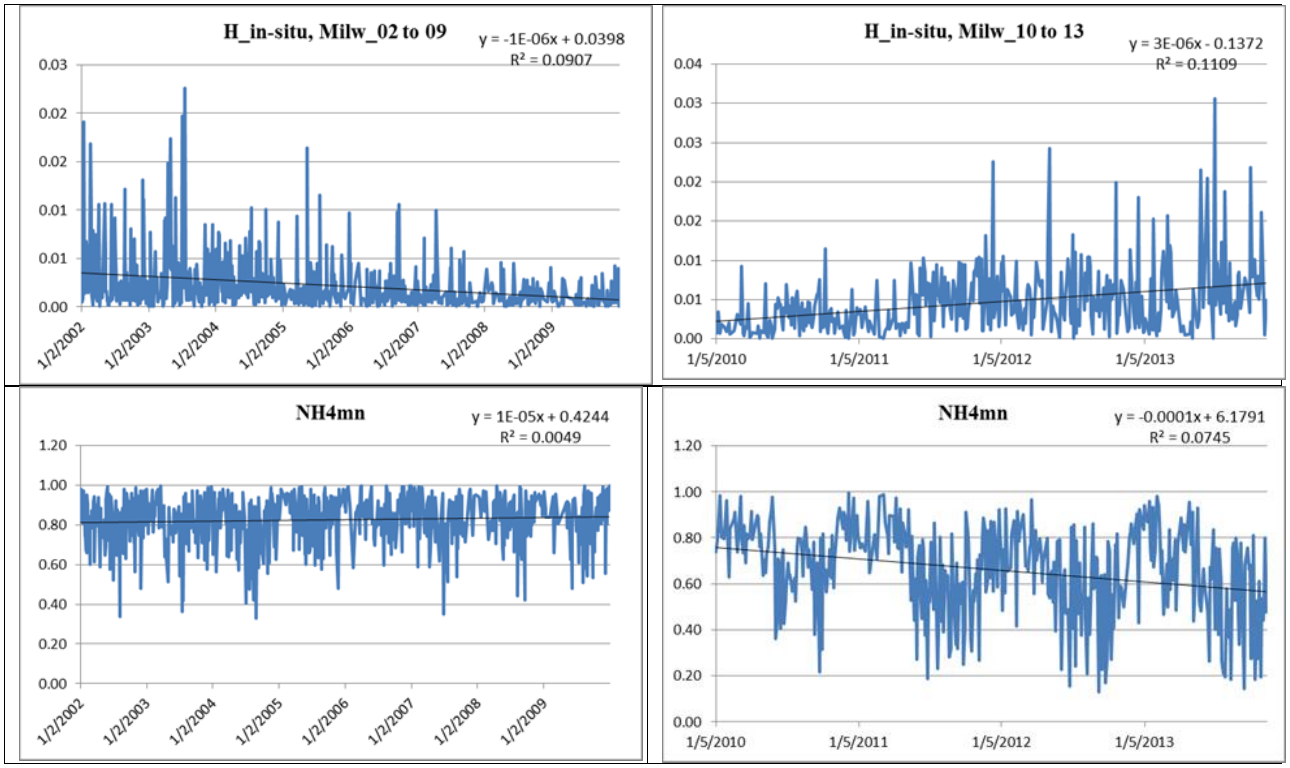


Figure 4.6 The Trend of Atmospheric Aerosol Acidity in Milwaukee (before and after 2009)

The p value for the trend of H_in-situ from 2002 to 2009 is 1.2E-17, at 95% confidence interval, and the p value for the trend of H_in-situ from 2010 to 2013 is 6.34E-11, at 95% confidence interval. The P value analysis indicated that both the downward and upward trends of H_in-situ were not insignificant. Further study is needed to determine if there is a permanent trend.

Investigating what actually caused that changes observed between 2009 and 2010 can provide useful information for the mechanism of aerosol acidity change.

This particle acidity increasing trend was observed at southeastern Unite States and many other locations where the air quality is impacted by SO2 emissions and lack of non-volatile cations (Weber et al., 2016).

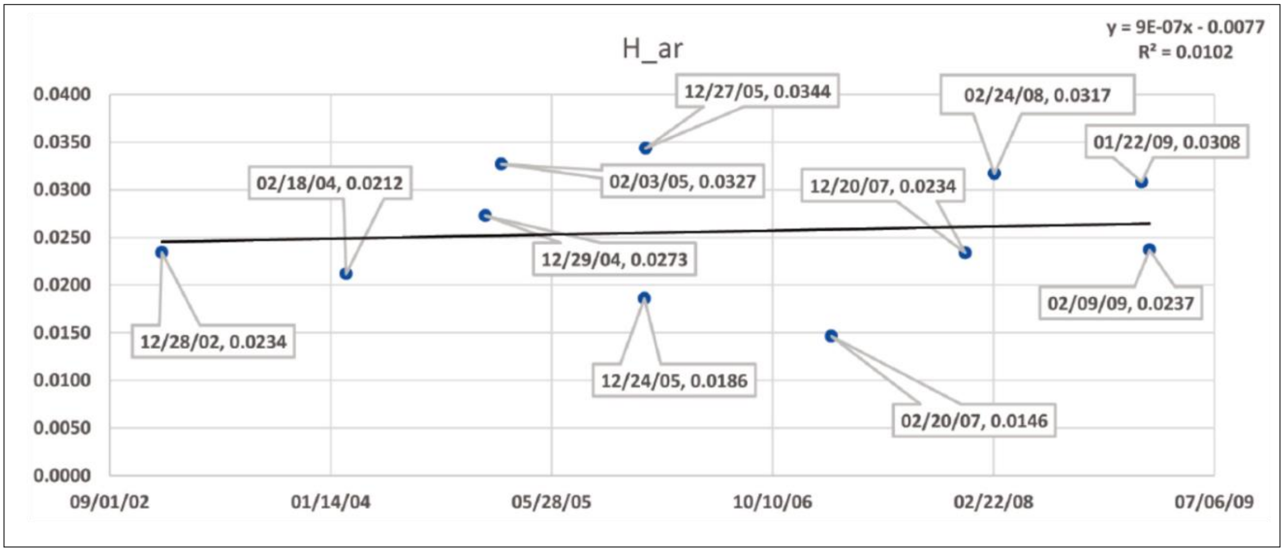


Figure 4.7. Winter Episode Aerosol Acidity Trend in Milwaukee

Another increasing trend of atmospheric aerosol acidity was observed during winter episode days in Milwaukee. Further monitoring and detailed study is necessary to determine if there is a permanent trend.

4.4.3. **Correlations between $[H^+]_{IN\text{-}SITU}$, $[H^+]_{AER}$ and NH4mn**

Since the $[H^+]_{IN\text{-}SITU}$ value is difficult to measure, the correlations of the estimated $[H^+]_{IN\text{-}SITU}$ with the two acid indexes, $[H^+]_{AER}$ and NH4mn, are explored to determine if $[H^+]_{IN\text{-}SITU}$ can be expressed as the function of $[H^+]_{AER}$ or NH4mn.

4.4.3.1. **$[H^+]_{IN\text{-}SITU}$ as a Function of $[H^+]_{AER}$**

It is found that only in winter $[H^+]_{IN\text{-}SITU}$ has good correlations with $[H^+]_{AER}$, but not other seasons. Under both AP and AR conditions, the R^2s of linear regression and polynomial regression for winter $[H^+]_{IN\text{-}SITU}$ and $[H^+]_{AER}$ at Milwaukee region are > 75%.

AP, Polynomial regression: $y = -8.6499x^2 + 1.7675x + 0.0046$, $R^2 = 0.778$

Linear regression: $y = 1.6788x + 0.0047$, $R^2 = 0.7775$

AR, Polynomial regression: $y = -56.15x^2 + 2.5019x + 0.0036$, $R^2 = 0.8047$

Linear regression: $y = 1.7365x + 0.0046$, $R^2 = 0.7743$

Where, $x = [H^+]_{AER}$, $y = [H^+]_{IN\text{-}SITU}$

4.4.3.2. **$[H^+]_{IN\text{-}SITU}$ as a Function of Aerosol Composition and Aerosol Water Content**

A two-stage polynomial model is selected to find a simple empirical model for describing the correlation between $[H^+]_{IN\text{-}SITU}$, composition of the system, H_2O content, and temperature. NH_4mn represents both “composition” and “acidic condition”. H_2O% is one of the outputs from EAIM modeling, indirectly associated with ambient RH. The temperature impact is reflected in the difference of seasonal data modeling results. Two equations, $[H^+]_{IN\text{-}SITU} = f([NH_4mn], [H_2O], [NH4mn]^2)$ and $[H^+]_{IN\text{-}SITU} = f([NH_4mn], [H_2\mathbf{O}], [H_2O]^2)$ are selected.

1). $[H^+]_{IN\text{-}SITU}$ = f([NH4mn], [H_2O], [NH4mn]^2)

Milwaukee Station:

$$[H^+]_{\text{in-situ}} = 0.00355 + 0.00187[NH_4mn] + 0.0371[H_2O] - 0.0377[NH_4mn][H_2O] - 0.00511[NH_4mn]^2 \quad (Winter) \qquad (1) \quad R^2 = 0.8945$$

Mayville Station:

$$[H^+]_{\text{in-situ}} = -0.0302 + 0.1[NH_4mn] + 0.0216[H_2O] - 0.0208[NH_4mn][H_2O] - 0.0717[NH_4mn]^2 \quad (Winter) \qquad (2) \quad R^2 = 0.6205$$

2). $[H^+]_{IN\text{-}SITU}$ = f([NH4mn], [H_2**O**], [H_2O]^2)

Milwaukee Station:

$$[H^+]_{\text{in-situ}} = 0.0073 - 0.0088[NH_4mn] + 0.0299[H_2O] - 0.0260[NH_4mn][H_2O] - 0.00168[H_2O]^2 \quad (Summer), \qquad (3) \quad R^2 = 0.6873$$

Mayville Station:

$$[H^+]_{\text{in-situ}} = 0.0044 - 0.0049[NH_4mn] + 0.0389[H_2O] - 0.0382[NH_4mn][H_2O] - 0.0013[H_2O]^2 \quad (Summer) \qquad (4) \quad R^2 = 0.8682$$

- **Discussion**

Ambient aerosols are a complex system, the composition of the system, the phase status and concentration of each individual component in the system, the meteorology conditions, such as temperature, RH, pH and etc., all play important roles to the status of the system.

Acidic aerosols are formed from oxidation of acidic gases, mainly SO_2 and NOx. These acidic gases, emitted from either natural or anthropogenic sources, are rapidly oxidized into more acidic forms, H_2SO_4 (sulfuric acid) and HNO_3 (nitric acid) in the air (Chang, 1987; Seinfeld, 2006; Tanner et al., 1981; US EPA). H_2SO_4 and HNO_3 are formed predominately from the reaction of OH with SO_2 and NO_2 via the homogeneous gas-phase reaction under sunlight, respectively. HNO_3 can also be formed via heterogeneous chemical reactions (John H. Seinfeld, 2006; Pathak et al., 2004). Depending on the availability of ambient ammonia, acid aerosol may be partially or totally neutralized. Also, depending on the composition of the acid aerosol and the RH, the partially or totally neutralized aerosols may exist in both solid and liquid phase, the partition coefficient is governed by the phase diagram of the system. The ammonium nitrate aerosol dissociate constant depends on temperature and RH (Tang, 1980). The ammonia-nitric acid partial pressure product is sensitive to relative humidity (RH) but not sensitive to pH. Thus, the aqueous NH_4NO_3 dissociation constant at a specific temperature and RH would characterize the ammonia-nitric acid partial pressure product of a slightly acidic ammonium nitrate solution (Stelson and Seinfeld, 1982b). The correlation formulas successfully reflect the effect of composition (NH4mn), RH ($H_2\mathbf{O}$) and temperature (formula (1) for winter and formula (4) for summer).

$[H^+]_{IN\text{-}SITU} = f([NH4mn], [H_2O], [NH4mn]^2)$ and $[H^+]_{IN\text{-}SITU} = f([NH4mn], [H_2O], [H_2O]^2)$ are better describe the correlations between $[H^+]_{IN\text{-}SITU}$ and other parameters in the acidic aerosol system. The linear relation between winter $[H^+]_{IN\text{-}SITU}$ and winter $([H^+]_{AER})$ is a special situation.

4.4.4. **Atmospheric Aerosol Acidity and OC and $PM_{2.5}$**

The positive correlations between concentration of OC and aerosol acidity were discovered from the chamber test and analysis of monitoring data. It is proposed that an acid-catalyzed heterogeneous reaction v be one important mechanism for the positive correlations between concentration of OC and aerosol acidity in the air (Chu, 2004; Jang et al., 2003; Jang et al., 2002; Jang and Kamens, 2001; Kroll et al., 2005; Zhang et al., 2007).

To investigate the relationship between aerosol acidity and OC, the relationships between OC and sulfate and between OC and H_{AER} are investigated.

4.4.4.1. **OC and Sulfate**

The OC over sulfate bin plots were made for each station to explore the correlations between OC and sulfate, see Figure 4.8 for an example. The sulfate bin is at a 0.003 (μmol m^{-3}) increment, the associated OC is the average of all the OC whose sulfate falls into that bin. The left y_axis is for the number of samples fell into the bean; the right y_axis is for concentration of OC ($\mu g/m^3$). There are two plots for each season, one for $NH_4^+/SO_4^{2-} < 1.5$ (AP) condition and another for $NH_4^+/SO_4^{2-} \geq 1.5$ (AR) condition.

1. Milwaukee Station

Figures 4.7-1 and 4.7-2 show how atmospheric concentration of OC corresponds to the variations of concentration of sulfate in Milwaukee region. The linear regression results are:

Milwaukee, NH_4^+/SO_4^{2-} <1.5, 235, >60%, All season, $y = 0.2487x + 1.9365$, $R^2 = 0.7928$

NH_4^+/SO_4^{2-} >1.5, 352, >60%, All season, $y = 0.2104x + 2.243$, $R^2 = 0.7063$

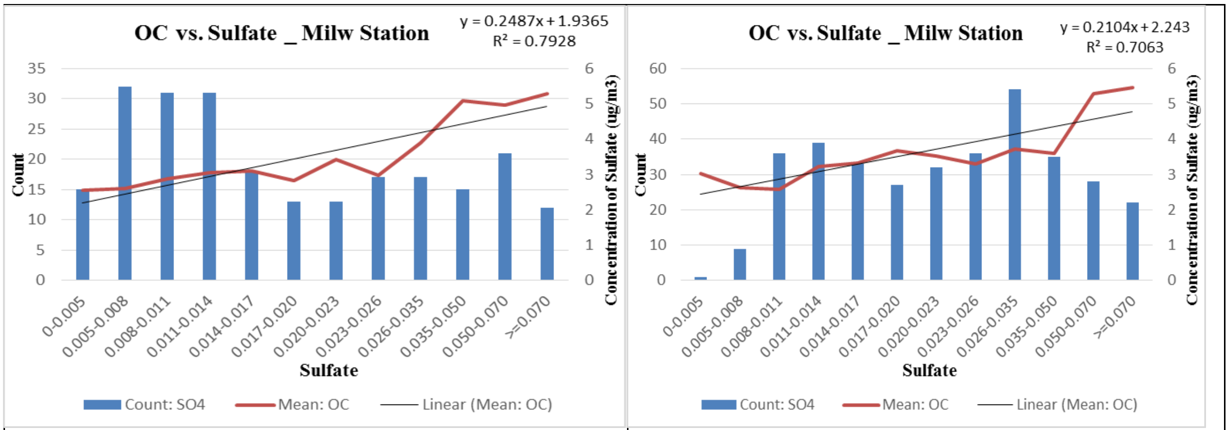


Figure 4.8-1 Milw <1.5, 235, >60%, All season

Figure 4.8-2 Milw >1.5, 352, >60%, All season

Figure 4.8 OC vs Sulfate _ Milw

- **Discussion:**

The regression results indicate that there are a positive correlations between ambient concentration of OC and concentration of sulfate, under both AP and AR conditions in Milwaukee area. The higher the concentration of sulfate is, the higher the concentration of OC is. Same regression was done for Wauk, Mayv and Perk stations. The results are summarized in Table 4.15.

Table 4.15. OC vs Sulfate Linerar Regression Coeff.

	Milwaukee			Waukesha			Mayville			Perkinstown		
	a	b	R^2	a	b	R^2	a	b	R^2	a	b	R^2
AP	0.249	1.937	0.793	0.180	3.071	0.466	0.162	1.757	0.760	0.253	1.620	0.735
AR	0.211	2.243	0.706	0.184	2.668	0.667	0.179	1.578	0.688	0.038	2.733	0.023

where a = slope and b = intercept.

- **Discussion:**

Data analysis for OC vs Sulfate has demonstrated significant positive correlations between OC and sulfate at four regions (except for Wauk under AP conditions and Perk under AR conditions).

From Table 4.15, Milwaukee region has the most significant correlations between OC and sulfate (a = 0.23 and R^2=0.75). The next is that from Waukesha area (a=0.18 and R^2= 0.57). The lower R^2 under AP conditions may be caused by the data fluctuation. The third one is from Mayville area (a=0.17 and R^2= 0.73).

OC contains both primary (POC) and secondary (SOA) organic carbons. The precursors for OC are biogenic and anthropogenic VOCs. From lab tests, Jang et al. evaluated the particle growth by the heterogeneous reaction of different VOC precursors (such as aldehydes) in chamber in darkness in the presence of acid catalysts with different composition and observed the production of organic particle increased by factors of 4 to 6 comparing to neutral aerosol systems (Jang et al., 2003; Jang et al., 2002; Jang and Kamens, 2001). From the analysis of field data, Chu found positive correlations between OC and sulfate and suggested that the sulfate catalyzed heterogeneous reactions which played a role in enhancing the SOA production(Chu, 2004). The correlations between OC and sulfate found from this study support the possibility of acidic – catalyst enhanced SOA formation mechanism proposed by Chu and Jang, etc. However, to confirm the proposed formation mechanism, sampling of SOA and VOC precursors are needed. In the changing world, the possibility of new VOC emissions are existing too.

4.4.4.2. **OC and H_{AER}**

Milwaukee Station:

Figures 4.9 and 4.10 demonstrated how atmospheric concentration of OC corresponds to the variations of atmospheric aerosol acidity (strong acid, $[H^+]_{AER}$) in Milwaukee region at summer and spring, respectively.

The $[H^+]_{AER}$ bin is at a 0.003 (μmol m^{-3}) increment, the associated OC is the average of the OC whose $[H^+]_{AER}$ falls into that bin. There are two plots for each season, one for $NH_4^+/SO_4^{2-} < 1.5$ (AP) condition and another for $NH_4^+/SO_4^{2-} \geq 1.5$ (AR) condition. Only the data with RH above seasonal DRH are used in the plot and linear regression. Comparing the OC vs $[H^+]_{AER}$ bin plot under AP conditions with that under AR conditions, one can see that, for all seasons, $[H^+]_{AER}$ has a bigger impact on concentration of OC under AP conditions and the higher the acidity, the higher the concentration of OC. For example, the slopes of the linear regression for summer data is 0.1344 under AP conditions verses 0.016 under AR conditions; and 0.2304 for AP conditions verses 0.0754 for AR conditions for spring and fall.

Under AP conditions, OC has shown some indication that it is higher when the $[H^+]_{AER}$ value is higher, but did not show a solid correlation between the acidity and OC. However, the OC over H_{AER} regression results in this study couldn’t deny nor support the proposed mechanisms that “An acid-catalyzed heterogeneous reaction could be one important mechanism that enhances the formation of SOA in the air”. To better test the hypothesis, SOA sampling along with the acidy measurement is needed.

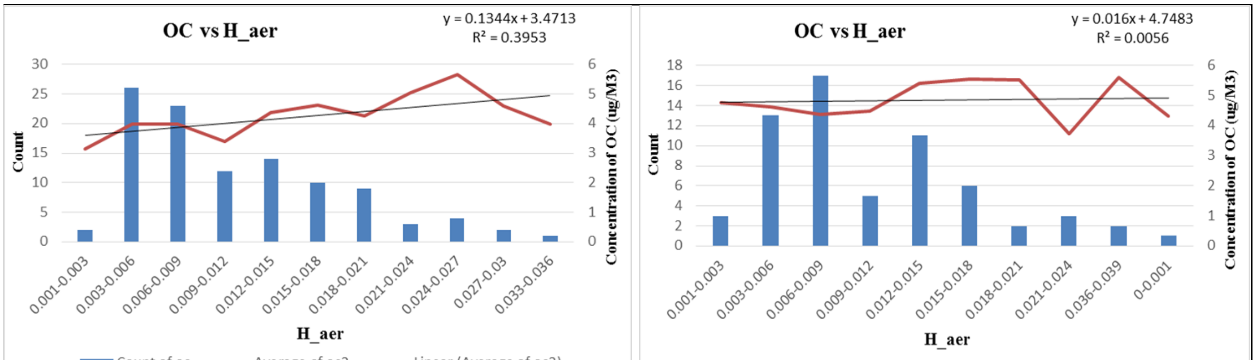


Figure 4.9-1. Summer, <1.5, RH > 60%, #=106	Figure 4.9-2. Summer, >1.5, >60%, #=63

Figure 4.9 OC vs H_aer _Milw (summer)

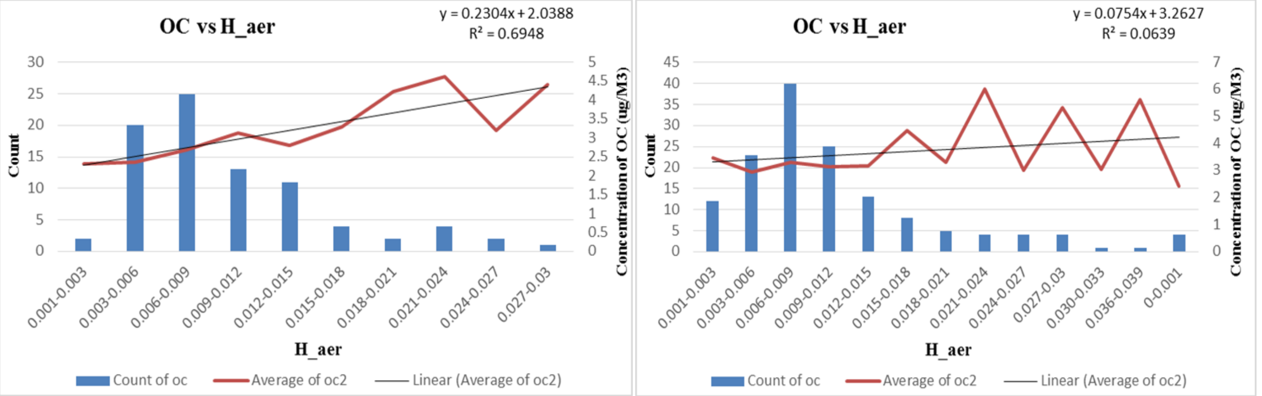


Fig. 4.10-1. Spring and Fall, <1.5, RH > 65%, #=84	Fig. 4.10-2 Spring & Fall >1.5, RH > 65%,#=144

Figure 4.10 OC vs H_aer _Milw (Spring)

4.4.4.3. Aerosol Acidity Impact on $PM_{2.5}$

Positive and significant correlations between $PM_{2.5}$ and H_{AER} are found for the data collected under AP conditions, in summer at Milw and Wauk stations only.

Figure 4.11 show how summer atmospheric concentration of $PM_{2.5}$ corresponds to the variations of atmospheric aerosol acidity (strong acid, $[H^+]_{AER}$) in Milwaukee area.

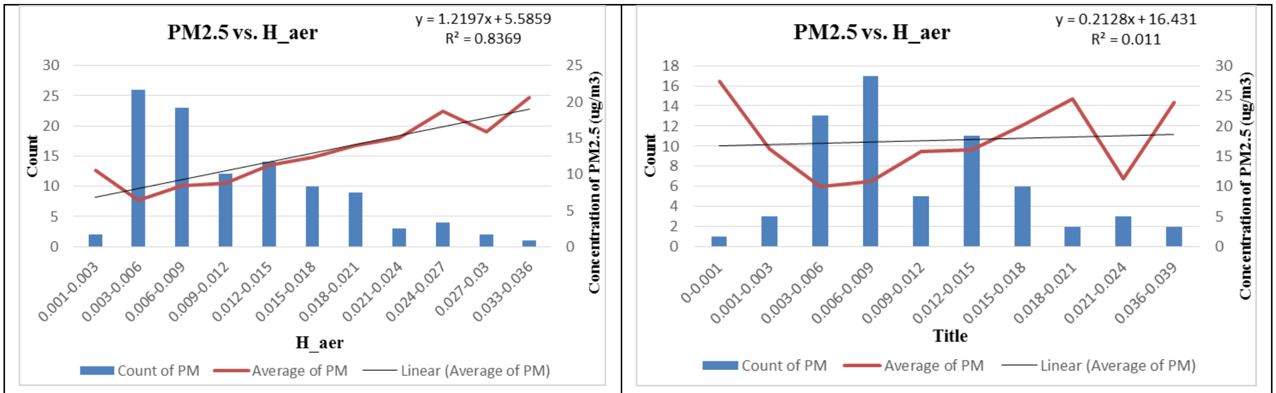


Figure 4.11-1 Summer, RH > 60%, <1.5, #=106

Figure 4.11-2. Summer, RH > 60%, >1.5, #=63

Figure 4.11 $PM_{2.5}$ vs H_aer _Milw

$[H^+]_{AER}$ has bigger impact to $PM_{2.5}$ concentration under AP conditions, the higher the acidity, the higher the concentration of $PM_{2.5}$ is.

Summer, RH > 60%, <1.5, #=106, $y = 1.2197x + 5.5859$, $R^2 = 0.8369$

Summer, RH > 60%, >1.5, #=63, $y = 0.2128x + 16.431$, $R^2 = 0.011$

- **Discussion:**

$PM_{2.5}$ vs. $[H^+]_{AER}$

Only summer $PM_{2.5}$ from Milw and Wauk, two urban and industrial areas, has shown significant correlations between OC and H_{AER} under AP conditions.

Temperature and sulfate together contributed to the significant correlations between summer $PM_{2.5}$ and H_{AER} in Milwaukee and Waukesha. The warm temperature is favorable to the production of biogenic VOC. The strong sunlight enhanced the photochemical reactions that converted SO_2 to SO_4^{2-} and the formation of SOA from VOCs. As discussed in previous sectors, sulfate is one major contribution to the aerosol acidity. In summer, both sulfates and OC are the major $PM_{2.5}$ components. The higher anthropogenic SO_2, NOx and VOC emissions from urban and industrial areas further enhanced above reactions.

Ambient aerosols are complex systems whose chemical and physical states are controlled by dynamic atmospheric conditions. The significant correlations between $PM_{2.5}$ and H_{AER} in Milwaukee and Waukesha are special cases.

4.5. Conclusion and Recommendation

Spatiotemporal variations of aerosol acidity were observed for all four stations with different patterns. The cause of the variations was complex and unique for each station. The major contributors are precursors, composition of the atmospheric aerosol, the pre-existing atmospheric acidic condition and the local meteorology conditions.

The increasing aerosol acidity trend is observed at the stations of Milw, Wauk and Perk. The data observation was terminated at Mayv station. From the timeseries of aerosol acidity observed at the other stations, the trend started turning up since 2009. Investigating what actually caused that swing observed between 2009 and 2010 could provide useful information for the mechanism of aerosol acidity change.

An increasing H_{AR} was found from winter episodes occurred in Milwaukee area. This trend is in consistent with the trend of H_{AER}, observed based on the whole data set at the other stations. The significance of this trend is, the acidity (H_{AR}) is calculated based on the higher ammonium scenario. This means, in Great Lakes Region, ammonia, the largest basic element in the atmosphere is no longer sufficient to balance the acidic gases generated by both human activity and nature.

In general, the H_{AER} value is higher under AP conditions and higher in urban and industrial areas. NH4mn has higher temporal variations as compared with that under AP conditions. The available ambient NH_3 as well as the content of the acidic aerosol play significant roles in the variations of neutralization degree. Under AR conditions, the winter NH4mn at Milw and Mayv, the urban and industrial region, are the highest among all seasons. Based on the neutralization degree, under AP conditions, summer has more days under more acidic conditions at all regions.

The knowledge of aerosol acidity distribution provides useful information to plan epidemiologic studies and therefore provide better human health benefits.

Significant correlations between concentration of sulfate and organic carbon are found at all regions, with different value of R^2. These relations are not sufficient to either deny or support the hypothesis that “An acid-catalyzed heterogeneous reaction could be one important mechanism that enhances the formation of SOA in the air”. SOA sampling is essential to establish the correlations between sulfate and SOA.

4.6. Reference

Chang, J.S., Brost, R.A., et al., 1987. A Three-Dimensional Eulerian Acid Deposition Model: Physical Concepts and Formulation. Journal of Geophysical Research 92, 14,681-614,700.

Chu, S.-H., 2004. PM2.5 episodes as observed in the speciation trends network, 31 ed. Elsevier Ltd, pp. 5237-5246.

Clegg, S.L., Brimblecombe, P., Wexler, A.S., 1998. Thermodynamic model of the system H+-NH4+-SO42--NO3--H2$ /O at tropospheric temperatures. Journal of Physical Chemistry A 102, 2137-2154.

Ephrath, J.E., Goudriaan, J., Marani, A., 1996. Modelling diurnal patterns of air temperature, radiation wind speed and relative humidity by equations from daily characteristics. Agricultural Systems 51, 377-393.

Gao, S., Keywood, M., Ng, N.L., Surratt, J., Varutbangkul, V., Bahreini, R., Flagan, R.C., Seinfeld, J.H., 2004. Low-molecular-weight and oligomeric components in secondary organic aerosol from the ozonolysis of cycloalkenes and alpha-pinene. Journal of Physical Chemistry A 108, 10147-10164.

He, K., Zhao, Q., Ma, Y., Duan, F., Yang, F., Shi, Z., Chen, G., 2012. Spatial and seasonal variability of PM2.5 acidity at two Chinese megacities: Insights into the formation of secondary inorganic aerosols. Atmospheric Chemistry and Physics 12, 1377-1395.

Hewitt, C.N.a.J., A.V., 2009. Atmospheric Science for Environmental Scientists. Wiley-Blackwell.

Jang, M., Lee, S., Kamens, R.M., 2003. Organic aerosol growth by acid-catalyzed heterogeneous reactions of octanal in a flow reactor. Atmospheric Environment 37, 2125-2138.

Jang, M.S., Czoschke, N.M., Lee, S., Kamens, R.M., 2002. Heterogeneous atmospheric aerosol production by acid-catalyzed particle-phase reactions. Science 298, 814-817.

Jang, M.S., Kamens, R.M., 2001. Atmospheric secondary aerosol formation by heterogeneous reactions of aldehydes in the presence of a sulfuric acid aerosol catalyst. Environmental Science & Technology 35, 4758-4766.

Jickells, T.D., An, Z.S., Andersen, K.K., Baker, A.R., Bergametti, C., Brooks, N., Cao, J.J., Boyd, P.W., Duce, R.A., Hunter, K.A., Kawahata, H., Kubilay, N., LaRoche, J., Liss, P.S., Mahowald, N., Prospero, J.M., Ridgwell, A.J., Tegen, I., Torres, R., 2005. Global iron connections between desert dust, ocean biogeochemistry, and climate. Science 308, 67-71.

John H. Seinfeld, S.N.P., 2006. Atmospheric Chemistry and Physics: From Air Pollution to Climate Change, 2nd Edition, p. 1332.

Khlystov, A., Stanier, C.O., Takahama, S., Pandis, S.N., 2005. Water content of ambient aerosol during the Pittsburgh air quality study. Journal of Geophysical Research-Atmospheres 110.

Koutrakis, P., Thompson, K.M., Wolfson, J.M., Spengler, J.D., Keeler, G.J., Slater, J.L., 1992. DETERMINATION OF AEROSOL STRONG ACIDITY LOSSES DUE TO INTERACTIONS OF COLLECTED PARTICLES - RESULTS FROM LABORATORY AND FIELD STUDIES. Atmospheric Environment Part a-General Topics 26, 987-995.

Kroll, J.H., Ng, N.L., Murphy, S.M., Varutbangkul, V., Flagan, R.C., Seinfeld, J.H., 2005. Chamber studies of secondary organic aerosol growth by reactive uptake of simple carbonyl compounds. Journal of Geophysical Research-Atmospheres 110.

Likens, G.E., Driscoll, C.T., Buso, D.C., 1996. Long-term effects of acid rain: Response and recovery of a forest ecosystem. Science 272, 244-246.

Nenes, A., Krom, M.D., Mihalopoulos, N., Van Cappellen, P., Shi, Z., Bougiatioti, A., Zarmpas, P., Herut, B., 2011. Atmospheric acidification of mineral aerosols: A source of bioavailable phosphorus for the oceans. Atmospheric Chemistry and Physics 11, 6265-6272.

Newberg, J.T., Matthew, B.M., Anastasio, C., 2005. Chloride and bromide depletions in sea-salt particles over the northeastern Pacific Ocean. Journal of Geophysical Research D: Atmospheres

110, 1-13.

Pathak, R.K., Louie, P.K.K., Chan, C.K., 2004. Characteristics of aerosol acidity in Hong kong. Atmospheric Environment 38, 2965-2974.

Pathak, R.K., Wu, W.S., Wang, T., 2009. Summertime PM2.5 ionic species in four major cities of China: nitrate formation in an ammonia-deficient atmosphere. Atmospheric Chemistry and Physics 9, 1711-1722.

Putaud, J.P., Van Dingenen, R., Alastuey, A., Bauer, H., Birmili, W., Cyrys, J., Flentje, H., Fuzzi, S., Gehrig, R., Hansson, H.C., Harrison, R.M., Herrmann, H., Hitzenberger, R., Huglin, C., Jones, A.M., Kasper-Giebl, A., Kiss, G., Kousa, A., Kuhlbusch, T.A.J., Loschau, G., Maenhaut, W., Molnar, A., Moreno, T., Pekkanen, J., Perrino, C., Pitz, M., Puxbaum, H., Querol, X., Rodriguez, S., Salma, I., Schwarz, J., Smolik, J., Schneider, J., Spindler, G., ten Brink, H., Tursic, J., Viana, Wiedensohler, A., Raes, F., 2010. A European aerosol phenomenology-3: Physical and chemical characteristics of particulate matter from 60 rural, urban, and kerbside sites across Europe. Atmospheric Environment 44, 1308-1320.

Saxena, P., Mueller, P.K., Kim, Y.P., Seinfeld, J.H., Koutrakis, P., 1993. Coupling thermodynamic theory with measurements to characterize acidity of atmospheric particles. Aerosol Science and Technology 19, 279-293.

Schlesinger, R.B., Graham, J.A., 1992. Health-effects of atmospheric acid aerosols - a model problem in inhalation toxicology and air-pollution risk assessment. Fundam. Appl. Toxicol. 18, 17-24.

Seinfeld, J.H.a.P., S.N., 2006. Atmospheric Chemistry and Physics - from Air Pollution to Climate Change.

Speizer, F.E., 1989. Studies of acid aerosols in 6 cities and in a new multi-city investigation - design issues. Environmental Health Perspectives 79, 61-67.

Stelson, A.W., Seinfeld, J.H., 1982a. Relative humidity and pH dependence of the vapor pressure of ammonium nitrate- nitric acid solutions at 25oC. Atmospheric Environment 16, 993-1000.

Stelson, A.W., Seinfeld, J.H., 1982b. Relative humidity and temperature dependence of ammonium nitrate dissociation constant. Atmospheric Environment 16, 983-992.

Tang, I.N., 1980. ON THE EQUILIBRIUM PARTIAL PRESSURES OF NITRIC-ACID AND AMMONIA IN THE ATMOSPHERE. Atmospheric Environment 14, 819-828.

Tang, I.N., Munkelwitz, H.R., 1993. COMPOSITION AND TEMPERATURE-DEPENDENCE OF THE DELIQUESCENCE PROPERTIES OF HYGROSCOPIC AEROSOLS. Atmospheric Environment Part a-General Topics 27, 467-473.

Tanner, R.L., Leaderer, B.P., Spengler, J.D., 1981. Acidity of atmospheric aerosols. Environmental Science & Technology 15, 1150-1153.

US EPA, Atmospheric Deposition of Sulfur and Nitrogen Compounds.

Yao, X., Yan Ling, T., Fang, M., Chan, C.K., 2006. Comparison of thermodynamic predictions for in situ pH in PM2.5. Atmospheric Environment 40, 2835-2844.

Zhang, Q., Jimenez, J.L., Worsnop, D.R., Canagaratna, M., 2007. A case study of urban particle acidity and its influence on secondary organic aerosol. Environmental Science and Technology 41, 3213-3219.

Ziemba, L.D., Fischer, E., Griffin, R.J., Talbot, R.W., 2007. Aerosol acidity in rural New England: Temporal trends and source region analysis. Journal of Geophysical Research D: Atmospheres 112.

CHAPTER 5. THE DAYS WITH ELEVATED $PM_{2.5}$ AND O_3

5.1. Introduction

The American Lung Association's State of the Air 2007 report released a clear warning to people living in the upper Midwest that the air quality was poor in both metropolitan areas and rural areas in the region. The report indicated that Wisconsin had the most failing grades on air quality in the Midwest region (Association, 2007). From the ambient $PM_{2.5}$ data collected from 2002 to 2013 in Wisconsin, the elevated 24-hr ambient concentration of $PM_{2.5}$ have occurred frequently at all seasons in different regions of Wisconsin. Many studies confirmed the significant impact of meteorological changes on the daily air quality in the Midwest (LADCO, 2009; Mickley et al., 2004). Dawson et al. forecasted that the summertime episodes would happen more frequently, more severely, and cover larger areas from the present to 2050 in the Midwest (Dawson et al., 2014; Dawson et al., 2009; Mickley et al., 2004).

Epidemiological studies have indicated a positive correlation between daily mortality and exposure to high concentrations ambient particles (Laden et al., 2000). It has been observed from the ambient air quality data collected in Wisconsin that when elevated levels of 24-hr $PM_{2.5}$ and 8-hr O_3 occur together, usually the concentration of sulfate and OC would be higher than when these two concentrations at a single occurrence. The potency of the mixture of high $PM_{2.5}$, O_3, sulfate and OC would be greater than the potency of its constituents (EPA, 2005; EPA/600/P-99/002bF, 2004; Hidy, 2011). Analyzing the daily episodes enables us to catch the characteristics of the worst-case scenario, thereby providing useful information for effective air quality management and health protection. The elevated $PM_{2.5}$ and O_3 data collected at stations in Milwaukee, Waukesha, Mayville and Perkinstown per CSN program from 2002 to 2013

(Mayville from 2002 to 2009 only) will be used in this study to examine the relationship between elevated air pollution events and the concurrent meteorological parameters to fully characterize elevated $PM_{2.5}$ events in Wisconsin.

The objective of this study is to improve our knowledge about:

1) The trend and characteristics of the short-term elevated $PM_{2.5}$ events;
2) The correlations between elevated $PM_{2.5}$ events and the meteorological condition;
3) The major factors that contribute to those short-term elevated air pollution events;

The Hypotheses of this study are:

1) Each episode is unique. Meteorological conditions and emission sources both have significant impact on the elevated air pollution events. The impact from meteorological parameters varies.
2) During the episode, each major $PM_{2.5}$ components is higher than its mean at normal condition. However, the elevation ratio of each component [(concentration of the component during an episode)/ (concentration of the component under normal conditions)] is different and depends on the season, the meteorological condition and the pre-existing atmospheric conditions.
3) However, the elevation ratio of each component [(concentration of the component during an episode)/ (concentration of the component under normal conditions)] is different and depends on the season, the meteorological condition and the pre-existing atmospheric conditions.

The implications of this study: Many aspects of global changes are expected to impact $PM_{2.5}$ pollution and its implications for environmental management. Studying the elevated $PM_{2.5}$

events provides the opportunity to obtain the information about the scale, the cause and the impact of air pollutions in a worst-case scenario. The estimated health risks are not evenly distributed among our populations. The economically disadvantaged, the elderly, the infant and those, whose health is already compromised are more sensitive to the poor air. Therefore, knowledge about the characteristics and variations of the worst air pollution events in the region and in adjacent regions provides useful information to lawmakers in establishing feasible and cost-effective plans to improve the ambient air quality and to protect human health.

5.2. Literature Review

Elevated $PM_{2.5}$ events have occurred in the Midwest for several decades. Recent ambient air monitoring data has shown that in northern cities of the upper Midwest, elevated $PM_{2.5}$ events have occurred more frequently in wintertime than in summertime (Katzman et al., 2010). Heo et al. (2013) analyzed speciated PM2.5 data collected from Madison, Milwaukee and Mayville, Wisconsin, and found that extreme events of elevated $PM_{2.5}$ occurred during times when air trajectories passed over ammonia emissions hotspots as well as large stationary emission sources, such as those located at Ohio River Valley and adjacent states.

Multiple epidemiological studies have shown an increase of daily mortality shortly after days with high ambient particle concentrations (Laden et al., 2000). Currently the available technology does not allow precise identification and quantification of the adverse influences of specific components or source-related mixtures on health impacts. Nevertheless, some studies have suggested a degree of differential toxicity happening with $PM_{2.5}$ – related emissions such as fine and ultrafine particles, specific metals and elemental carbon (Kelly and Fussell, 2012; Maynard et al., 2007). Short-term (hours or days) exposure to particles can aggravate lung disease causing asthma attacks and acute bronchitis, increase susceptibility to respiratory infections, and cause heart attacks and arrhythmias in people with heart disease. Even healthy people may experience temporary symptoms, such as irritation of the eyes, nose and throat, coughing, chest tightness and shortness of breath (http://www.sparetheair.com/).

Since the state of the atmosphere determines the development, transport, dispersion, and deposition of air pollutants (Ebi and McGregor, 2008), it is essential to understand the local meteorological conditions when considering reduction of the elevated air pollutants in a region. Studies on the elevated $PM_{2.5}$ in the Midwest indicated that high daily concentrations are driven by specific meteorological conditions, rather than by the changes of emissions (LADCO, 2009).

Modeling focused on the impacts on air quality by climate change indicated that the cyclone frequency has played a critical role on short-term pollution episodes rather than on the seasonal mean concentrations (Mickley et al., 2004). The model simulations by Dawson et al. predicted the possible increasing in severity of the summertime episodes, episodes frequency and the size of the areas where the more frequent and more severe episodes could happen from present to 2050 in Midwest (Dawson et al., 2014; Dawson et al., 2009).

During episodes the secondary aerosols are the dominating majority with the spatial and temporal variations on the characteristics. SOA and sulfates are the two major secondary $PM_{2.5}$ components that would be very high during elevated $PM_{2.5}$ events in summertime. SOA constitutes approximately 20 to 60 percent of the OC in the southeastern US (Blanchard et al., 2008; Lim and Turpin, 2002). Meteorological conditions have big impact on the time of occurrence, scale and duration of the episodes. One way that climate change affects the air quality is its ability to change the local meteorology, such as, temperature, relative humidity

(RH), etc. Since the impact on concentration of $PM_{2.5}$ caused by the changes of meteorology could be negated at a long-term (Monson et al., 2007; Possell and Hewitt, 2011; Rosenstiel et al., 2003), studying the elevated $PM_{2.5}$ episode could catch the dynamics of the worst case scenario, which could provide useful information for an efficient air quality management and health protection plans.

5.3. Experimental Method

Speciated $PM_{2.5}$, $PM_{2.5}$ and O_3 data collected from 2002 to 2009 at Stations of Milwaukee, Mayville, Waukesha and Perkingstown per CSN program were analyzed for this study. See Chapter 2 for details about the location, the geographical and economical background of the regions where the four stations are located and how the air samples were collected and analyzed. The ambient air quality data for the days with elevated $PM_{2.5} \geq 35$ µg /m^{3}and the days with both elevated $PM_{2.5}$ and O_3 (≥35 µg /m^3 and ≥ 0.075 ppb) were selected in this study.

The days of the $PM_{2.5}$ exceedance at the four stations and the days with both $PM_{2.5}$ and O_3 exceedance at Milwaukee and Mayville are listed in tables 5.1, 5.2, and 5.3 for comparing the scope and frequency of the exceedance at the four stations.

The mean concentrations of $PM_{2.5}$, its major components and aerosol acidities and the means of the same parameters for the days when $PM_{2.5}$ is ≥ 35 µg/m^3 and the days when $PM_{2.5}$ is between 30 µg/m^3 and 35 µg/m^3, and the same parameters for the days when both the elevated $PM_{2.5}$ and O_3 occurred are listed in Table 5.4 to Table 5.8 for exploring and comparing the variations and trends of the different episodes at the four station.

This study has also investigated the relationships among meteorology, sulfate, organic carbon

(OC) and O_3 using speciated $PM_{2.5}$ and O_3 data collected at Milwaukee and Mayville station. The meteorological parameters, including relative humidity, ambient temperature, wind speed, wind direction were obtained from Midwestern Regional Climate Center (MRCC). The meteorology data were recorded at hourly intervals.

PC Windows-based HYsplit_4 (Hybrid Single – Particle Lagrangian Integrated Trajectory (HYSPLIT)) model (Draxler, 2014) was downloaded from NOAA website to model the air parcel transported to Stations of Milwaukee, Mayville and Perkinstown. HYSPLIT_ back trajectory were calculated using the National Weather Service (NWS), National Center for Environmental Prediction (NCEP)'s Eta Data Assimilation System (EDAS) Model Data. The EDAS data, digital data set DSI-6141, was archived at the National Climatic Data Center (NCDC) and obtained from the National Oceanic and Atmospheric Administration's Air Resources Labotory (NOAA-ARL) in this study. It is an intermittent assimilation system consisting of successive 3 hourly Eta model forecasts and Optimum Interpolation analyses on a 40 km grid. The Air Resources Laboratory (ARL) extracts every second grid point to produce a 3 hourly 80 km grid, which is archived at NCDC. Major parameters in EDAS are (1) Surface parameters and (2) Upper air parameters.

The meteorological model data, already converrted into a HYSPLIT compatible format, were stored in the ARL analysis data archive on ARL web server. The ARL analysis consists of output from the Global Data Analysis System (GDAS) and the NAM Data Analysis System (NDAS - previously called EDAS) covering much of North America. During the modeling, the direct access to these data files via FTP is "hardwired" into the GUI for the calculation of the back trajectories and for further frequencey analysis. The height of the air parcel trajectory is calculated based on half of mixing height (MH).

The back trajectories (BT) from stations of Milwaukee, Mayville and Perkinstown were calculated for tracing the source region and source category of the episodes.

The frequency analysis was performed using the back trajectories several days before the episodes to explore the meteorology impact on the area before the episodes. The frequency ($F_{i,j}$) is calculated by:

$$\mathrm{F}_{\mathrm{i,j}} = 100 \sum \mathrm{T}_{\mathrm{i,j}} / N$$

Where, $T_{i,j}$ is the number of trajectories that fall within each grid cell that covers the area. The trajectory frequency (F) is the sum of the number of trajectories (T) passing through each (i,j) grid cell divided by the total number (N) of trajectories analyzed. In this calculation, all trajectories are counted once in the source location grid cell and each trajectory is counted once per intersecting grid cell.

5.4. Results and Discussion

5.4.1. The Scale and Frequency of the Elevations

Thresholds of 35, 30 and 25 $\mu g/m^3$ were selected as criteria to categorize the elevated $PM_{2.5}$ events. The frequencies of high $PM_{2.5}$ days occurring at the four stations are summarized in Table 5.1. Table 5.2 lists the number of days at Milwaukee and Mayville with $O_3 > 0.075$ ppm. Table 5.3 lists the days when both $PM_{2.5}$ exceeds 35 $\mu g/m^3$ and O_3 exceeded the 0.070 ppm.

Table 5.1. Frequency of above designated concentration (2002 to 2009) at each station

Stations and sampling interval	≥35 $\mu g/m^3$				30 ~ 35 $\mu g/m^3$				25 ~ 30 $\mu g/m^3$			
Milwaukee (every 3rd day) (From 2002 to 2009)	21				15				38			
	Win	Spr	Su	Fall	Win	Spr	Su	Fall	Win	Spr	Su	Fall
	11	2	3	5	6	1	3	5	5	8	14	11
Mayville (every 3rd day) (From 2002 to 2009)	15				10				23			
	Win	Spr	Su	Fall	Win	Spr	Su	Fall	Win	Spr	Su	Fall
	7	4	2	2	6	2	0	2	4	5	7	7
Waukesha (every 6th day) (From 2002 to 2009)	11				9				22			
	Win	Spr	Su	Fall	Win	Spr	Su	Fall	Win	Spr	Su	Fall
	6	1	3	1	2	3	1	3	2	3	7	10
Perkinstown (every 6th day) (From 2005 to 2009)	3				7				6			
	Win	Spr	Su	Fall	Win	Spr	Su	Fall	Win	Spr	Su	Fall
	1	1	1	0	1	2	4	0	2	0	2	2

Table 5.2. Elevated Ozone Days

Stations (sampling interval)	≥0.075 ppm	0.075 > ppm O_3 ≥ 0.070 ppm	0.070 ppm > O_3 ≥ 0.065 ppm
Milwaukee (Maximum 8hr)	15	5	20
Mayville (Maximum 8hr)	4	5	5

Table 5.3. Elevated both $PM_{2.5}$ and O_3 (2002 to 2009) days at Milw and Mayv stations:

Station	Milwaukee	Mayville

Date	6/27/05	5/30/07	9/8/02	8/2/05	9/10/05	6/27/05	8/2/05	9/3/04
$PM_{2.5}$($\mu g/m^3$)	48.1	47.4	43.2	41.9	38.0	43.8	36.3	35.6
Ozone (ppm)	0.096	0.079	0.093	0.102	0.082	0.0875	0.07	0.070

At the stations of Wauk and Perk, samples were taken every 6th day. O_3 samples were not collected at station Perk. This study focuses mainly on the variations of characteristics and trends between Milwaukee and Mayville areas, an urban and industrial area and an agricultural area, respectively. Conditions in Waukesha and Perkinstown are used for comparing the different local impact.

Table 5.4 and 5.5 are the mean concentrations of all $PM_{2.5}$, its major components, aerosol acidities (Normal mean) at Milwaukee and Mayville and the means of same parameters for the days when the $PM_{2.5}$ is ≥ 35 $\mu g/m^3$ (35 mean) and the means for the days when $PM_{2.5}$ is between 30 $\mu g/m^3$ and 35 $\mu g/m^3$ (30 mean).

Table 5.6 to 5.8 (after the Reference of this Chapter) lists the seasonal mean concentrations of $PM_{2.5}$, its major components, as well as the associated aerosol acidities at each station and the same parameters for the days with elevated $PM_{2.5}$ and O_3 at the four stations.

Table 5.4. Seasonal Means of Normal, ≥35 and between 30 and 35 _ Milwaukee

Season	**Winter**	**Mean35**	**Mean30**	**Spring**	**Mean35**	**Mean30**	**Summer**	**Mean35**	**Mean30**	**Fall**	**Mean35**	**Mean30**
PM$_{2.5}$	13.629	39.891	32.917	10.127	42.350	30.500	11.957	42.667	30.767	11.140	39.820	31.600
Ozone	0.024	0.017	0.013	0.041	0.079	0.047	0.047	0.087	0.055	0.031	0.047	0.031
SO$_4$	0.022	0.051	0.060	0.022	0.117	0.097	0.030	0.189	0.088	0.025	0.137	0.084
NO$_3$	0.072	0.258	0.206	0.039	0.145	0.168	0.014	0.037	0.020	0.033	0.113	0.073
NH$_4$	0.109	0.391	0.334	0.075	0.398	0.360	0.060	0.364	0.163	0.073	0.354	0.230
Anions	0.116	0.360	0.327	0.083	0.380	0.361	0.074	0.414	0.196	0.083	0.387	0.242
EC	0.478	1.085	0.772	0.392	0.696	0.631	0.518	0.987	0.484	0.629	1.274	1.126
OC	3.522	5.878	5.455	3.090	8.285	4.260	4.771	7.107	7.187	3.838	7.932	6.730
NH4mn	0.881	1.080	1.022	0.833	1.049	0.996	0.721	0.902	0.740	0.822	0.931	0.937
NO$_3$/SO$_4$	1.675	2.720	1.925	0.883	0.779	0.867	0.292	0.165	0.109	0.792	0.834	0.949
NH$_4$/SO$_4$	2.400	4.039	2.986	1.588	1.879	1.860	0.933	1.062	0.829	1.486	1.769	1.796
H_ar	0.011	0.026	0.030	0.011	0.059	0.048	0.015	0.094	0.044	0.012	0.069	0.042
H_aer	0.007	-0.030	-0.007	0.009	-0.019	0.001	0.014	0.050	0.033	0.010	0.033	0.012
T	270.0	272.9	272.3	280.9	290.0	284.7	294.6	297.9	297.2	284.8	290.6	288.8
DPT	265.5	269.8	269.8	274.5	285.0	277.6	288.1	290.8	290.9	278.8	286.1	283.1
WBT	268.7	271.8	271.4	278.1	287.0	281.1	290.7	293.2	293.2	281.9	287.9	286.0
RH	0.718	0.808	0.836	0.672	0.747	0.629	0.687	0.661	0.686	0.692	0.761	0.717
S	0.681	1.608	1.892	0.692	3.635	2.980	0.996	6.147	2.927	0.809	4.090	2.711
Al	0.015	0.010	0.011	0.024	0.041	0.007	0.035	0.009	0.108	0.022	0.014	0.016
Ca	0.031	0.055	0.044	0.036	0.077	0.041	0.045	0.106	0.096	0.044	0.071	0.089
Si	0.037	0.064	0.053	0.067	0.159	0.084	0.077	0.023	0.100	0.055	0.101	0.143
Ti	0.003	0.004	0.004	0.003	0.011	0.003	0.004	0.011	0.005	0.003	0.004	0.008
Fe	0.065	0.147	0.178	0.071	0.182	0.120	0.086	0.241	0.077	0.091	0.202	0.183
K	0.050	0.086	0.108	0.042	0.084	0.115	0.106	0.094	2.054	0.052	0.194	0.121
Cu	0.003	0.005	0.005	0.003	0.015	0.002	0.005	0.006	0.032	0.004	0.008	0.015
Cr	0.004	0.002	0.015	0.003	0.005	0.001	0.003	0.008	0.002	0.003	0.001	0.010
Zn	0.014	0.035	0.045	0.011	0.021	0.028	0.012	0.037	0.025	0.015	0.042	0.032
As	0.001	0.001	0.002	0.001	0.001	0.002	0.001	0.001	0.004	0.001	0.006	0.002
Se	0.001	0.001	0.003	0.001	0.002	0.004	0.001	0.003	0.002	0.001	0.004	0.004
Br	0.004	0.005	0.005	0.004	0.014	0.004	0.010	0.016	0.036	0.005	0.010	0.005
Cl	0.052	0.073	0.074	0.011	0.019	0.065	0.011	0.025	0.526	0.013	0.146	0.018
Co	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
Pb	0.004	0.007	0.008	0.004	0.011	0.007	0.005	0.012	0.014	0.004	0.030	0.011
Mn	0.005	0.018	0.013	0.004	0.014	0.006	0.005	0.022	0.008	0.006	0.015	0.007
Ni	0.001	0.001	0.003	0.001	0.002	0.000	0.002	0.006	0.001	0.001	0.002	0.005
Sr	0.001	0.002	0.001	0.001	0.002	0.001	0.002	0.002	0.028	0.001	0.003	0.002
V	0.001	0.001	0.002	0.001	0.002	0.002	0.002	0.001	0.008	0.002	0.002	0.002

Table 5.5. Seasonal Means of Normal, ≥35 and between 30 and 35 _ Mayville

Season	**Winter**	**Mean35**	**Mean30**	**Spring**	**Mean35**	**Mean30**	**Summer**	**Mean35**	**Mean30**	**Fall**	**Mean35**	**Mean30**
PM$_{2.5}$	12.766	39.643	31.900	10.473	39.500	32.450	10.772	49.867	31.90	10.400	42.200	32.550
Ozone	0.031	0.031	0.027	0.046	0.047	0.060	0.049	0.072	0.027	0.036	0.044	0.081
SO$_4$	0.021	0.054	0.044	0.024	0.045	0.086	0.029	0.170	0.044	0.028	0.114	0.154
NO$_3$	0.077	0.271	0.227	0.045	0.089	0.149	0.016	0.039	0.227	0.037	0.199	0.042
NH$_4$	0.110	0.395	0.322	0.087	0.184	0.325	0.068	0.340	0.322	0.085	0.444	0.328
Anions	0.118	0.379	0.315	0.093	0.179	0.321	0.075	0.379	0.315	0.093	0.427	0.351
EC	0.266	0.520	0.432	0.240	0.293	0.425	0.265	0.481	0.432	0.339	1.127	0.631
OC	2.315	4.186	3.700	2.414	4.570	5.130	3.613	4.533	3.700	2.831	6.175	5.535
NH4mn	0.880	1.037	1.017	0.886	0.957	1.012	0.847	0.914	1.017	0.857	1.045	0.937
NO$_3$/SO$_4$	1.845	2.581	2.870	0.928	1.009	0.913	0.345	0.161	2.870	0.892	1.865	0.138
NH$_4$/SO$_4$	0.880	3.724	3.960	0.886	1.933	1.930	0.847	1.069	3.960	0.857	3.222	1.066
H_ar	0.010	0.027	0.022	0.012	0.023	0.043	0.015	0.085	0.022	0.014	0.057	0.077
H_aer	0.008	-0.017	-0.007	0.007	-0.005	-0.004	0.007	0.039	-0.007	0.008	-0.017	0.022
T	268.0	271.0	272.0	280.2	284.7	286.7	294.0	297.3	272.0	283.8	287.1	298.1
DPT	264.0	268.0	268.9	273.7	277.0	281.1	287.9	291.3	268.9	278.5	282.9	291.7
WBT	266.9	269.9	270.9	277.4	280.9	283.7	290.3	293.3	270.9	281.1	284.8	293.9
RH	0.742	0.292	0.291	0.670	0.291	0.290	0.707	0.291	0.291	0.722	0.292	0.293
s	0.653	1.699	1.387	0.745	1.456	2.525	0.967	5.427	1.387	0.885	3.505	5.100
Al	0.016	0.040	0.032	0.019	0.038	0.009	0.025	0.008	0.032	0.016	0.044	0.008
Ca	0.026	0.035	0.046	0.023	0.029	0.031	0.028	0.041	0.046	0.034	0.049	0.077
Si	0.029	0.041	0.044	0.064	0.079	0.088	0.058	0.062	0.044	0.045	0.076	0.079
Ti	0.003	0.004	0.003	0.003	0.003	0.002	0.003	0.003	0.003	0.003	0.005	0.005
Fe	0.029	0.064	0.107	0.033	0.043	0.067	0.035	0.050	0.107	0.034	0.103	0.087
k	0.057	0.078	0.081	0.040	0.057	0.083	0.052	0.051	0.081	0.044	0.106	0.076
Cu	0.002	0.004	0.004	0.003	0.002	0.002	0.004	0.010	0.004	0.002	0.010	0.002
Cr	0.003	0.003	0.015	0.002	0.001	0.001	0.003	0.001	0.015	0.002	0.002	0.002
Zn	0.008	0.022	0.019	0.007	0.009	0.018	0.006	0.009	0.019	0.008	0.036	0.019
As	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.002	0.001	0.001	0.003	0.003
Se	0.001	0.001	0.002	0.001	0.001	0.001	0.001	0.002	0.002	0.001	0.005	0.003
Br	0.002	0.004	0.006	0.003	0.002	0.004	0.002	0.003	0.006	0.002	0.006	0.004
Cl	0.022	0.045	0.059	0.011	0.019	0.033	0.006	0.014	0.059	0.015	0.664	0.005
Pb	0.003	0.004	0.005	0.004	0.005	0.004	0.004	0.003	0.005	0.004	0.015	0.004
Mn	0.002	0.004	0.005	0.002	0.002	0.003	0.002	0.002	0.005	0.002	0.004	0.004
Ni	0.001	0.002	0.004	0.001	0.001	0.001	0.001	0.001	0.004	0.001	0.002	0.001
Sr	0.001	0.001	0.002	0.001	0.001	0.001	0.001	0.001	0.002	0.001	0.003	0.002
V	0.001	0.001	0.001	0.001	0.001	0.003	0.002	0.002	0.001	0.001	0.002	0.002

- Discussion:

Frequency: The elevated $PM_{2.5}$ episodes had happened more often at each season in Milwaukee area than that happened in Mayville area. At summer episodes, concentration of $PM_{2.5}$ at Milwaukee is usually higher than that in Mayville, while during winter episodes, the concentration of $PM_{2.5}$ at Milwaukee is not always higher. The high $PM_{2.5}$ and high O_3 days had occurred more often in Milwaukee than that in Mayville.

$PM_{2.5}$: For both stations, the mean concentration of $PM_{2.5}$ is the lowest in spring. However, during the episodes, the elevated concentration of $PM_{2.5}$ does not have seasonal trend, the highest could be at any season.

Sulfate: In Milwaukee area, the summer normal mean concentration of sulfate is 1.5 times that for winter normal mean concentration, while the summer 35 mean is 3.15 times of winter 35 mean. The summer 35 mean concentration of sulfate is 6.30 times of summer normal mean, while winter 35 mean is 2.73 times of winter normal mean. The sulfate means at Mayville area has a pattern similar to that in Milwaukee. The summer normal mean is 1.38 times of winter normal mean, while the summer 35 mean is 3.15 times of winter 35 mean. The summer 35 mean concentration of sulfate is 5.86 times of summer normal mean, whilewinter 35 mean is 2.38 times of winter normal mean. However, the content of sulfate at each $PM_{2.5}$ episode varies widely without seasonal correlation. Table 5.10 listed the variations in comparing the different “means”.

Nitrate: At Milw station, the winter normal mean is 5.1 times of summer normal mean and winter 35 mean is 6.97 times of summer 35 mean. Winter 35 mean is 3.6 times of winter normal mean, which summer 35 mean is 2.6 times of summer normal mean. Summer has the lowest nitrate, while winter has the highest, including the concentration during episodes. Mayv has similar patterns. The winter normal mean is 4.8 times of summer normal mean and winter 35 mean is 4.63 times of summer 35 mean. Winter 35 mean is 3.5 times of winter normal mean, while summer 35 mean is 3.5 times of summer normal mean.

Table 5.10. Variations between normal mean and episode mean for sulfate and nitrate

Sulfate	Range	Summer normal /Winter normal	Summer 35 mean /Winter 35 mean	Winter 35 mean/ Winter normal mean	Summer 35 mean / Summer normal mean
Milw	0.022 ~ 0.030 (μg/m3) (w) 0.06 ~ 0.189 (μg/m3) (s.)	1.51	3.15	2.73	6.30
Mayv	0.021 ~ 0.029 (μg/m3) (w,) 0.054 ~ 0.170 (μg/m3) (s.)	1.38	3.15	2.38	5.86
Nitrate		Winter normal / Summer normal	Winter 35 mean / Summer 35 mean	Winter 35 mean/ Winter normal mean	Summer 35 mean / Summer normal mean
Milw	0.072 ~ 0.258 (μg/m3) (w) 0.014 ~ 0.037 (μg/m3) (s.)	5.14	6.97	3.58	2.64
Mayv	0.077 ~ 0.271 (μg/m3) (w) 0.016 ~ 0.039 (μg/m3) (s.)	4.81	6.95	3.51	2.44

Note: Normal mean – the mean of all data in that season, including the episodes
35 mean – the mean of $PM_{2.5}$ whose concentration is ≥ 3.5 $\mu g/m^3$

EC: At the Milw station, for each season, the 35 mean concentration of EC is about 2 times the normal mean concentration of EC. EC emission is mainly associated with fuel consumption. The increased EC during episodes indicated two possibilities, the additional contribution from the regional emissions sources, and/or the stagnant air during the episodes caused poor dispersion and accumulations of EC in the air. The ratio of 35 mean of EC to normal mean of EC at Mayv varies from 1.22 (spring) to 3.32 (fall). Mayv station is located in an agricultural field. The higher fall ratio could be caused by the increased agricultural activities at autumn harvest season.

OC: The concentration of normal mean OC and 35 mean OC in Milw are higher than those in Mayv.

Neutralization (NH_4mn): - At Milw area, the neutralization degrees are above 80% except for summer, when it is 72%. Mayv area has higher neutralization degree.

H_aer: - For both station, the summer 35 mean has the highest H_aer

In general, the elevated $PM_{2.5}$ had happened in Milwaukee more often, with higher concentration compared with Mayville. On comparing means, there are some similarities, even though the ratios from Milwaukee are slightly higher than those in Mayville, such as seasonal 35 means for sulfate. The details of episodes listed in Table 5.6 to Table 5.9 indicate that each episode is unique. In order to have a better understanding of the major influencing factors, four types of $PM_{2.5}$ episodes are selected for further detailed discussion in the next sections.

5.4.2. **Elevated $PM_{2.5}$ Events**

5.4.2.1. **Late Spring Episode (05/30/2007)**

This is an early summer episode that covers the four stations. On 05/30/2007, $PM_{2.5}$ were 47.4 μg/m^3, 38.6 μg/m^3, 41.2 μg/m^3 and 41.4 μg/m^3, at Milwaukee, Mayville, Waukesha and Perkinstown, respectively. Figure 5.1 illustrates the air parcel movement on 05/30/2007 and between 05/15/2007 to 05/30/2007 to stations of Milw (latitude: 43.000; longitude: -87.735), Mayv (latitude: 43.439; longitude: -88. 528), and Perk (latitude: 45.204; longitude: -90.600). Figure 5.1-1 is for the 3-day back trajectories from stations Milw, Mayv and Perk from 05/27/2007 to 05/30/2007. Figure 5.1-2 is frequency map for the 2-day back trajectories from station Perk from 05/15/2007 to 05/31/2007. Figure 5.1-3 and Figure 5.1-4 are the are frequency maps by 2-day back trajectories from stations Milw and Mayv, respectively.

Table 5. 10 lists the compostion of $PM_{2.5}$ collected on 05/30/2007.

Table 5.11. The compostion of elevated $PM_{2.5}$ from four stations on 05/30/2007

	$PM_{2.5}$	**Ozone**	**SO_4**	**NO_3**	**NH_4**	**Anions**	**EC**	**OC**	**NH_4mn**	**NH_4/SO_4**	**H_ar**	**RH**	**T**
Milw	47.4	0.079	0.152	0.068	0.382	0.372	0.912	10.1	1.026	1.257	0.076	0.635	295.6
Mayv	38.6	0.068	0.108	0.047	0.294	0.264	0.398	10.2	1.116	1.360	0.054	0.662	297.0
Wauk	41.2	0.066	0.111	0.043	0.279	0.266	0.678	11.8	1.052	1.254	0.056	0.653	296.7
Perk	41.4	na	0.060	0.018	0.134	0.137	0.387	8.15	0.976	1.121	0.030	0.827	294.2

The frequency map identifies the areas where the trajectories have frequently passed before the episode. The frequecncy map is used in this study to explore possible emission source regions that had bult up the background concentration at Milwaukee, Mayville, Waukesha and Perkinstown before the episode. From Figure 5.1- 2, for Perk, the areas where trajectories passing more than 10% are: Minnesota, Iowa, middle part of Missouri and northwestern

Wisconsion. The >1% frequency trajectories were started from Gulf Mexico states: Texas, louisiana, Mississipi and Alabama.

Back trajetory (BT) here is used to trace the emission source region of the episode. The 3-days back trajectory started from Perk at the day of the episode ended at Gulf of Mexico. In another words, the trajectory started from Gulf of Mexico three days before the episode, passing Louisiana, Okaloma, Missouri, Iowa then entered Perk at 05/30/2007. For convenience, all the back trajectories are described from its endpoint.

From Figure 5.1-3, for Milw, the areas where more than 10% of trajectories have passed are: Illinois, northwestern corner of Indiana, southeastern corner of Missori and southeastern Wisconsin, including Lake Michigan. The >1% trajectories have passed area covers Gulf of Mexico, Texas, Louisiana, Mississipi, Alabama and northern Florida. The 3-days back trajectory from Milw started from Gulf of Mexico, passing Louisiana, Arkansas, Tennessee, Kentucky, Illinois, Indiana, Ohio then along the IL and IN border, Lake Michigan, then entered Milwaukee.

From Figure 5.1-4, for Mayv, the areas where more than 10% of trajectories had passed are: Minnisota, Illinois, southeastern corner of Missori and south-central Wisconsin, including Lake Michigan. The >1% of trajectories had passed are from Gulf Mexico, Louisiana, Mississipi, Alabama, Missouri and Iowa. The 3-day back trajectory started from Mayv started from Mississippi, passing Louisiana, Arkansas, Missouri, Illinois, Indiana, back to IL, then entered Mayv.

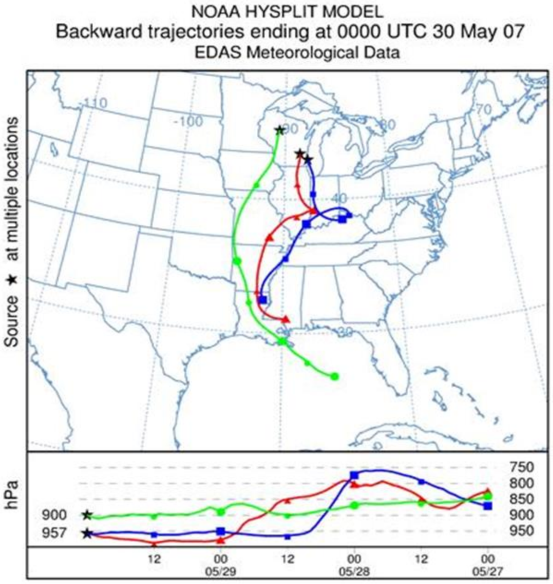


Figure 5.1-1 HYSPLIT Trajectories, blue, Milwaukee; red, Mayville; green, Perkinstown

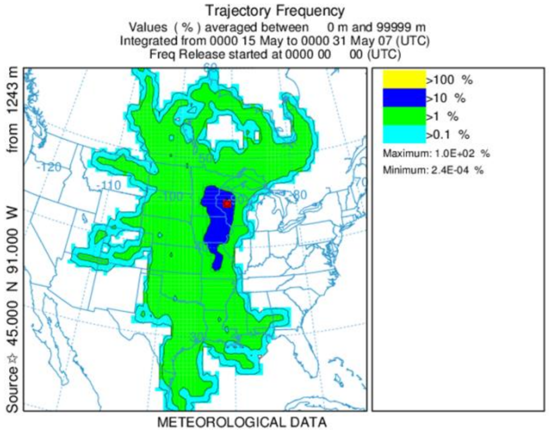


Figure 5.1-2 Perkinstown

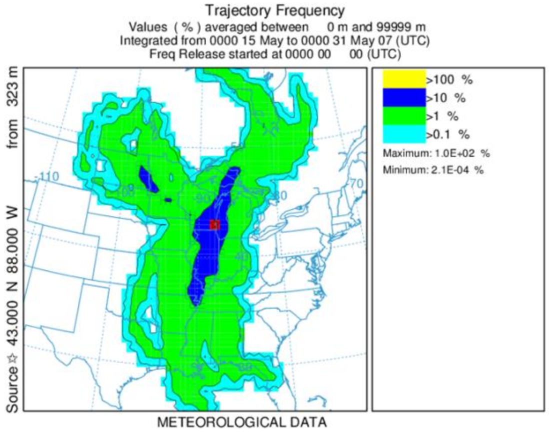


Figure 5.1-3 Milwaukee

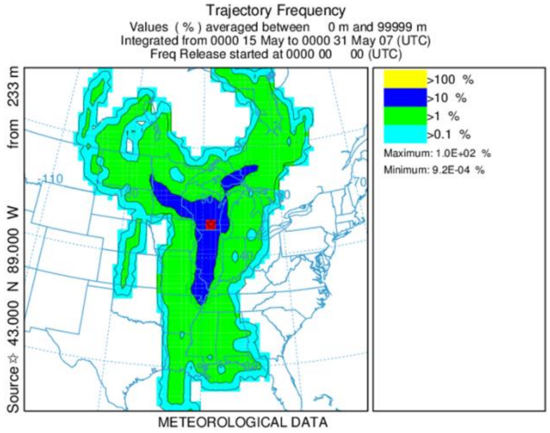


Figure 5.1-4 Mayville

Figure 5.1 Early Summer Elevated $PM_{2.5}$ Event _ 05/30/2007

The different pathes very well explained why the composition of the $PM_{2.5}$ for Perk was so different from the compostion for Milw and Mayv and why Milw and Mayv had so higher concentration of sulfate. This back trajectory towards to Milwaukee had passed all the high SO_2 sources in that region, Ohio valley, northern Illinoi and Indiana. This could explain why the molar SO_4 content was so high (0.152 mole/m^3). Earlier data (1999 to 2002) indicated that the high sulfate days in most of the urban areas were associated with trajectories that passed through the Ohio River Valley and the high sulfate in Milwaukee was influenced by emissions from northern Illinois and Indiana (LADCO, 2003).

The air parcel toward Mayv avoided these two famous sulfate emissions areas, but still passed the industrial areas and picked up the emissions from the industries at Missouri and Illinois. All three trajectories had passed Gulf of Mexico and several oil states, which well explained the high OC content in the $PM_{2.5}$. This episode carried the highest OC content when compared with other episodes.

5.4.2.2. **Winter Episode (02/24/2008)**

This is a winter episode. During the 02/24/2008 episode, $PM_{2.5}$ were 36 µg/m^3, 42.7 µg/m^3, 35.6 µg/m^3 and 40.2 µg/m^3, at Milwaukee, Mayville, Waukesha and Perkinstown, respectively. Figure 5.2 illustrates the air parcel movements on 02/24/2008 and between 02/03/2008 to 02/27/2008 from stations of Milw (latitude: 43.000; longitude: -87.735), Mayv (latitude: 43.439; longitude: -88. 528), and Perk (latitude: 45.204; longitude: -90.600). Figure 5.2-1 is for the 3-day back trajectories from stations Milw, Mayv and Perk from 02/03/2008 to 02/27/2008. Figure 5.2-2 is frequency map for the 2-day back trajectories from station Perk from 02/03/2008 to 02/27/2008. Figure 5.2-3 and Figure 5.2-4 are the are frequency maps by 2-day back trajectories from stations Milw and Mayv, respectively. Table 5.12 listed the composition of $PM_{2.5}$ collected on 02/24/2008

Table 5.12. The compostion of elevated $PM_{2.5}$ on 02/24/2008

	$PM_{2.5}$	SO_4	NO_3	NH_4	Anions	EC	OC	NH_4mn	NH_4/SO_4	H_ar	RH	T
Milw	36	0.063	0.258	0.412	0.385	0.553	4.36	1.072	3.253	0.032	0.706	269.7
Mayv	42.7	0.066	0.306	0.476	0.438	0.338	3.93	1.086	3.608	0.033	0.291	267.8
Wauk	35.6	0.057	0.237	0.360	0.351	0.391	4.24	1.025	3.159	0.028	0.807	267.8
Perk	40.2	0.060	0.339	0.487	0.458	0.421	4.03	1.062	4.073	0.030	0.812	268.2

From Figure 5.2-2, for Perk, the areas where more than 10% of trajectories have passed are: Minnisota, Iowa and northwestern Wisconsin. The >1% of trajectories have passed areas are Iowa and Missouri. The 3-day back trajectory before the episode started from southwestern Wisconsin, passing Iowa, Minnesota, then enters Perk.

From Figure 5.2-3, for Milw, the areas where more than 10% of trajectories had passed are: Most part of Wisconsin, eastern Iowa and northern Illinois. The >1% trajectories are Iowa and Missouri, IL, IN and OH. The 3-day back trajectory started from northern Indiana, passing northern Illinois, then southwestern Wisconsin.

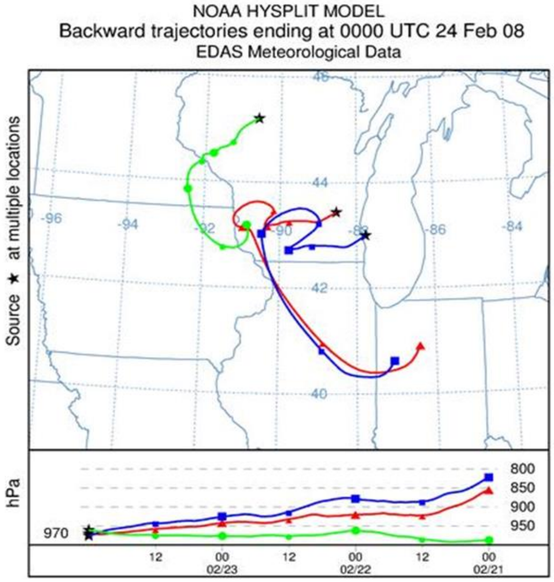


Figure 5.2-1 HYSPLIT Trajectories, blue, Milwaukee; red, Mayville; green, Perkinstown

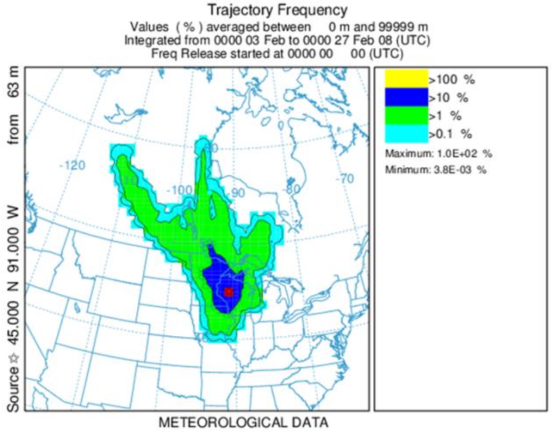


Figure 5.2-2 Perkinstown

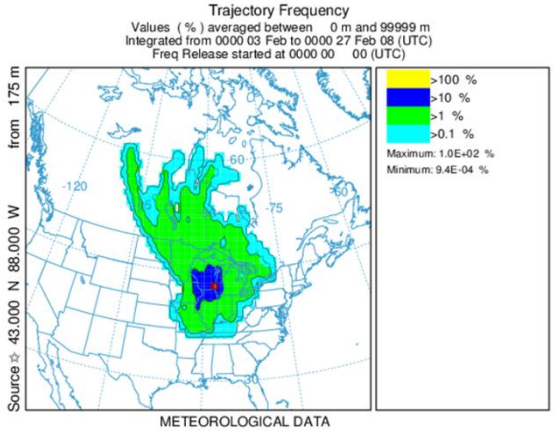


Figure 5.2-3 Milwaukee

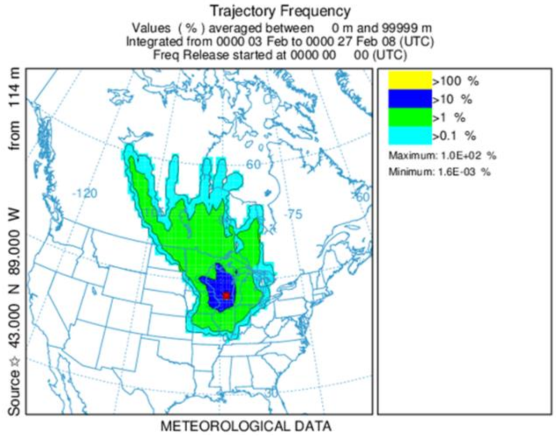


Figure 5.2-4 Mayville

Figure 5.2 Winter Elevated $PM_{2.5}$ Event _ 02/24/2008

From Figure 5.2-4, for Mayv, the areas where more than 10% trajectories have passed are: Most part of Wisconsin, eastern Iowa and northern Illinois. The area where >1% trajectories have passed are Iowa, Missouri, IL, IN and MI. The 3-day back trajectory of episode is similar to the one from station Milw, except for the part in southwestern Wisconsin.

In this episode, the concentration of $PM_{2.5}$ at Mayv and Perk were higher than that in Milw and Wauk. Comparing the four back trajectories, the travel in southwester part of Wisconsin of the air parcels from Mayv and Perk may have brought higher concentration of $PM_{2.5}$ to Mayv and Perk – if other conditions are all same, the impact from local source is larger than that from a distant emissions source (eq for dispersion model). The largest uncertainty in Upper Midwest winter episode is the emission of NH3 and the partitioning of NH_3 to $NH4^+$ as indicated in LADCO's 2009 study, "the variability in NH_3 emissions, the balance of daytime and nighttime nitrate production, NOx control or nitrate control and how the snow and fog affect the formation of $PM_{2.5}$ (LADCO, 2010)".

From the trajectory map, this episode does not involve long distance transported primary air pollutants. This is a an example of how the winter low-pressure system raised the concentration of locally emitted primary air pollutants in urban and rural area, as well as how the preferential partitioning and the nighttime chemical reactions enhanced the formation of secondary nitrate and ammonium aerosols in the whole region.

The trajectories initiated at the regions with significant emission sources of SO_2 and NOx, like the northern Illinois and Indiana. Once the acids in the air arrived at the regions with NH_3 emission sources, the SO_4^{2-} and NO_3^- not only react with NH_4^+ to form $PM_{2.5}$, the acidic environment being favorable to more NH_3 release from manure.

5.4.2.3. **Summer Episodes (06/27/2005 and 08/02/2005)**

06/27/2005 and 08/02/2005 are the two episode with exceedence of both $PM_{2.5}$ and O_3. Table5.13 listed the composition of $PM_{2.5}$ and O_3 collected on 06/27/2005 and 08/02/2005.

Table 5.13. The composition of $PM_{2.5}$ when both $PM_{2.5}$ and O_3 are high

		$PM_{2.5}$	**O_3**	**SO_4**	**NO_3**	**NH_4**	**Anions**	**EC**	**OC**	**NH_4mn**	**NH_4/SO_4**	**H_ar**	**RH**	**T**
06/27/05	Milw	48.1	0.096	0.237	0.033	0.456	0.507	1.17	8.7	0.899	0.961	0.119	0.628	300.4
06/27/05	Mayv	43.8	0.088	0.231	0.030	0.452	0.492	0.499	5.26	0.919	0.979	0.116	0.291	301.1
08/02/05	Milw	41.9	0.102	0.249	0.016	0.414	0.514	1.17	6.83	0.806	0.832	0.124	0.630	300.1
08/02/05	Mayv	36.3	0.070	0.199	0.031	0.350	0.428	0.523	5.02	0.818	0.881	0.099	0.292	299.5

Figure 5.3 illustrates the air parcel movements on 06/27/2005, between 06/24/2005 to 06/30/2005 and between 06/12/2005 to 06/29/2005 from stations of Milw (latitude: 43.000; longitude: -87.735) and Mayv (latitude: 43.439; longitude: -88. 528). Figure 5.3-1 is for the 3-day back trajectories from stations Milw, Mayv and Perk from 06/24/2005 to 06/27/2005. Figure 5.3-2 is the frequency map for the 2-day back trajectories from station Milw from 06/24/2005 to 06/30/2005. Figure 5.3-3 and Figure 5.3-4 are the frequency maps by 2-day back trajectories from stations Milw and Mayv from 06/12/2005 to 06/29/2005, respectively.

Figure 5.4 illustrates the air parcel movements on 08/02/2005, between 07/17/2005 to 08/05/2005 from station Mayv (latitude: 43.439; longitude: -88. 528) and between 07/03/2005 to 07/31/2005 and between 08/01/2005 to 08/05/2005 from stations of Milw (latitude: 43.000; longitude: -87.735). Figure 5.4-1 is for the 3-day back trajectories from stations Milw, Mayv and Perk from 07/30/2005 to 08/02/2005. Figure 5.4-2 is frequency map for the 2-day back trajectories from station Mayv from 07/17/2005 to 08/02/2005. Figure 5.4-3 and Figure 5.4-4 are the frequency maps by 2-day back trajectories from station Milw from 07/03/2005 to 07/31/2005 and from 08/01/2005 to 08/05/2005, respectively.

Compare Table 5.12 with Table 5.11 (05/30/ 2007), we can see that at these two episodes sulfate is almost doubled, nitrate is almost halfed, particles were less neutralized, more acidic and EC was up 20 ~ 30%. The temperature were about 4°F higher and RH is relatively lower. 06/27/2005 had higher $PM_{2.5}$ and OC than that on 08/02/2005. This could be caused by both the accumulations before the episode and the path of the air parcel at the day of the episode. Milw had higher concentration of $PM_{2.5}$ and O_3 and other $PM_{2.5}$ components than those in Mayv.

During these two episodes, the higher temperature (301°K) created an increase in electricity demand for air conditioning. The higher energy consumption led to more fossil fuel combustion (EC up 20 ~ 30%) and therefore, more SO_2 emissions. In addition to the higher concentration of OH under warm temperature, strong summer sunlight is favored SO_4^{2-} formation. From the frequency map, the >10% of trajectories have passed the higher SO_2 emission source region, like northern Illinois, northern Indiana and southeastern Wisconsin. The higher frequency (>10%) trajectories had also passed the major NH_3 emission source region, like Iowa, Missouri and southern Wisconsin. The highly acidic gasses and particles would have reacted with the NH_3/NH_4^+ to form ammonium sulfate. The acidic atmosphere is also favored the release of NH_3.

It was observed in 1970s that Midwestern sulfate source areas are a major cause of widespread summertime haze in the eastern U.S (Ferman et al., 1981; Wolff et al., 1981, 1982). Even though SO_2 emissions decreased significantly over Midwestern and Northeastern US since a 1990s, the continued population growth and demand for energy has caused the haze to remain problem in the region. The satellite-based Moderate Resolution Imaging Spectroradiometer (MODIS) monitored the haze building up in Midwest and moving to Northeast during the June 20 to 28, 2002 events (Engel-Cox et al., 2004). Elevated concentrations of ozone, sulfate, and particulate organic carbon have been observed frequently in Southeastern US since 1999 (Blanchard et al., 2013).

From Figure 5.3-1, the 3-day back trajectory from Milwaukee was initiated from northeastern of Oklahoma, crossed Missouri, themiddle of IL, Lake Michigan, and then entered Milwaukee. The 3-day back trajectory from Mayville was initiated from southwestern IL, crossing northern IL, Lake Michigan, then went to Mayville. The frequency maps for Milwaukee and Mayville are similar, covering eastern Iowa, northern IL, part of Lake Michigan and southeastern Wisconsin.

From Figure 5.4-1, the 3-day back trajectory from Milwaukee was initiated in northeaster Minnesota, passed northern IN, northern IL, and then entered Milwaukee. The 3-day trajectory from Mayville was initiated in northern IN, crossed IL, and then entered southern WI. The frequency maps for Milw and Mayv are similar, covering northern IL, northwestern IN and southeastern WI (see 5.3-2 for Mayville). Figure 5.4-3 covers the area of >10% trajectories have passed from July 3 to July 31, 2005 and Figure 5.4-4 covers the area of >10% trajectories have passed from Aug 1 to Aug 5, 2005, both of these figures are for Milwaukee. The difference of these two maps indicated that more trajectories came from IL and IN as well as part of Missouri the days before the Aug. 2 episode.

The higher temperature and RH are the favored conditions for SOA formation. Studies have revealed that the changes in temperature, wind speed, relative humidity (RH), mixing height, and

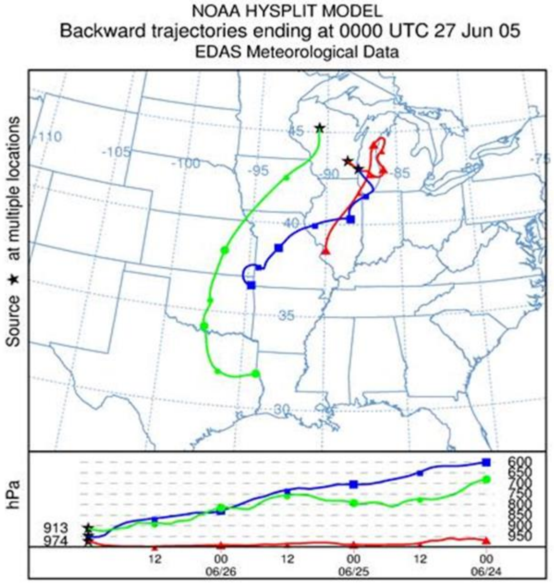


Figure 5.3-1 HYSPLIT Trajectories, blue, Milwaukee; red, Mayville; green, Perkinstown

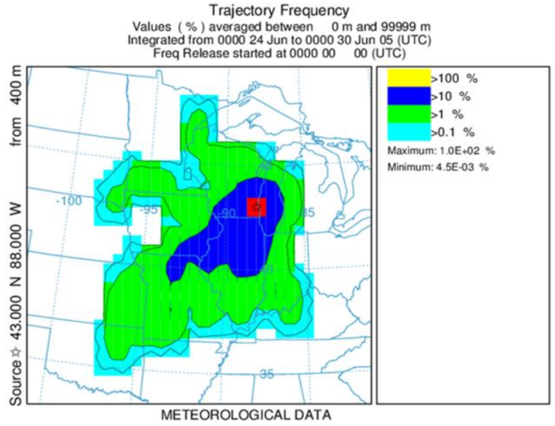


Figure 5.3-2 Milwaukee

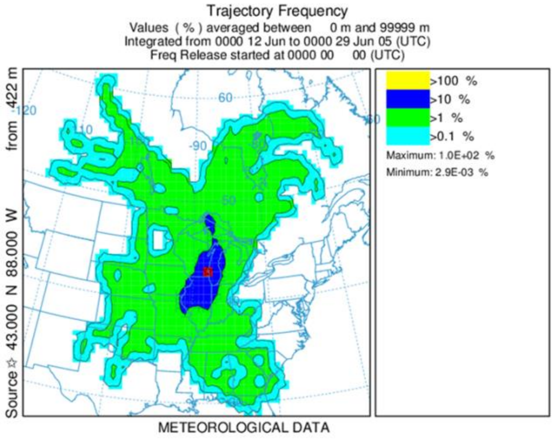


Figure 5.3-3 Milwaukee

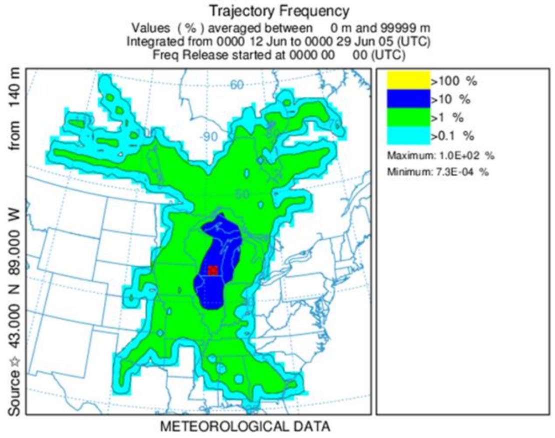


Figure 5.3-4 Mayville

Figure 5.3. Summer episode with both higher $PM_{2.5}$ and O_3 _ 06/27/2005

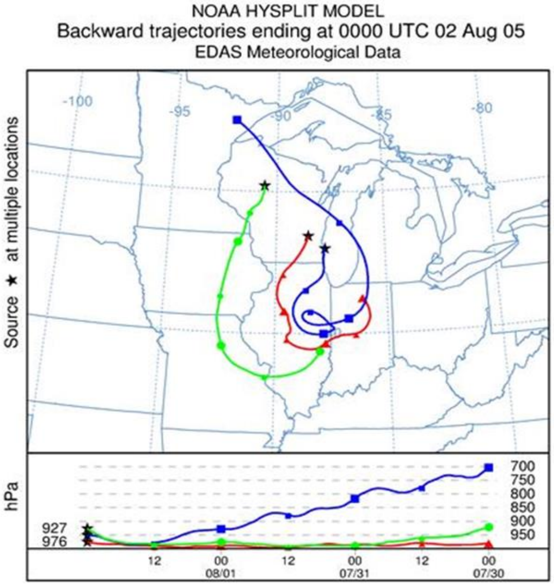


Figure 5.4-1 HYSPLIT Trajectories, blue, Milwaukee; red, Mayville; green, Perkinstown

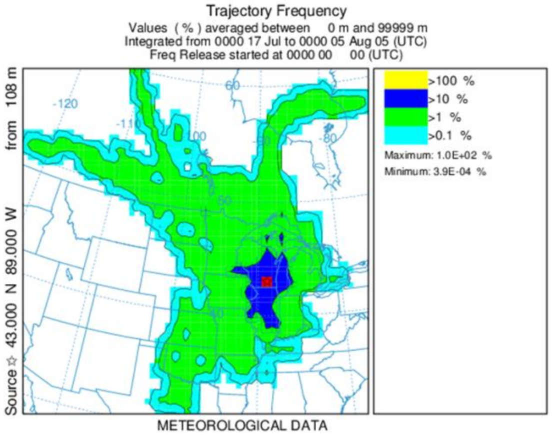


Figure 5.4-2 Mayville

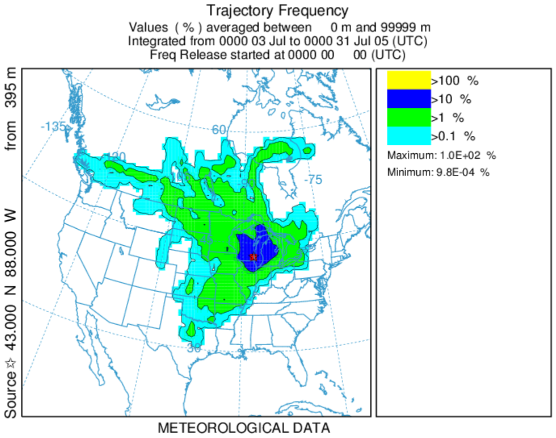


Figure 5.4-3 Milwaukee before 08/02/2005

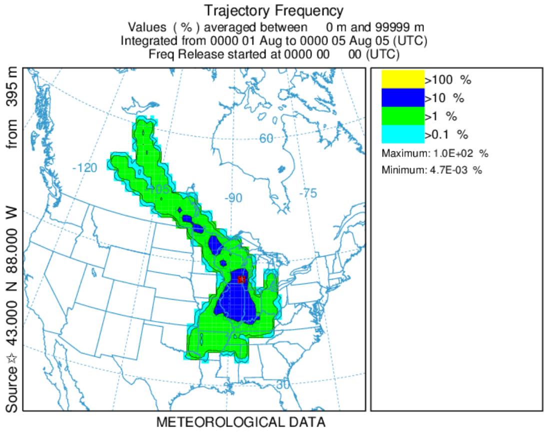


Figure 5.4-4 Milwaukee around 08/02/2005

Figure 5.4. Summer episode with both higher PM2.5 and O3 _ 08/02/2005

precipitation and air circulations have the strongest effects on changes in $PM_{2.5}$ concentrations (Tai et al., 2010). Temperature plays a significant role in air pollution through its effect on emission of biogenic organic compounds (precursors for secondary organic compound and O_3), on formation of sulfate and nitrate (secondary inorganic compound) of $PM_{2.5}$ and its effect on chemical reaction rate (Dawson et al., 2007; Stelson and Seinfeld, 1982). Gao, et al found from their study on air qualities during two haze days in Beijing that both the low wind speed and high relative humidity were in favor of the accumulation of locally emitted and regionally transported air pollutants from anthropogenic sources, as well as the formation of secondary $PM_{2.5}$ in the air (Gao et al., 2015).

The higher O_3 is an indicator that SOA is higher too. The formation of SOA is much more complicated than the formation of sulfate. Larger portion of SOA is produced by atmospheric reactions involving volatile organic compounds (VOCs) (Hallquist et al., 2009), which are mainly non-methane organic compound (NMOC) of anthropogenic and biogenic origins. The major anthropogenic sources of NMOC are related to fossil fuel combustion (vehicle exhaust, heat generation, and industrial processes), storage and distribution of fuel and solvent use (Mukund et al., 1996; Theloke and Friedrich, 2007). Lab tests found that inorganic acids, such as sulfuric acid, could catalyze particle-phase heterogeneous reactions of atmospheric organic carbonyl species (Jang et al., 2003; Jang et al., 2002), under the condition of low RH and strongly acidic inorganic seed compositions (Czoschke and Jang, 2006). The acidic seed catalyzed particle phase reactions of VOC result in a substantial SOA mass growth through a series of chemical reactions (Jang et al., 2004). Higher temperature and strong sunlight create ideal conditions for the formation of sulfate and SOA and the acidic sulfate seed further catalyzed the formation of SOA. The favorable meteorological condition is one major contributor to the observed higher sulfate and OC during these high $PM_{2.5}$ and O_3 episodes. **The Trends**

5.4.3.1. **Ozone and meteorology conditions**

1. O_3 and wind direction (2005)

Figures 5.5 and 5.6 illustrate the correlation between ozone and wind direction for the data collected in Milwaukee and Mayville in 2005. For the 2002 to 2009 period, 2005 was a year when more NAAQS exceedances had occurred.

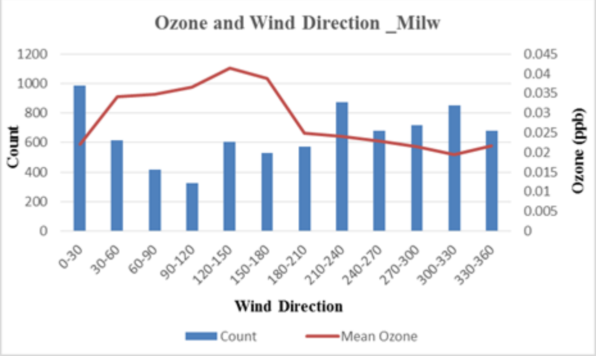


Figure 5.5 -1. Four season_Milw_2005

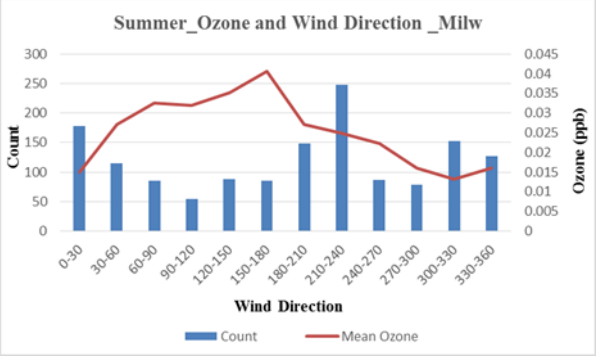


Figure 5.5 -2. Summer_Milw_2005

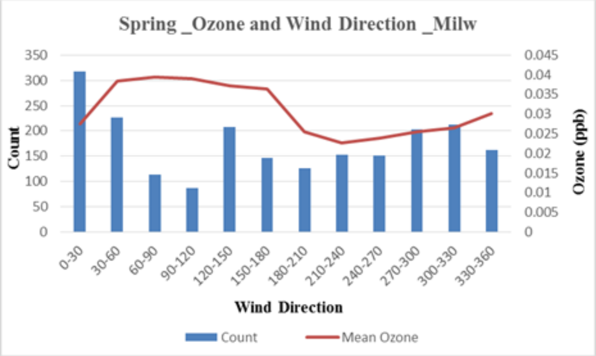


Figure 5.5 -3. Spring_Milw_2005

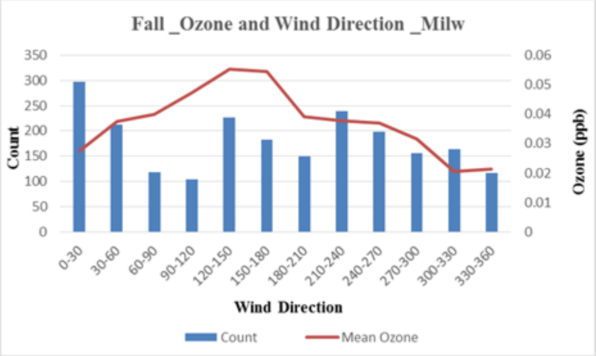


Figure 5.5 -4. Fall_Milw_2005

Figure 5.5. The concentration of Ozone and wind direction _ Milwaukee

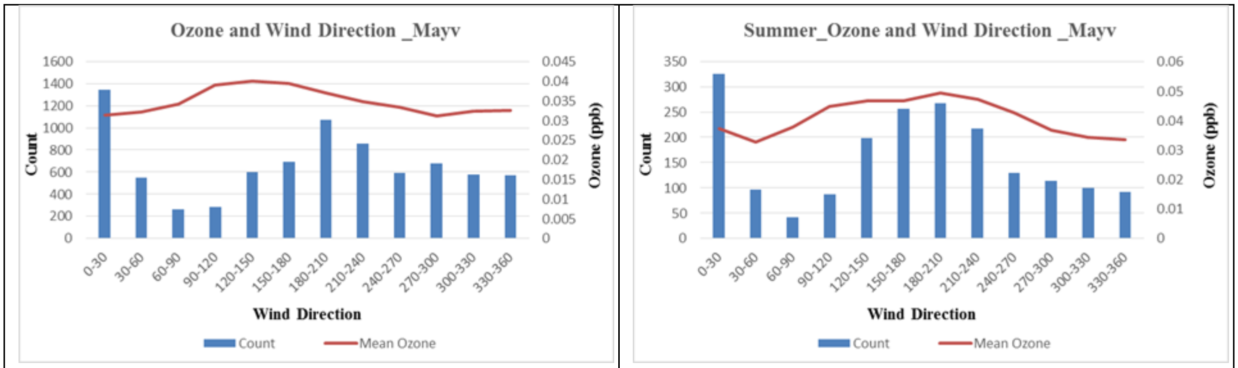


Figure 5.6 -1. Four season_Mayv_2005

Figure 5.6 -2. Summer_Mayv_2005

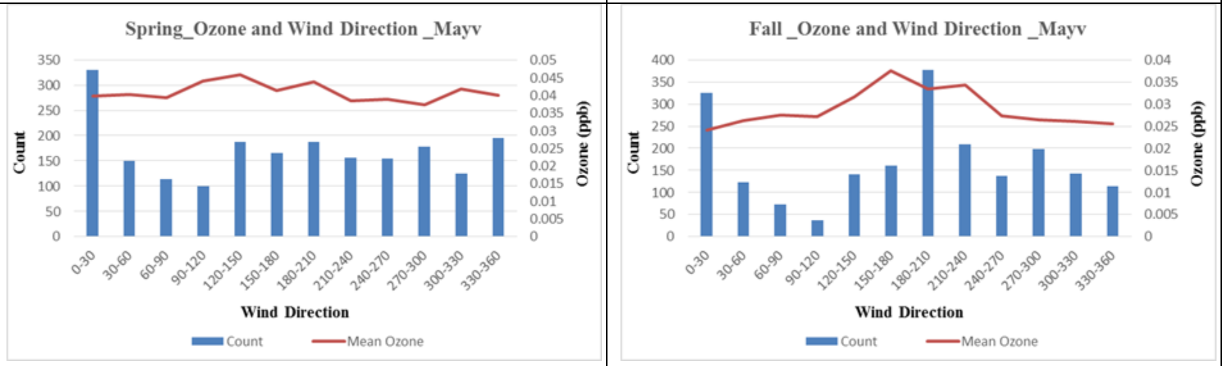


Figure 5.6 -3. Spring_Mayv_2005

Figure 5.6 -4. Fall_Mayv_2005

Figure 5.6. The concentration of Ozone and wind direction _ Mayville

Comparing Figure 5.5 with Figure 5.6, it is apparent that the concentration of ozone in Milwaukee was more sensitive to the change of wind direction than the concentration of ozone to the change of wind direction in Mayville.

In Mayville O_3 data was collected for 12- months. In spring, the response of concentration of O_3 to change in wind speed was flat. In summer and fall, there was a very mild response when wind direction is in the range 150° to 270°.

Ozone was measured from May to September in Milwaukee. Only one month's (May) data was used for spring plot and only one month (September) was used for fall plot. Looking closely at the summer correlation plot, the concentration of ozone started increasing with wind direction from 0° until 180°. From 180° to 210°, there is a sharp drop in concentration of ozone. Then slowly drops until 330°. Milwaukee is sitting on the western shoreline of Lake Michigan. This phenomena is due to the impact of "Lake Breeze". Under wind direction of 0° to 180°, air blows from Lake to the shoreline.

The lake breeze occurs when the land is warmer than the lake water and it typically begins to penetrate inland at about 8~9 AM CST (Dye et al., 1995). The land breeze develops late at about 10~11 PM CST and remains until the afternoon lake breeze is formed. The hypothesis is the morning land breeze transports ozone precursor created by rush hour traffic or emitted from industries to the lake where stable air favors the formation of ozone. Afternoon lake breezes transport the ozone back over land and cause high levels of ozone along the Lake Michigan shoreline traffic (LYONS, 1973). Lennartson and Schwartz (2002) found that 82% of ozone exceedances in Wisconsin were correlated with the lake breeze.

2. Ozone, Sulfate and OC

Sulfate, OC and O_3 collected at Milwaukee and Mayville from 2002 to 2009 were analyzed for the yearly trend. As showed in Figure 5.7, for the period of 2002 to 2009, O_3, OC and sulfate collected in Milwaukee all had the decreasing trends.

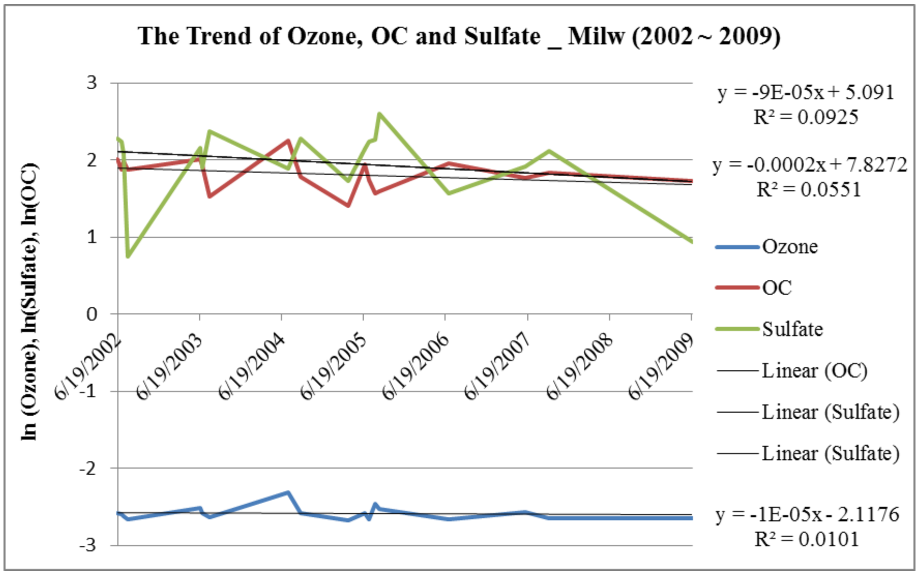


Figure 5.7. The trends of O_3, OC and Sulfate at Milwaukee (2002 to 2009)

For the period 2002 to 2013, the concentration of sulfate and O3 in Milwaukee have different trend. Sulfate is decreasing, while O3 is increasing (see Figure 5.8). The analytical method for OC has changed since 2009, so the two OC data sets are not comparable.

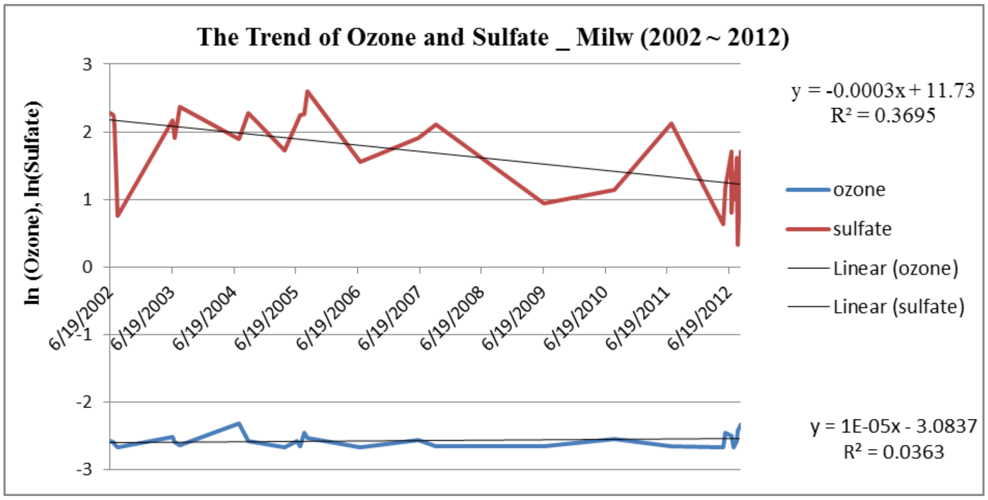


Figure 5.8. The trends of O_3 and Sulfate at Milwaukee (2002 to 2013)

For O_3, OC and sulfate collected in Mayville from 2002 to 2009, the concentrations of OC and sulfate were increasing, while O3 was decreasing.

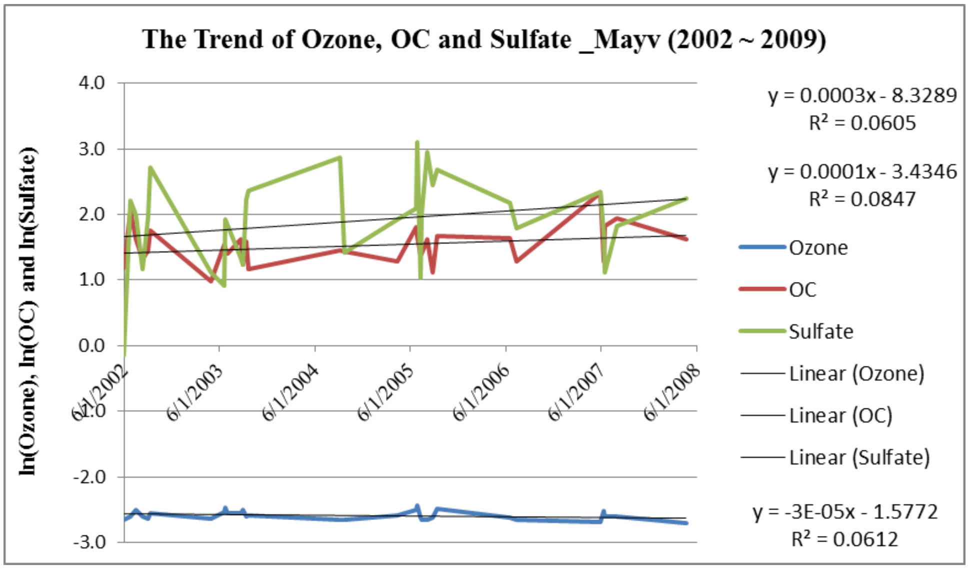


Figure 5.9. The trends of O_3, OC and Sulfate at Mayville (2002 to 2009)

From the monitoring data collected in Milwaukee, when both $PM_{2.5}$ and O_3 are high, sulfate is usually high. Studies found that urban areas are VOC limited in ozone formation and nonurban areas are NOx limited where O_3 increases with NOx and is insensitive to changes of hydrocarbons (Sillman, 1999). The higher sulfate acted as a catalyst in enhancing SOA formation at summer episodes, when other favorable conditions coexist. As discussed in Chapter 2. The future trend of $PM_{2.5}$ in Milwaukee is decreasing in sulfate and increasing in OC. These conditions support the trend of higher OC in the future.

5.4.3.2. **The Trend of Atmospheric Aerosol Acidity During Episodes**

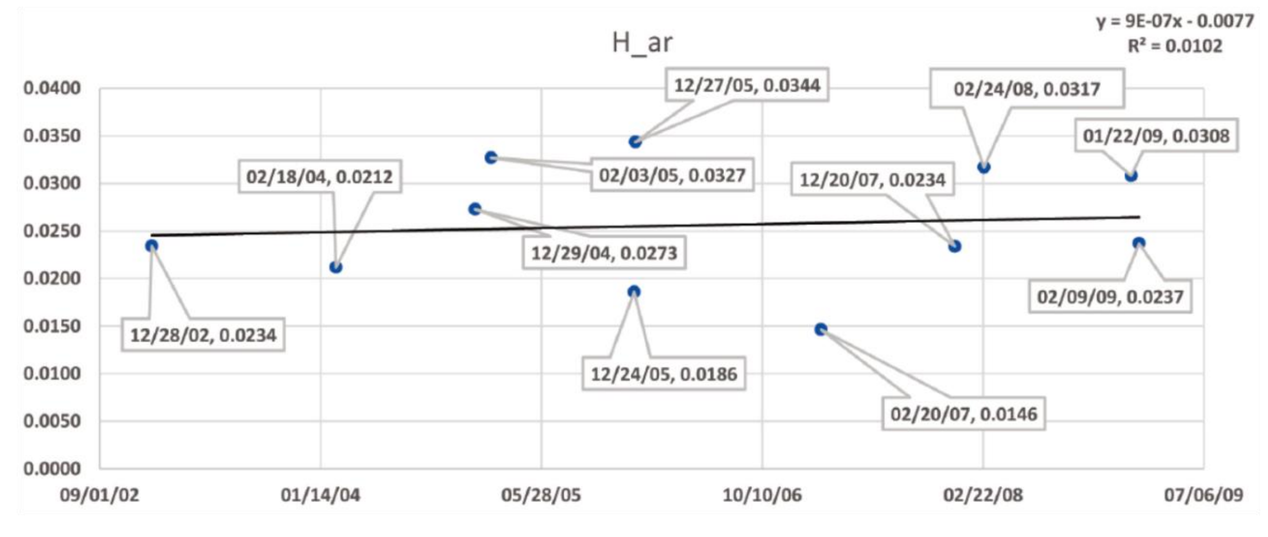


Figure 5.10. Winter Episode Aerosol Acidity Trend in Milwaukee

See Section 4.4.2, Chapter 4 for discussion.

5.5. Conclusion

An increasing trend of ammonium rich aerosol acidity was observed based on the winter episode data for Milwaukee from 2002 to 2009. This trend is in consistent with the trend of H_{AER}, observed based on the wholde data set at the other stations. However, the specific significance of this founding is, it means, in Great Lake Region, ammonia, the largest basic element in the atmosphere, is no longer sufficient to balance the acidic gases generated by both human activity and nature.

Elevated $PM_{2.5}$ events are caused by both emission sources and meteorological conditions. The emission sources include both local and long distance transported primary air pollutants. On studying the characteristics of the episode, the background concentration as well as the contribution of air pollutants on the day of the episode are equally important.

Meteorological conditions and emission sources both have significant impact on the elevated air pollution events. However, it is the meteorological conditions that contributed to the uniqueness of each episode, such as the difference between episodes of 05/30/2007 and 06/27/2005.

During the episode, each major $PM_{2.5}$ components is higher than its mean at normal condition. However, the elevation ratio of each component [(concentration of the component during an episode)/ (concentration of the component under normal conditions)] is different and depends on the season, the meteorological condition and the pre-existing atmospheric conditions.

Milwaukee has a higher number of episodes and higher concentration of $PM_{2.5}$ during the episode. The urban emissions and the special meteorological conditions caused by Lake Michigan are the major contributors.

Even though “Lake Breeze” is a more complicated meteorological phenomena than just a breeze that blows pollutants onshore from the Lake, the positive correlation between the O_3 and wind direction was observed, which helps set the stage for elevated air pollution events.

There are trends in comparing the mean concentrations of elevated $PM_{2.5}$ events, but each one episode is unique. There is not seasonal cap for the highs of the episodes.

The mean concentration of $PM_{2.5}$ has a decreasing trend in the future, due to decreasing production-related emissions. However, as mentioned previously, the decreasing trend of mean concentration of $PM_{2.5}$ does not put any cap on the highs of the episode. As epidemiological studies indicate the positively correlations between the short-term exposure and negative health impact, prevention of human exposure to elevated air pollutions episodes, especially for the economically disadvantaged, the elderly, the infant and those, whose health is already compromised, become essential.

5.6. Reference:

Association, A.L., 2007. Annual Report Card on Air Quality in Upper Midwest Shows Cause for Concern, Prompts Call for Government, Industry and Individual Action.

Blanchard, Hidy, G.M., Tanenbaum, S., Edgerton, E., Hartsell, B., Jansen, J., 2008. Carbon in southeastern U.S. aerosol particles: Empirical estimates of secondary organic aerosol formation. Atmospheric Environment 42, 6710-6720.

Blanchard, C.L., Hidy, G.M., Tanenbaum, S., Edgerton, E.S., Hartsell, B.E., 2013. The Southeastern Aerosol Research and Characterization (SEARCH) study: Temporal trends in gas and PM concentrations and composition, 1999-2010. Journal of the Air and Waste Management Association 63, 247-259.

Czoschke, N.M., Jang, M.S., 2006. Acidity effects on the formation of alpha-pinene ozone SOA in the presence of inorganic seed. Atmospheric Environment 40, 4370-4380.

Dawson, J.P., Adams, P.J., Pandis, S.N., 2007. Sensitivity of PM2.5 to climate in the Eastern US: a modeling case study. Atmospheric Chemistry and Physics 7, 4295-4309.

Dawson, J.P., Bloomer, B.J., Winner, D.A., Weaver, C.P., 2014. Understanding the meteorological drivers of us particulate matter concentrations in a changing climate. Bulletin of the American Meteorological Society 95, 520-532.

Dawson, J.P., Racherla, P.N., Lynn, B.H., Adams, P.J., Pandis, S.N., 2009. Impacts of climate change on regional and urban air quality in the eastern United States: Role of meteorology. Journal of Geophysical Research-Atmospheres 114.

Draxler, R.R., 2014. HYSPLIT_4 User's Guide. NOAA Technical Memorandum ERL ARL-230,, p. 35.

Dye, T.S., Roberts, P.T., Korc, M.E., 1995. Observations of transport processes for ozone and ozone precursors during the 1991 lake-Michigan ozone study. Journal of Applied Meteorology 34, 1877-1889.

Ebi, K.L., McGregor, G., 2008. Climate Change, Tropospheric Ozone and Particulate Matter, and Health Impacts. Environmental Health Perspectives 116, 1449-1455.

Engel-Cox, J.A., Holloman, C.H., Coutant, B.W., Hoff, R.M., 2004. Qualitative and quantitative evaluation of MODIS satellite sensor data for regional and urban scale air quality. Atmospheric Environment 38, 2495-2509.

EPA, U., 2005. Understanding Particle Pollution.

EPA/600/P-99/002bF, 2004. Air Quality Criteria for Particulate Matter, p. 1148.

Ferman, M.A., Wolff, G.T., Kelly, N.A., 1981. The nature and sources of haze in the shenandoah valley-blue ridge mountains area. Journal of the Air Pollution Control Association 31, 1074-1082.

Gao, J.J., Tian, H.Z., Cheng, K., Lu, L., Zheng, M., Wang, S.X., Hao, J.M., Wang, K., Hua, S.B., Zhu, C.Y., Wang, Y., 2015. The variation of chemical characteristics of PM2.5 and PM10 and formation causes during two haze pollution events in urban Beijing, China. Atmospheric Environment 107, 1-8.

Hallquist, M., Wenger, J.C., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., Dommen, J., Donahue, N.M., George, C., Goldstein, A.H., Hamilton, J.F., Herrmann, H., Hoffmann, T., Iinuma, Y., Jang, M., Jenkin, M.E., Jimenez, J.L., Kiendler-Scharr, A., Maenhaut, W., McFiggans, G., Mentel, T.F., Monod, A., Prevot, A.S.H., Seinfeld, J.H., Surratt, J.D., Szmigielski, R., Wildt, J., 2009. The formation, properties and impact of secondary organic aerosol: current and emerging issues. Atmospheric Chemistry and Physics 9, 5155-5236.

Heo, J., McGinnis, J.E., de Foy, B., Schauer, J.J., 2013. Identification of potential source areas for elevated PM2.5, nitrate and sulfate concentrations. Atmospheric Environment 71, 187-197.

Hidy, G.M., et al. , 2011. Technical Challenges of Multipollutant Air Quality Management.

Jang, M., Czoschke, N.M., Northcross, A.L., 2004. Atmospheric organic aerosol production by heterogeneous acid-catalyzed reactions. Chemphyschem 5, 1647-1661.

Jang, M., Lee, S., Kamens, R.M., 2003. Organic aerosol growth by acid-catalyzed heterogeneous reactions of octanal in a flow reactor. Atmospheric Environment 37, 2125-2138.

Jang, M.S., Czoschke, N.M., Lee, S., Kamens, R.M., 2002. Heterogeneous atmospheric aerosol production by acid-catalyzed particle-phase reactions. Science 298, 814-817.

Katzman, T.L., Rutter, A.P., Schauer, J.J., Lough, G.C., Kolb, C.J., Van Klooster, S., 2010. PM2.5 and PM10-2.5 Compositions during Wintertime Episodes of Elevated PM Concentrations across the Midwestern USA. Aerosol and Air Quality Research 10, 140-U113.

Kelly, F.J., Fussell, J.C., 2012. Size, source and chemical composition as determinants of toxicity attributable to ambient particulate matter. Atmospheric Environment 60, 504-526.

LADCO, 2003. PM2.5   in the Upper Midwest.

LADCO, 2009. Conceptual Model of PM2.5 Episodes in the Midwest _ Lake michigan Air Directors Consortium (LADCO), p. 37.

LADCO, 2010. Episodic Air Pollution in Wisconsin (LADCO Winter Nitrate Study) and Georgia (SEARCH Network) During Jan-Mar 2009 Phase I Report.

Laden, F., Neas, L.M., Dockery, D.W., Schwartz, J., 2000. Association of fine particulate matter from different sources with daily mortality in six US cities. Environmental Health Perspectives 108, 941-947.

Lennartson, G.J., Schwartz, M.D., 2002. The lake breeze-ground-level ozone connection in eastern Wisconsin: A climatological perspective. International Journal of Climatology 22, 1347-1364.

Lim, H.-J., Turpin, B.J., 2002. Origins of primary and secondary organic aerosol in Atlanta: Results of time-resolved measurements during the Atlanta Supersite Experiment. Environmental Science and Technology 36, 4489-4496.

LYONS, W.A., OLSSON, LARS E. , 1973. Detailed Mesometeorological Studies of Air

Pollution Dispersion in the Chicago Lake Breeze. MWRv 101.

Maynard, D., Coull, B.A., Gryparis, A., Schwartz, J., 2007. Mortality risk associated with short-term exposure to traffic particles and sulfates. Environmental Health Perspectives 115, 751-755.

Mickley, L.J., Jacob, D.J., Field, B.D., Rind, D., 2004. Effects of future climate change on regional air pollution episodes in the United States. Geophysical Research Letters 31, 1-4.

Monson, R.K., Trahan, N., Rosenstiel, T.N., Veres, P., Moore, D., Wilkinson, M., Norby, R.J., Volder, A., Tjoelker, M.G., Briske, D.D., Karnosky, D.F., Fall, R., 2007. Isoprene emission from terrestrial ecosystems in response to global change: minding the gap between models and observations. Philosophical Transactions of the Royal Society a-Mathematical Physical and Engineering Sciences 365, 1677-1695.

Mukund, R., Kelly, T.J., Spicer, C.W., 1996. Source attribution of ambient air toxic and other VOCs in Columbus, Ohio. Atmospheric Environment 30, 3457-3470.

Possell, M., Hewitt, C.N., 2011. Isoprene emissions from plants are mediated by atmospheric CO2 concentrations. Global Change Biol. 17, 1595-1610.

Rosenstiel, T.N., Potosnak, M.J., Griffin, K.L., Fall, R., Monson, R.K., 2003. Increased CO2 uncouples growth from isoprene emission in an agriforest ecosystem. Nature 421, 256-259.

Sillman, S., 1999. The relation between ozone, NOx and hydrocarbons in urban and polluted rural environments. Atmospheric Environment 33, 1821-1845.

Stelson, A.W., Seinfeld, J.H., 1982. Relative humidity and temperature dependence of ammonium nitrate dissociation constant. Atmospheric Environment 16, 983-992.

Tai, A.P.K., Mickley, L.J., Jacob, D.J., 2010. Correlations between fine particulate matter (PM2.5) and meteorological variables in the United States: Implications for the sensitivity of PM2.5 to climate change. Atmospheric Environment 44, 3976-3984.

Theloke, J., Friedrich, R., 2007. Compilation of a database on the composition of anthropogehic

VOC emissions for atmospheric modeling in Europe. Atmospheric Environment 41, 4148-4160.

Wolff, G.T., Kelly, N.A., Ferman, M.A., 1981. On the sources of summertime haze in the eastern-united-states. Science 211, 703-705.

Wolff, G.T., Kelly, N.A., Ferman, M.A., 1982. Source regions of summertime ozone and haze episodes in the eastern-united-states. Water Air and Soil Pollution 18, 65-81.

Table 5.6 Milwaukee High Days

Winter	**High $PM_{2.5}$ days**											
	Mean	12/27/05	02/20/07	02/03/05	12/29/04	12/20/07	02/24/08	02/18/04	12/24/05	12/28/02	02/09/09	12/13/02
$PM_{2.5}$	13.63	47.8	46.6	43.8	43.4	36.5	36	36	35.7	35.6	35.6	34.9
O_3	0.0242	0.0076	0.0236	0.0198	0.0048	0.0255		0.0113	0.0226		0.0264	
SO_4_m	0.0220	0.0687	0.0293	0.0654	0.0545	0.0467	0.0634	0.0424	0.0372	0.0468	0.0474	0.0730
NO_3_m	0.0716	0.1172	0.2887	0.2935	0.2984	0.2838	0.2580	0.2951	0.2339	0.2484	0.2387	0.2226
NH_4_m	0.1086	0.2611	0.3903	0.4424	0.4307	0.5544	0.4125	0.3803	0.2916	0.3448	0.3459	0.3692
Anions	0.1156	0.2547	0.3472	0.4243	0.4075	0.3773	0.3848	0.3799	0.3082	0.3421	0.3334	0.3685
EC	0.4777	0.736	0.797	0.971	0.995	0.875	0.553	0.565	1.32	0.63	0.534	0.78
OC	3.5216	2.8	6.1	7.26	6.43	8.37	4.36	4.15	6.15	6.52	3.56	5.94
NH_4mn	0.8808	1.0253	1.1241	1.0427	1.0572	1.4692	1.0718	1.0011	0.9462	1.0081	1.0375	1.0019
NO_3/SO_4	1.6754	0.8533	4.9346	2.2450	2.7349	3.0365	2.0352	3.4830	3.1463	2.6510	2.5197	1.5250
NH_4/SO_4	2.4004	1.9002	6.6711	3.3836	3.9484	5.9304	3.2530	4.4881	3.9233	3.6805	3.6518	2.5298
H_ar	0.0110	0.0344	0.0146	0.0327	0.0273	0.0234	0.0317	0.0212	0.0186	0.0234	0.0237	0.0365
H_aer	0.0070	-0.0065	-0.0431	-0.0181	-0.0233	-0.1770	-0.0276	-0.0004	0.0166	-0.0028	-0.0125	-0.0007
T	270.03	274.25	274.78	273.32	270.94	273.83	269.67	272.56	275.01	273.93	276.69	275.99
DPT	265.46	273.49	271.10	268.79	268.88	270.55	264.92	267.91	274.11	270.78	273.99	273.74
WBT	268.69	274.02	273.30	271.68	270.27	272.56	268.11	270.80	274.71	272.77	275.62	275.01
RH	71.78	95.00	77.08	72.63	86.29	79.13	70.58	72.46	94.25	80.00	82.79	85.54

Table 5.6-(2). Milwaukee

	Spring	High $PM_{2.5}$ days		Summer	High $PM_{2.5}$ days			Fall	High $PM_{2.5}$ days				
	Mean	05/30/07	03/16/03	Mean	06/27/05	08/02/05	06/18/09	Mean	09/08/02	11/25/06	09/03/04	09/10/05	11/07/06
$PM_{2.5}$	10.13	47.4	37.3	11.96	48.1	41.9	38	11.14	43.2	42.5	38.7	38	36.7
O_3	0.0415	0.0788	na	0.0471	0.096	0.10225	0.06238	0.0308	0.09263	0.00381	0.04625	0.08163	0.00819
SO_4_m	0.0220	0.1520	0.0829	0.0296	0.2373	0.2488	0.0797	0.0248	0.2321	0.0438	0.1520	0.1884	0.0697
NO_3_m	0.0393	0.0684	0.2210	0.0143	0.0327	0.0163	0.0626	0.0330	0.0353	0.2226	0.1110	0.0473	0.1482
NH_4_m	0.0747	0.3820	0.4147	0.0598	0.4562	0.4141	0.2223	0.0729	0.4086	0.3171	0.3731	0.3748	0.2966
Anions	0.0833	0.3723	0.3867	0.0735	0.5074	0.5139	0.2221	0.0826	0.4996	0.3102	0.4149	0.4241	0.2877
EC	0.3918	0.912	0.48	0.5184	1.17	1.17	0.621	0.6294	0.7	1.84	1.32	0.93	1.58
OC	3.0897	10.1	6.47	4.7710	8.7	6.83	5.79	3.8382	7.89	11.5	8.5	4.62	7.15
NH_4mn	0.8329	1.0258	1.0724	0.7213	0.8991	0.8059	1.0011	0.8217	0.8178	1.0222	0.8992	0.8837	1.0309
NO_3/SO_4	0.8825	0.2250	1.3332	0.2920	0.0690	0.0327	0.3924	0.7923	0.0761	2.5392	0.3650	0.1254	1.0625
NH_4/SO_4	1.5884	1.2566	2.5022	0.9332	0.9612	0.8322	1.3939	1.4861	0.8800	3.6178	1.2274	0.9945	2.1262
H_ar	0.0110	0.0760	0.0414	0.0148	0.1187	0.1244	0.0399	0.0124	0.1161	0.0219	0.0760	0.0942	0.0349
H_aer	0.0086	-0.0096	-0.0280	0.0137	0.0512	0.0998	-0.0002	0.0097	0.0910	-0.0069	0.0418	0.0493	-0.0089
T	280.89	295.59	284.43	294.63	300.3602	300.0824	293.1853	284.76	297.35	280.92	293.99	298.18	282.58
DPT	274.55	288.00	281.98	288.14	292.3972	292.0731	287.7988	278.83	291.01	276.15	291.66	291.52	280.13
WBT	278.10	290.89	283.02	290.68	295.0361	294.7583	289.8761	281.90	293.23	278.74	292.40	293.81	281.29
RH	67.19	63.5	85.88	68.72	62.83	63.00	72.52	69.22	68.58	72.50	87.08	67.54	84.88

Table 5.7 Mayville High Days

	Winter	**High $PM_{2.5}$ days**							**Spring**	**High $PM_{2.5}$ days**		**Summer**	**High $PM_{2.5}$ days**	
	Mean	02/18/04	02/03/05	02/24/08	12/20/07	01/21/07	12/13/02	12/29/04	Mean	03/01/03	05/30/07	Mean	06/27/05	08/02/05
$PM_{2.5}$	12.77	43.8	43.5	42.7	38.8	37	36.1	35.6	10.47	39.4	38.6	10.77	43.8	36.3
O_3	0.0310	0.0493	0.0350	0.0570	0.0243	0.0173	0.0195	0.0181	0.0458	0.0379	0.0684	0.0487	0.0875	0.07
SO_4_m	0.0207	0.0478	0.0656	0.0660	0.0447	0.0293	0.0711	0.0536	0.0243	0.0509	0.1083	0.0295	0.2311	0.1988
NO_3_m	0.0765	0.3580	0.3548	0.3064	0.3048	0.1292	0.1903	0.2500	0.0447	0.2871	0.0473	0.0165	0.0298	0.0308
NH_4_m	0.1105	0.4640	0.5156	0.4762	0.4197	0.1824	0.3254	0.3831	0.0866	0.3875	0.2944	0.0680	0.4524	0.3504
Anions	0.1180	0.4536	0.4860	0.4384	0.3941	0.1877	0.3325	0.3572	0.0933	0.3889	0.2638	0.0754	0.4920	0.4285
EC	0.2656	0.396	0.667	0.338	0.694	0.14	0.68	0.723	0.2400	0.46	0.398	0.2652	0.499	0.523
OC	2.3153	3.91	4.31	3.93	3.87	4.17	5.15	3.96	2.4142	4.43	10.2	3.6134	5.26	5.02
NH_4mn	0.8797	1.0230	1.0609	1.0862	1.0648	0.9718	0.9787	1.0724	0.8856	0.9965	1.1160	0.8472	0.9194	0.8177
NO_3/SO_4	1.8445	3.7467	2.7051	2.3215	3.4128	2.2082	1.3383	2.3315	0.9277	2.8198	0.2182	0.3447	0.0646	0.0775
NH_4/SO_4	0.8797	4.8556	3.9307	3.6077	4.6986	3.1176	2.2885	3.5727	0.8856	3.8063	1.3595	0.8472	0.9787	0.8811
H_ar	0.0104	0.0239	0.0328	0.0330	0.0223	0.0146	0.0355	0.0268	0.0122	0.0255	0.0541	0.0147	0.1155	0.0994
H_aer	0.0076	-0.0104	-0.0296	-0.0378	-0.0255	0.0053	0.0071	-0.0259	0.0067	0.0014	-0.0306	0.0074	0.0397	0.0781
T	268.04	271.68	273.46	267.78	272.25	267.19	274.46	270.08	280.18	272.35	297.03	293.98	301.13	299.48
DPT	263.96	268.02	269.55	263.65	269.19	264.78	272.51	268.00	273.72	265.71	288.67	287.90	292.58	292.21
WBT	266.86	270.31	272.03	266.56	271.12	266.47	273.67	269.36	277.36	270.11	291.78	290.30	295.36	294.64
RH	74.25	29.24	29.36	29.14	29.14	29.20	29.10	29.32	66.98	29.07	29.18	70.70	29.15	29.19

Table 5.8 Waukesha High Days

	Winter	**High $PM_{2.5}$ days**				**Spring**	**High $PM_{2.5}$ days**		**Summer**	**High $PM_{2.5}$ days**	
	Mean	12/29/04	02/03/05	12/20/07	02/24/08	Mean	05/30/07	03/16/03	Mean	06/27/05	08/02/05
$PM_{2.5}$	14.27	44.3	44.2	41.8	35.6	11.33	41.2	33.1	12.92	43.8	39.7
O_3	NA	na	na	na	na	0.0415	0.066	na	0.0437	0.084	0.072
SO_4_m	0.0205	0.0523	0.0629	0.0456	0.0569	0.0217	0.1114	0.0765	0.0295	0.2134	0.1936
NO_3_m	0.0695	0.2935	0.2838	0.3177	0.2371	0.0394	0.0427	0.1919	0.0144	0.0237	0.0152
NH_4_m	0.0976	0.4136	0.4186	0.6043	0.3598	0.0713	0.2794	0.3332	0.0574	0.4008	0.3116
Anions	0.1106	0.3980	0.4096	0.4089	0.3510	0.0828	0.2655	0.3449	0.0734	0.4505	0.4024
EC	0.4845	1.28	0.795	1.18	0.391	0.4514	0.678	0.5	0.6496	0.901	0.924
OC	3.6948	7.07	7.26	5.21	4.24	3.4687	11.8	5.84	4.8595	6.02	5.93
NH_4mn	0.8186	1.0390	1.0219	1.4778	1.0251	0.7920	1.0523	0.9659	0.6948	0.8897	0.7742
NO_3/SO_4	3.4764	2.8085	2.2572	3.4841	2.0818	1.8096	0.1919	1.2542	0.6063	0.0555	0.0391
NH_4/SO_4	4.5517	3.9570	3.3284	6.6265	3.1593	3.0461	1.2542	2.1773	1.8028	0.9391	0.8045
H_ar	0.0103	0.0261	0.0314	0.0228	0.0285	0.0109	0.0557	0.0383	0.0148	0.1067	0.0968
H_aer	0.0130	-0.0155	-0.0090	-0.1954	-0.0088	0.0115	-0.0139	0.0118	0.0160	0.0497	0.0908
T	268.00	270.54	269.99	273.14	267.79	279.74	296.69	281.07	291.96	296.51	296.17
DPT	264.83	269.71	267.42	270.41	264.78	274.13	289.44	279.82	287.38	293.25	292.56
WBT	267.18	270.40	269.15	272.00	266.82	277.32	292.22	280.76	289.27	294.36	294.08
RH	79.37	94.00	82.88	82.55	80.71	70.95	65.28	92.28	77.03	82.13	80.50

Table 5.7-(2) Mayville (continued) Table 5.8-(2) Waukesha (continued)

Table 5.9 Perkinstown High Days

	Fall	**High $PM_{2.5}$ days**		**Fall**	**High $PM_{2.5}$ days**				**Winter**		**Spring**	
	Mean	11/25/06	09/03/04	Mean	11/25/06	11/07/06	11/17/04		Mean	02/24/08	Mean	05/30/07
$PM_{2.5}$	10.40	48.8	35.6	12.12	46	36.5	33.5	$PM_{2.5}$	9.01	40.2	7.47	41.4
O_3	0.0357	0.018	0.07038	0.0355	na	na	na	O_3	na	na	na	na
SO_4_m	0.0280	0.0454	0.1832	0.0231	0.0408	0.0641	0.0616	SO_4_m	0.0158	0.0598	0.0177	0.0599
NO_3_m	0.0370	0.3193	0.0777	0.0354	0.2403	0.1547	0.1310	NO_3_m	0.0439	0.3387	0.0229	0.0177
NH_4_m	0.0850	0.4851	0.4030	0.0681	0.3315	0.2495	0.1974	NH_4_m	0.0635	0.4867	0.0483	0.1342
Anions	0.0930	0.4101	0.4442	0.0817	0.3219	0.2829	0.2542	Anions	0.0754	0.4582	0.0583	0.1375
EC	0.3392	1.61	0.644	0.7031	1.56	1.74	0.859	EC	0.2142	0.421	0.1742	0.387
OC	2.8312	8.05	4.3	4.1082	12.8	7.79	5.21	OC	2.2395	4.03	2.2135	8.15
NH_4mn	0.8569	1.1828	0.9074	0.7045	1.0298	0.8818	0.7764	NH_4mn	0.7382	1.0623	0.7189	0.9760
NO_3/SO_4	0.8922	3.5179	0.2121	1.6779	2.9444	1.2060	1.0625	NO_3/SO_4	1.3351	2.8341	0.5604	0.1482
NH_4/SO_4	0.8569	5.3438	1.0999	2.6718	4.0620	1.9452	1.6012	NH_4/SO_4	1.7979	4.0730	1.1668	1.1207
H_ar	0.0140	0.0227	0.0916	0.0116	0.0204	0.0321	0.0308	H_ar	0.0079	0.0299	0.0088	0.0299
H_aer	0.0080	-0.0750	0.0411	0.0136	-0.0096	0.0334	0.0569	H_aer	0.0119	-0.0286	0.0101	0.0033
T	283.77	278.95	295.29	282.11	282.21	282.64	286.58	T	265.28	268.18	280.13	294.50
DPT	278.47	275.45	290.41	277.88	278.39	280.11	285.96	DPT	262.04	265.29	273.03	291.17
WBT	281.15	277.33	292.21	280.29	280.54	281.38	285.96	WBT	264.45	267.21	277.31	292.37
RH	72.21	29.19	29.22	77.07	77.58	85.44	95.88	RH	78.67	81.17	64.67	82.71

CHAPTER 6. CONCLUSION AND RECOMMENDATION

6.1. Summary of Key Findings

This is the first comprehensive study on Wisconsin $PM_{2.5}$ data in investing the $PM_{2.5}$ problems in the state. In this study, large amount available $PM_{2.5}$ data sets were analyzed with different methods from different aspects to explore the characteristics of $PM_{2.5}$ in different regions in the state, and to explore the variations of the characteristics among different regions. The patterns of the variations are examined and important changes on the patterns are discovered. In addition, during above study, a systematic approach was developed for future analyzing the broadly available air quality monitoring data collected by EPA and State agency. These data carrying useful information but were overlooked.

The ambient $PM_{2.5}$ and its components collected at Milwaukee (urban), Waukesha (industrial), Mayville (agriculture) and Perkinstown (rural/forests) from 2002 to 2009 are analyzed to study the characteristics of ambient $PM_{2.5}$ at regions which are not too far apart located in one state. The patterns of the variation among the regions and the changes of the patterns are investigated as well. The diversified economy, diversified geography and long Great Lake coastline, and the frequently exceedance in ambient air quality standards, made the ambient $PM_{2.5}$ collected in Wisconsin an interesting case to study.

In addition to the ambient air quality data, meteorological parameters collected at the four monitoring stations located in different regions within Wisconsin are analyzed to support the examination of the spatial and temporal characteristics of concentration and composition of ambient $PM_{2.5}$ and its components in Wisconsin. Receptor model, PMF, is employed in the study to identify the potential emission sources of ambient $PM_{2.5}$ in the regions of Wisconsin. Since aerosol acidity has played a significant role in affecting human health and the formation of $PM_{2.5}$, aerosol acidity distribution in the regions is studied using the long term collected $PM_{2.5}$ data. Finally, the different scenarios of elevated $PM_{2.5}$ events are discussed for the courses of the events, the trends of the elevated $PM_{2.5}$ events observed at different region of Wisconsin.

6.1.1. Findings from Variation Study (Chapter 2)

Ambient concentration of $PM_{2.5}$ at the four stations has clear seasonal variations. Like many Midwest areas, winter has higher nitrate, summer has higher sulfate and OC. The significance of spatial variations among Milw, Wauk, Mayv and Perk depends on seasons, locations where the comparison made and the physical and chemical property of the air pollutant. The variations between Perk and other three stations are significant for all elements and at all seasons. Local emission sources and meteorological conditions are the major contributors to the significance of the variations.

It is found that the downward trend of ambient concentration of $PM_{2.5}$, nitrate and sulfate in the period of 2005 to 2009 was mainly due to the decreasing emissions associated with the reduced fuel combustion. During the same period, the relatively flat ambient OC concentration and increasing OC composition were observed. This change in pattern highlighted the need for changing $PM_{2.5}$ reduction strategies.

Another observed change on the variation pattern is the increase of ambient concentration of winter $PM_{2.5}$ and nitrate alone without the increase of sulfate in the same period. This phenomenon was very likely contributed by additional non-fuel combustion related N-emissions sources in the region during the period.

Lake Breeze is the major cause of the contrast between shoreline and inland regions. The relative humidity and temperature difference between Milwaukee and other regions have contributed to the higher frequency of elevated $PM_{2.5}$ events in Milwaukee than other stations.

6.1.2. **Finding from PMF Application (Chapter 3)**

PMF effectively resolved 6 to 8 sources of the $PM_{2.5}$ for each station area. The common emission sources identified by PMF at the four stations are:

1) Secondary nitrate sources (mobile and stationary sources; fossil fuel combustion emissions such as power plants; paper mills; foundries and non-fuel combustion related N emissions);
2) Secondary sulfate sources (mobile and stationary sources);
3) Soil sources;
4) Organic carbon (OC) sources

The OM/EC ratio in the PMF estimated OC factor at each station clearly distinguished diesel emission from gasoline emission and other OC emissions. The diesel emissions contain a large amount of the elemental carbon fractions. The OC emission factor strongly influenced by diesel emissions has lower OM/EC ratio (less than 2) while OM/EC from rural area which was less impacted by the impact of diesel fuel combustion, the ratio is higher than 3.4.

PMF can help in identifying new potential emission factors, such as the Lead emission factor in Milwaukee. Comparing the CPF plots for the emission factors of secondary nitrate and sulfate sources estimated by PMF pointed out different pictures for these two major inorganic $PM_{2.5}$ components. The CPF plot for nitrates clearly indicated there are additional emissions sources category for nitrate.

Soil source has very strong local characteristics, from the composition and the concentration of the major soil ingredients, like Ca, Si, Al, Ti, etc. There soil sources, in many cases, are "contaminated" by other emission categories, such as soil + quarry emissions, soil + traffic emissions.

6.1.3. **Finding from Aerosol Acidity study (Chapter 4)**

An increasing trend of aerosol acidity was observed at the four regions in Wisconsin based on four season data. A further study is needed to determine if the increasing is a permanent trend.

An increasing trend of aerosol acidity was observed for winter episodes in Milwaukee, regardless the concentration of the $PM_{2.5}$ at the episode. Other stations didn't have enough days to examine the trend.

Spatiotemporal variations of aerosol acidity were observed for all four stations with different patterns. The cause of the variations was complex and unique for each station. The major contributors are composition of the atmospheric aerosol, the pre-existing atmospheric acidic condition and the local meteorology conditions.

In general, the H_{AER} value is higher under AP conditions and higher in urban and industrial areas. The available ambient NH_3 as well as the content of the acidic aerosol play significant roles in the variations of neutralization degree. Under AR conditions, the winter NH_4mn at Milwaukee and Mayville, the urban and industrial region, are the highest among all seasons. Based on the neutralization degree, under AP conditions, summer has more days under more acidic conditions at all regions.

The knowledge of aerosol acidity distribution provides useful information to plan epidemiologic studies and therefore helps the epidemiologic studies provide better human health benefits.

Significant correlations between concentration of sulfate and organic carbon are found at all regions, with different value of R^2. However, these relations are not sufficient to either deny or support the hypothesis that “An acid-catalyzed heterogeneous reaction could be one important mechanism that enhances the formation of SOA in the air”. SOA sampling is essential to establish the correlations between sulfate and SOA.

6.1.4. **Finding from Elevated $PM_{2.5}$ Events Study (Chapter 5)**

Elevated $PM_{2.5}$ events are caused by both emission sources and meteorological conditions. The emission sources include both local and long distance transported primary air pollutants. On studying the characteristics of the episode, the background concentration as well as the contribution of air pollutants on the day of the episode are equally important.

Meteorological conditions that contributed to the uniqueness of each episode. Such as the difference between episodes of 05/30/2007 and 06/27/2005.

Milwaukee has a higher number of episodes and higher concentration of $PM_{2.5}$ during the episode. The urban emissions and the special meteorological conditions caused by Lake Michigan are the major contributors.

Even though “Lake Breeze” is a more complicated meteorological phenomena than just a breeze that blows pollutants onshore from the Lake, the correlation between the O_3 and wind direction helps set the stage for elevated air pollution events.

There are trends in comparing the mean concentrations of elevated $PM_{2.5}$ events, but each one episode is unique. There is not seasonal cap for the highs of the episodes.

6.2. Recommendation for Future Work

The trends of aerosol acidity need to be further studied. An decreasing trend was observed from station Mayville based on the data from 2002 to 2009. The data collection was terminated at the end of 2009 at station Mayville. The time series for station Milwaukee, Waukesha and Perkinstown showed a downward then an upward curve between 2009 to 2010. Investigating what actually caused that change between 2009 and 2010 could provide useful information for the mechanism of aerosol acidity changes. The increasing trend of aerosol acidity during winter episode need to be further studied as well.

"The effects of air pollution on the cardiovascular system account for the largest portion of the public health and economic benefits of the Clean Air Act. The relationship between long-term exposure to $PM_{2.5}$ and cardiovascular health effects has been determined as causal (U.S. EPA, 2009; Brook et al., 2010) based on a number of epidemiological studies. A long-term prospective studies can inform and reduce uncertainties about the concentration-response relationship, especially at low ambient concentrations of $PM_{2.5}$" [EPA-G2016-STAR-B1]. Studies have indicated that the severe health impact of $PM_{2.5}$ is not its mass but its ingredients. The toxicity of metals becomes more potent at acidic conditions. The concentration of aerosol acidity is not proportional to the mass of $PM_{2.5}$. EPA has collected more than 10 years' speciated $PM_{2.5}$ data nationwide, which provides a good data set for studying $PM_{2.5}$ on the cardiovascular system at low ambient concentrations of $PM_{2.5}$. Including the concentration of atmospheric aerosol acidity with the concentration of $PM_{2.5}$ provides more accurate concentration-response relationship.

The mean concentration of $PM_{2.5}$ has a decreasing trend based on 2002 to 2009. The mean concentration of O_3 has a decreasing trend based on 2002 to 2009 data, but an increasing trend if extend data being involved in the analysis to 2013. Acknowledging either 7 or 10 year is a relatively short database in which to draw conclusion on air quality change, or climate change. It is very helpful for future study to find out what is the cause that makes the trend decreasing or increasing in a short period.

PMF analysis has its limitations in identifying potential emissions sources, especially for identifying the regional pollutants. Analyze the ambient air quality monitoring data collected at the study area, develop the updated and localized source profile can help identifying the potential emissions sources. For example, particulate Fe/Mg ratio could provide signature of oil-derived combustion aerosol, the particulate V/Se ratio could provide signature of coal vs. oil derived aerosol on the regional scale and the particulate As/Se ratio could provide signature of western vs. eastern coal derived aerosols (Rubin, 1999).

Trace metals are good tracers of local industrial emissions (Moreno et al., 2006). Collecting trace metal data and incorporating the metals in urban areas that are influenced by local industrial activities can help separating local and regional emission impact. $PM_{2.5}$ concentration is very sensitive to temperature, wind speed, absolute humidity, mixing height and precipitation (Dawson et al., 2007). Meteorological parameter based techniques, such as HYSPLIT could support to improved source apportionment of $PM_{2.5}$.

6.3. References

Dawson, J.P., Adams, P.J., Pandis, S.N., 2007. Sensitivity of ozone to summertime climate in the eastern USA: A modeling case study. Atmospheric Environment 41, 1494-1511.

Moreno, T., Querol, X., Alastuey, A., Viana, M., Salvador, P., de la Campa, A.S., Artinano, B., de la Rosa, J., Gibbons, W., 2006. Variations in atmospheric PM trace metal content in Spanish towns: Illustrating the chemical complexity of the inorganic urban aerosol cocktail. Atmospheric Environment 40, 6791-6803.

Rubin, E.S., 1999. Toxic releases from power plants. Environmental Science & Technology 33, 3062-3067.

Long-term Exposure to Air Pollution and Development of Cardiovascular Disease, 2016, EPA-G2016-STAR-B1.

CHAPTER 7. APPENDIX

7.1. Appendix A

7.1.1. Speciated $PM_{2.5}$ Data

Table AA2.1 Yearly seasonal composition of $PM_{2.5}$ _ Mayville (2002 ~2009)

				Winter								Spring				
NH4%	2002	2003	2004	2005	2006	2007	2008	2009	2002	2003	2004	2005	2006	2007	2008	2009
mean	0.1325	0.1361	0.1405	0.1608	0.1449	0.1422	0.1449	0.1543	0.1485	0.1448	0.1444	0.1536	0.1296	0.1438	0.1485	0.1298
count	29	29	28	29	29	27	28	16	28	31	26	30	29	30	29	26
Std	0.0429	0.0326	0.0404	0.0390	0.0395	0.0380	0.0452	0.0332	0.0454	0.0406	0.0312	0.0515	0.0501	0.0464	0.0398	0.0395
5th	0.0697	0.0646	0.0762	0.1174	0.0809	0.0816	0.0643	0.0983	0.0698	0.0817	0.0979	0.0682	0.0373	0.0706	0.0722	0.0671
95th	0.2102	0.1741	0.1944	0.2060	0.1928	0.1926	0.2095	0.1927	0.2113	0.2110	0.1855	0.2129	0.2086	0.2096	0.1963	0.1801
				Summer								Fall				
NH4%	2002	2003	2004	2005	2006	2007	2008	2009	2002	2003	2004	2005	2006	2007	2008	2009
mean	0.1136	0.1044	0.1006	0.1023	0.1091	0.1013	0.0971	0.0944	0.1391	0.1327	0.1263	0.1487	0.1247	0.1303	0.1200	0.1446
count	30	29	29	26	29	30	29	25	30	29	28	30	30	29	28	11
Std	0.0470	0.0420	0.0494	0.0555	0.0451	0.0498	0.0517	0.0421	0.0420	0.0444	0.0450	0.0373	0.0414	0.0488	0.0360	0.0425
5th	0.0458	0.0375	0.0285	0.0220	0.0458	0.0326	0.0336	0.0369	0.0563	0.0670	0.0650	0.0791	0.0649	0.0628	0.0625	0.0914
95th	0.1694	0.1716	0.1908	0.1839	0.1866	0.1817	0.1817	0.1659	0.1890	0.1968	0.1958	0.1976	0.1827	0.1874	0.1807	0.2058

				Winter								Spring				
NO3%	2002	2003	2004	2005	2006	2007	2008	2009	2002	2003	2004	2005	2006	2007	2008	2009
mean	0.3525	0.3266	0.3167	0.3663	0.3228	0.3312	0.3231	0.3504	0.2667	0.2938	0.2446	0.2799	0.2152	0.2404	0.2432	0.2026
count	29	29	28	29	29	27	28	16	28	31	26	30	29	30	29	26
Std	0.1019	0.1084	0.1023	0.1069	0.1250	0.1115	0.1047	0.1056	0.1158	0.1282	0.0820	0.1224	0.1237	0.1385	0.0973	0.0995
5th	0.1652	0.1298	0.1752	0.2002	0.1059	0.1435	0.1590	0.1800	0.0752	0.0862	0.1207	0.1010	0.0344	0.0492	0.1054	0.0704
95th	0.4795	0.4571	0.4646	0.5282	0.5014	0.4865	0.4482	0.4810	0.4090	0.4904	0.3579	0.4874	0.3872	0.4475	0.4000	0.3556
				Summer								Fall				

NO3%	2002	2003	2004	2005	2006	2007	2008	2009	2002	2003	2004	2005	2006	2007	2008	2009
mean	0.1165	0.1134	0.1136	0.0878	0.0900	0.0822	0.0967	0.0886	0.2579	0.2360	0.2239	0.2103	0.2180	0.1895	0.1664	0.1581
count	30	29	29	26	29	30	29	25	30	29	28	30	30	29	28	11
Std	0.0942	0.0831	0.0784	0.0691	0.0602	0.0599	0.0700	0.0652	0.1333	0.1150	0.1258	0.1097	0.1187	0.1320	0.1006	0.1143
5th	0.0444	0.0331	0.0408	0.0275	0.0319	0.0206	0.0273	0.0356	0.0686	0.0768	0.0583	0.0732	0.0525	0.0388	0.0511	0.0501
95th	0.3166	0.2640	0.3020	0.1968	0.2098	0.1617	0.2478	0.2338	0.4687	0.3917	0.4154	0.3775	0.3891	0.4089	0.3409	0.3551

				Winter								Spring				
SO4%	2002	2003	2004	2005	2006	2007	2008	2009	2002	2003	2004	2005	2006	2007	2008	2009
mean	0.1643	0.1698	0.1918	0.1784	0.1772	0.1626	0.1588	0.1602	0.2515	0.2454	0.2391	0.2398	0.2165	0.2221	0.2282	0.2548
count	29	29	28	29	29	27	28	16	28	31	26	30	29	30	29	26
Std	0.0745	0.0747	0.0753	0.0672	0.0592	0.0641	0.0698	0.0652	0.0653	0.0877	0.0796	0.0843	0.0801	0.0716	0.0618	0.0847
5th	0.0848	0.0737	0.0896	0.0862	0.0895	0.0763	0.0820	0.0826	0.1670	0.1248	0.1166	0.1321	0.0630	0.1156	0.1382	0.1401
95th	0.2862	0.2954	0.3033	0.2781	0.2621	0.2861	0.2885	0.2494	0.3436	0.4072	0.3562	0.4035	0.3347	0.3063	0.3229	0.3662
				Summer								Fall				
SO4%	2002	2003	2004	2005	2006	2007	2008	2009	2002	2003	2004	2005	2006	2007	2008	2009
mean	0.2564	0.2451	0.2397	0.2765	0.2478	0.2292	0.2133	0.2249	0.2604	0.2407	0.2372	0.2871	0.2116	0.2293	0.2223	0.3059
count	30	29	29	26	29	30	29	25	30	29	28	30	30	29	28	11
Std	0.0826	0.0925	0.1047	0.1320	0.0926	0.1024	0.0995	0.0743	0.1343	0.1040	0.0996	0.0952	0.0785	0.0889	0.0987	0.0971
5th	0.1020	0.1171	0.0975	0.0800	0.0886	0.0972	0.0770	0.1257	0.1261	0.0980	0.1014	0.1563	0.0881	0.1194	0.0996	0.1927
95th	0.3489	0.3805	0.4258	0.5035	0.3853	0.4100	0.3656	0.3484	0.4344	0.4312	0.4341	0.4271	0.3470	0.3829	0.3980	0.4531

				Winter								Spring				
EC%	2002	2003	2004	2005	2006	2007	2008	2009	2002	2003	2004	2005	2006	2007	2008	2009
mean	0.0230	0.0286	0.0266	0.0219	0.0249	0.0284	0.0253	0.0214	0.0232	0.0227	0.0264	0.0285	0.0227	0.0402	0.0258	0.0301
count	29	29	28	29	29	27	28	16	28	31	26	30	29	30	29	26
Std	0.0166	0.0122	0.0137	0.0104	0.0157	0.0197	0.0090	0.0072	0.0249	0.0155	0.0105	0.0167	0.0140	0.0260	0.0123	0.0257
5th	0.0054	0.0130	0.0065	0.0101	0.0047	0.0035	0.0098	0.0132	0.0026	0.0068	0.0124	0.0100	0.0005	0.0088	0.0117	0.0016
95th	0.0547	0.0500	0.0492	0.0374	0.0499	0.0679	0.0394	0.0342	0.0412	0.0407	0.0436	0.0561	0.0451	0.0890	0.0501	0.0918
				Summer								Fall				
EC%	2002	2003	2004	2005	2006	2007	2008	2009	2002	2003	2004	2005	2006	2007	2008	2009

mean	0.0189	0.0249	0.0317	0.0249	0.0280	0.0317	0.0370	0.0376	0.0325	0.0363	0.0376	0.0382	0.0497	0.0388	0.0433	0.0450
count	30	29	29	26	29	30	29	25	30	29	28	30	30	29	28	11
Std	0.0131	0.0142	0.0125	0.0234	0.0143	0.0173	0.0231	0.0320	0.0351	0.0239	0.0217	0.0217	0.0297	0.0154	0.0240	0.0212
5th	0.0032	0.0045	0.0181	0.0031	0.0091	0.0115	0.0143	0.0000	0.0072	0.0155	0.0129	0.0138	0.0188	0.0182	0.0158	0.0154
95th	0.0408	0.0555	0.0536	0.0452	0.0475	0.0588	0.0659	0.0893	0.0578	0.0802	0.0861	0.0838	0.1134	0.0612	0.0820	0.0705

				Winter								Spring				
OC%	2002	2003	2004	2005	2006	2007	2008	2009	2002	2003	2004	2005	2006	2007	2008	2009
mean	0.2666	0.2676	0.2213	0.1816	0.2170	0.2005	0.2027	0.2288	0.2874	0.2756	0.2373	0.2720	0.2455	0.2623	0.3331	0.3585
count	29	29	28	29	29	27	28	16	28	31	26	30	29	30	29	26
Std	0.1096	0.1068	0.1016	0.0883	0.0949	0.1166	0.0845	0.1132	0.1512	0.1204	0.0963	0.1312	0.1211	0.0993	0.2229	0.1653
5th	0.1362	0.1253	0.1068	0.0983	0.1075	0.1015	0.1187	0.1386	0.1643	0.1225	0.1228	0.1074	0.0747	0.1315	0.1339	0.1626
95th	0.4377	0.4387	0.3894	0.3102	0.3911	0.3996	0.3555	0.3935	0.4679	0.4562	0.3739	0.5145	0.4361	0.4283	0.8662	0.6569
				Summer								Fall				
OC%	2002	2003	2004	2005	2006	2007	2008	2009	2002	2003	2004	2005	2006	2007	2008	2009
mean	0.4051	0.3727	0.4148	0.3648	0.3885	0.4023	0.4441	0.5511	0.3318	0.3215	0.3090	0.3405	0.3238	0.2948	0.4242	0.4021
count	30	29	29	26	29	30	29	25	30	29	28	30	30	29	28	11
Std	0.2122	0.1579	0.1570	0.1753	0.1467	0.1731	0.2060	0.1865	0.1496	0.1668	0.1789	0.1742	0.1422	0.1460	0.1935	0.1679
5th	0.2016	0.1842	0.1976	0.1226	0.2010	0.1475	0.1876	0.2532	0.1861	0.1455	0.1209	0.1727	0.1623	0.1397	0.2027	0.2031
95th	0.7126	0.5772	0.6706	0.6341	0.6396	0.6829	0.7715	0.8404	0.5603	0.6151	0.6765	0.7105	0.6182	0.5161	0.7665	0.6412

Table AA2.2 Yearly seasonal composition of $PM_{2.5}$ _ Milwaukee (2002 ~2009)

	Winter								Spring							
NH4%	2002	2003	2004	2005	2006	2007	2008	2009	2002	2003	2004	2005	2006	2007	2008	2009
mean	0.1388	0.1300	0.1408	0.1617	0.1514	0.1619	0.1528	0.1558	0.1492	0.1396	0.1317	0.1504	0.151	0.1385	0.1526	0.119
count	29	29	30	27	25	27	29	30	28	29	31	31	25	31	31	29
Std	0.1159	0.0981	0.1355	0.0995	0.0928	0.1365	0.0998	0.1219	0.1109	0.1438	0.1031	0.1141	0.1332	0.1106	0.1326	0.0872
5th	0.0294	0.0430	0.0274	0.0442	0.0315	0.0217	0.0507	0.0259	0.0204	0.0224	0.0167	0.0311	0.0451	0.0292	0.0183	0.0353
95th	0.3809	0.3139	0.4471	0.3465	0.2921	0.4176	0.3263	0.3768	0.3706	0.4241	0.3067	0.3300	0.4166	0.2578	0.4273	0.3028
	Summer								Fall							
NH4%	2002	2003	2004	2005	2006	2007	2008	2009	2002	2003	2004	2005	2006	2007	2008	2009
mean	0.1100	0.1059	0.0869	0.1228	0.0917	0.1153	0.0907	0.0765	0.1408	0.1301	0.1293	0.1331	0.1142	0.1379	0.1187	0.1291
count	31	30	31	29	31	31	30	28	30	28	30	29	30	29	29	30
Std	0.0824	0.0829	0.0823	0.1288	0.0764	0.1131	0.0766	0.0894	0.1271	0.1169	0.1274	0.1134	0.1091	0.1153	0.1077	0.1332
5th	0.0136	0.0208	0.0086	0.0131	0.0176	0.0074	0.0151	0.0150	0.0209	0.0265	0.0192	0.0118	0.0136	0.0197	0.0205	0.0212
95th	0.2474	0.2540	0.2555	0.3986	0.2239	0.3568	0.2438	0.2106	0.3692	0.3532	0.3586	0.3152	0.3416	0.3367	0.3104	0.4155

	Winter								Spring							
NO3%	2002	2003	2004	2005	2006	2007	2008	2009	2002	2003	2004	2005	2006	2007	2008	2009
mean	0.3484	0.2988	0.3291	0.3639	0.3117	0.3579	0.3094	0.3507	0.2705	0.2699	0.2541	0.281	0.2361	0.2263	0.2551	0.1758
count	29	29	30	27	25	27	29	30	28	29	31	31	25	31	31	29
Std	0.2852	0.2170	0.3447	0.2216	0.2056	0.2745	0.2178	0.295	0.2251	0.2938	0.2387	0.2437	0.2226	0.1859	0.2652	0.2018
5th	0.0858	0.0669	0.0538	0.0944	0.0368	0.0489	0.0665	0.0408	0.0168	0.0295	0.0313	0.0489	0.0468	0.0238	0.0215	0.0227
95th	0.9218	0.7178	1.1461	0.7367	0.5825	0.9672	0.6162	0.9338	0.7256	0.8667	0.7577	0.7042	0.6310	0.4879	0.8155	0.5038
	Summer								Fall							
NO3%	2002	2003	2004	2005	2006	2007	2008	2009	2002	2003	2004	2005	2006	2007	2008	2009
mean	0.0959	0.0785	0.0898	0.0679	0.0588	0.0906	0.0792	0.0647	0.2123	0.2075	0.1829	0.1396	0.1892	0.1839	0.168	0.2144
count	31	30	31	29	31	31	30	28	30	28	30	29	30	29	29	30
Std	0.0845	0.0556	0.0881	0.0567	0.0461	0.103	0.0741	0.082	0.1956	0.1659	0.1822	0.1196	0.2417	0.2061	0.1658	0.2732
5th	0.0125	0.0152	0.0136	0.0133	0.0100	0.0086	0.0120	0.0174	0.0212	0.0428	0.0205	0.0122	0.0183	0.0222	0.0169	0.0116
95th	0.2600	0.1727	0.2691	0.1658	0.1251	0.3090	0.2125	0.1610	0.5801	0.5059	0.5517	0.3755	0.6437	0.6286	0.4649	0.6481

				Winter									**Spring**			
SO4%	2002	2003	2004	2005	2006	2007	2008	2009	2002	2003	2004	2005	2006	2007	2008	2009
mean	0.1464	0.1460	0.1512	0.2066	0.1732	0.1299	0.1624	0.1428	0.2336	0.2177	0.2012	0.2212	0.2485	0.2099	0.229	0.1788
count	29	29	30	27	25	27	29	30	28	29	31	31	25	31	31	29
Std	0.0906	0.1036	0.0884	0.2219	0.0901	0.0685	0.1004	0.0824	0.1319	0.1709	0.1295	0.1435	0.1968	0.2032	0.1605	0.0836
5th	0.0583	0.0638	0.0628	0.0488	0.0693	0.0426	0.0703	0.0447	0.0767	0.0625	0.0533	0.0664	0.0860	0.0795	0.0550	0.0722
95th	0.2828	0.2851	0.3114	0.3507	0.3506	0.2561	0.3734	0.2853	0.4879	0.6205	0.4249	0.4421	0.6909	0.3739	0.5159	0.3239
				Summer								Fall				
SO4%	2002	2003	2004	2005	2006	2007	2008	2009	2002	2003	2004	2005	2006	2007	2008	2009
mean	0.2677	0.2705	0.2163	0.3417	0.2438	0.2575	0.2163	0.1814	0.2560	0.2324	0.2517	0.2766	0.1795	0.2335	0.2128	0.2118
count	31	30	31	29	31	31	30	28	30	28	30	29	30	29	29	30
Std	0.1818	0.2059	0.1832	0.371	0.1828	0.2407	0.1673	0.1716	0.3177	0.2429	0.268	0.2821	0.1292	0.1891	0.2166	0.1758
5th	0.0449	0.0688	0.0462	0.0445	0.0454	0.0287	0.0480	0.0577	0.0591	0.0524	0.0462	0.0357	0.0349	0.0461	0.0521	0.0567
95th	0.6081	0.6276	0.6357	1.1984	0.5779	0.8222	0.5583	0.4517	0.7990	0.8050	0.7681	0.7341	0.4347	0.5709	0.6692	0.5712

				Winter								Spring				
EC%	2002	2003	2004	2005	2006	2007	2008	2009	2002	2003	2004	2005	2006	2007	2008	2009
mean	0.0300	0.0367	0.0331	0.0294	0.0325	0.0318	0.0327	0.0387	0.0344	0.0320	0.0378	0.0361	0.0368	0.0405	0.0331	0.0357
count	29	29	30	27	25	27	29	20	28	29	31	31	25	31	31	29
Std	0.0158	0.0164	0.0130	0.0179	0.0191	0.0159	0.0114	0.0537	0.0244	0.0187	0.022	0.0224	0.0201	0.0208	0.0193	0.0211
5th	0.0102	0.0191	0.0146	0.0111	0.0119	0.0105	0.0153	0.0110	0.0099	0.0098	0.0124	0.0110	0.0121	0.0072	0.0083	0.0130
95th	0.0553	0.0705	0.0498	0.0671	0.0572	0.0614	0.0505	0.0651	0.0761	0.0688	0.0742	0.0799	0.0616	0.0746	0.0717	0.0789
				Summer								Fall				
EC%	2002	2003	2004	2005	2006	2007	2008	2009	2002	2003	2004	2005	2006	2007	2008	2009
mean	0.0322	0.0398	0.048	0.0355	0.0398	0.0436	0.0504	0.0451	0.0446	0.0502	0.0495	0.0481	0.0488	0.0517	0.0623	0.0508
count	31	30	31	29	31	31	30	28	30	28	30	29	30	29	29	13
Std	0.0184	0.0218	0.0262	0.0205	0.0194	0.0205	0.0231	0.0217	0.0275	0.0276	0.0291	0.0287	0.0334	0.0255	0.0345	0.0389
5th	0.0083	0.0144	0.0145	0.0045	0.0074	0.0176	0.0215	0.0135	0.0157	0.0174	0.0088	0.0129	0.0095	0.0219	0.0199	0.0058
95th	0.0641	0.0780	0.0974	0.0695	0.0697	0.0736	0.0875	0.0747	0.0743	0.1075	0.1020	0.0918	0.1079	0.0958	0.1343	0.1114

	Winter								**Spring**							
OC%	2002	2003	2004	2005	2006	2007	2008	2009	2002	2003	2004	2005	2006	2007	2008	2009
mean	0.2680	0.2730	0.2323	0.1905	0.2162	0.2137	0.2062	0.3814	0.2517	0.3231	0.2639	0.2679	0.2719	0.2687	0.312	0.326
count	29	29	30	27	25	27	29	20	28	29	31	31	25	31	31	29
Std	0.1061	0.1100	0.0819	0.0765	0.0742	0.0941	0.0688	0.6233	0.1041	0.1303	0.1393	0.1077	0.1004	0.1733	0.1228	0.1278
5th	0.1310	0.1710	0.1221	0.0924	0.1180	0.1080	0.1232	0.1208	0.1400	0.1691	0.1067	0.1420	0.1613	0.1372	0.1593	0.1912
95th	0.4487	0.4074	0.3658	0.3232	0.3351	0.3937	0.3138	0.6389	0.4592	0.5474	0.5290	0.5044	0.4482	0.6226	0.4893	0.5470
	Summer								Fall							
OC%	2002	2003	2004	2005	2006	2007	2008	2009	2002	2003	2004	2005	2006	2007	2008	2009
mean	0.3661	0.3780	0.3922	0.3013	0.3327	0.3536	0.474	0.4975	0.2826	0.3160	0.3202	0.256	0.297	0.2911	0.3907	0.3528
count	31	30	31	29	31	31	30	28	30	28	30	29	30	29	29	13
Std	0.1203	0.1202	0.1521	0.0811	0.1289	0.1121	0.1504	0.2579	0.1233	0.1000	0.1351	0.0982	0.1613	0.1217	0.1971	0.1623
5th	0.2182	0.1999	0.2055	0.1987	0.1262	0.1996	0.2628	0.2116	0.1170	0.1649	0.1746	0.1188	0.1481	0.1621	0.1557	0.1798
95th	0.5619	0.5889	0.6069	0.4347	0.4962	0.5427	0.7128	1.0274	0.5428	0.4799	0.5690	0.4195	0.5212	0.5038	0.6917	0.6076

Table AA2.3 Yearly seasonal composition of $PM_{2.5}$ _ Perkinstown (2002 ~2009)

	Winter								**Spring**							
NH4	2002	2003	2004	2005	2006	2007	2008	2009	2002	2003	2004	2005	2006	2007	2008	2009
Mean	0.1179	0.1181	0.1144	0.1337	0.1132	0.1144	0.1157	0.1292	0.1145	0.0990	0.1135	0.1431	0.0926	0.0927	0.1319	0.1044
count	28	19	15	15	16	13	15	15	30	15	14	15	15	16	16	14
Std	0.0648	0.0595	0.0529	0.0352	0.0480	0.0485	0.0506	0.0380	0.0399	0.0547	0.0486	0.0550	0.0540	0.0500	0.0576	0.0438
5th	0.0319	0.0271	0.0391	0.0713	0.0491	0.0512	0.0580	0.0725	0.0631	0.0280	0.0608	0.0703	0.0179	0.0316	0.0543	0.0517
95th	0.2276	0.2004	0.1873	0.1764	0.1840	0.1840	0.1942	0.1791	0.1704	0.1725	0.1843	0.2168	0.1738	0.1694	0.2028	0.1705
	Summer								Fall							
NH4	2002	2003	2004	2005	2006	2007	2008	2009	2002	2003	2004	2005	2006	2007	2008	2009
Mean	0.0757	0.0569	0.0571	0.0734	0.0350	0.0645	0.0893	0.0384	0.1125	0.1038	0.0948	0.0763	0.0983	0.0749	0.0730	0.1016
count	29	16	15	15	14	14	15	15	29	13	13	16	15	15	15	15
Std	0.0417	0.0379	0.0456	0.0583	0.0282	0.0433	0.0943	0.0384	0.0475	0.0468	0.0389	0.0492	0.0470	0.0469	0.0404	0.0626
5th	0.0145	0.0066	0.0084	0.0071	0.0059	0.0143	0.0035	0.0047	0.0438	0.0371	0.0417	0.0145	0.0440	0.0195	0.0220	0.0298
95th	0.1378	0.1069	0.1352	0.1764	0.0780	0.1201	0.2466	0.1037	0.1849	0.1632	0.1588	0.1579	0.1639	0.1548	0.1330	0.2140

	Winter								Spring							
NO3	2002	2003	2004	2005	2006	2007	2008	2009	2002	2003	2004	2005	2006	2007	2008	2009
Mean	0.3099	0.2592	0.1995	0.2901	0.2158	0.2587	0.2339	0.2585	0.1940	0.1457	0.1704	0.2568	0.0982	0.1256	0.2054	0.1520
count	28	19	15	15	16	13	15	15	30	15	14	15	15	16	16	14
Std	0.1722	0.1422	0.1401	0.1520	0.1427	0.1482	0.1411	0.1268	0.1553	0.0981	0.1354	0.1541	0.1093	0.1493	0.1371	0.1237
5th	0.0518	0.0635	0.0618	0.0608	0.0241	0.0697	0.0624	0.1077	0.0471	0.0381	0.0337	0.0793	0.0084	0.0125	0.0314	0.0142
95th	0.5849	0.4523	0.4798	0.4860	0.4109	0.4559	0.4627	0.4433	0.3617	0.3037	0.3869	0.5018	0.3169	0.3952	0.3872	0.3464
	Summer								Fall							
NO3	2002	2003	2004	2005	2006	2007	2008	2009	2002	2003	2004	2005	2006	2007	2008	2009
Mean	0.0538	0.0409	0.0466	0.0479	0.0163	0.0401	0.0425	0.0421	0.1941	0.1674	0.1590	0.1138	0.1592	0.1152	0.0770	0.1271
count	29	16	15	15	14	14	15	15	29	13	13	16	15	15	15	15
Std	0.0305	0.0324	0.0386	0.0346	0.0090	0.0317	0.0255	0.0342	0.1267	0.1316	0.1213	0.1217	0.1395	0.1113	0.0679	0.1301
5th	0.0184	0.0154	0.0161	0.0134	0.0044	0.0106	0.0131	0.0081	0.0525	0.0281	0.0258	0.0267	0.0323	0.0214	0.0209	0.0231
95th	0.1144	0.1197	0.1070	0.1056	0.0302	0.0981	0.0853	0.0960	0.4071	0.3504	0.3548	0.2730	0.3526	0.3400	0.2266	0.4171

				Winter								**Spring**				
SO4	2002	2003	2004	2005	2006	2007	2008	2009	2002	2003	2004	2005	2006	2007	2008	2009
Mean	0.2072	0.1964	0.2226	0.1903	0.2003	0.1659	0.1769	0.2004	0.3119	0.2501	0.2325	0.2608	0.2368	0.1991	0.2604	0.2283
count	28	19	15	15	16	13	15	15	30	15	14	15	15	16	16	14
Std	0.1218	0.0956	0.0726	0.0676	0.0600	0.0569	0.0699	0.1018	0.1680	0.0838	0.0304	0.0785	0.1111	0.0662	0.0643	0.0798
5th	0.0774	0.0925	0.1213	0.1132	0.1050	0.0832	0.1078	0.0929	0.1721	0.1297	0.1931	0.1693	0.0712	0.0970	0.1774	0.1285
95th	0.4582	0.3849	0.3264	0.2971	0.2761	0.2497	0.3073	0.3859	0.5119	0.3956	0.2848	0.3797	0.4091	0.2847	0.3814	0.3389
				Summer								Fall				
SO4	2002	2003	2004	2005	2006	2007	2008	2009	2002	2003	2004	2005	2006	2007	2008	2009
Mean	0.2253	0.2109	0.1932	0.2572	0.1092	0.1888	0.2579	0.1385	0.2509	0.2469	0.2267	0.2052	0.1948	0.1760	0.2142	0.2413
count	29	16	15	15	14	14	15	15	29	13	13	16	15	15	15	15
Std	0.0964	0.0873	0.0960	0.1155	0.0717	0.1047	0.2314	0.0704	0.0860	0.0930	0.0759	0.0748	0.0730	0.0633	0.0969	0.0804
5th	0.0819	0.0885	0.0516	0.1063	0.0205	0.0596	0.0693	0.0486	0.1227	0.1554	0.1357	0.1151	0.1137	0.1075	0.0940	0.1353
95th	0.3756	0.3290	0.3282	0.4526	0.2165	0.3129	0.6368	0.2327	0.3874	0.4276	0.3327	0.3096	0.3396	0.2815	0.3618	0.3700

				Winter								Spring				
EC	2002	2003	2004	2005	2006	2007	2008	2009	2002	2003	2004	2005	2006	2007	2008	2009
Mean	0.0219	0.0274	0.0312	0.0279	0.0270	0.0322	0.0274	0.0237	0.0241	0.0174	0.0278	0.0291	0.0258	0.0335	0.0238	0.0331
count	28	19	15	15	16	13	15	10	29	14	14	15	15	16	16	14
Std	0.0150	0.0192	0.0184	0.0120	0.0188	0.0227	0.0129	0.0113	0.0200	0.0089	0.0093	0.0133	0.0217	0.0284	0.0172	0.0225
5th	0.0061	0.0085	0.0112	0.0155	0.0040	0.0052	0.0099	0.0110	0.0041	0.0063	0.0130	0.0111	0.0049	0.0012	0.0075	0.0074
95th	0.0516	0.0526	0.0651	0.0476	0.0581	0.0692	0.0525	0.0421	0.0504	0.0324	0.0416	0.0498	0.0657	0.0764	0.0564	0.0685
				Summer								Fall				
EC	2002	2003	2004	2005	2006	2007	2008	2009	2002	2003	2004	2005	2006	2007	2008	2009
Mean	0.0206	0.0200	0.0265	0.0149	0.0154	0.0214	0.0284	0.0358	0.0241	0.0222	0.0405	0.0382	0.0437	0.0418	0.0571	0.0639
count	26	16	15	15	14	14	15	15	29	13	13	16	15	15	15	8
Std	0.0202	0.0094	0.0095	0.0157	0.0120	0.0143	0.0111	0.0246	0.0122	0.0117	0.0208	0.0295	0.0200	0.0278	0.0402	0.0404
5th	0.0006	0.0090	0.0134	0.0002	0.0004	0.0066	0.0140	0.0001	0.0105	0.0073	0.0172	0.0039	0.0201	0.0019	0.0038	0.0227
95th	0.0605	0.0357	0.0374	0.0418	0.0318	0.0438	0.0476	0.0747	0.0446	0.0413	0.0751	0.0952	0.0815	0.0831	0.1211	0.1248

				Winter								**Spring**				
OC	2002	2003	2004	2005	2006	2007	2008	2009	2002	2003	2004	2005	2006	2007	2008	2009
Mean	0.3561	0.3337	0.3314	0.2377	0.2710	0.2634	0.3062	0.2251	0.4782	0.3228	0.3045	0.3103	0.3378	0.2617	0.3828	0.3558
count	28	19	15	15	16	13	15	10	29	14	14	15	15	16	16	14
Std	0.2444	0.2043	0.2131	0.0637	0.1278	0.1386	0.1351	0.0805	0.2984	0.1175	0.1364	0.1681	0.1643	0.0943	0.2098	0.1653
5th	0.1571	0.1479	0.1420	0.1243	0.1377	0.1190	0.1487	0.1317	0.1854	0.1694	0.1271	0.1537	0.1013	0.1566	0.1629	0.1369
95th	0.6075	0.6897	0.6353	0.3138	0.4835	0.4788	0.4887	0.3412	1.0750	0.5306	0.5018	0.6197	0.6053	0.3997	0.7671	0.5931
				Summer								Fall				
OC	2002	2003	2004	2005	2006	2007	2008	2009	2002	2003	2004	2005	2006	2007	2008	2009
Mean	0.4556	0.4956	0.4249	0.5214	0.4266	0.4210	0.4943	0.7115	0.4358	0.3484	0.3410	0.4807	0.4078	0.4308	0.8546	0.7715
count	26	16	15	15	14	14	15	15	29	13	13	16	15	15	15	8
Std	0.1693	0.2441	0.1227	0.5097	0.2140	0.1422	0.2089	0.3244	0.3210	0.1526	0.1670	0.3366	0.1819	0.1842	0.8573	0.4877
5th	0.2405	0.2487	0.3059	0.1744	0.1169	0.2647	0.2556	0.3125	0.1663	0.1703	0.1444	0.1777	0.1795	0.1624	0.2174	0.2281
95th	0.7444	0.9063	0.6793	1.2080	0.7488	0.6384	0.8590	1.2033	0.8995	0.5820	0.6531	1.0621	0.6644	0.7037	2.2098	1.5296

Table AA2.4. Yearly seasonal mean concentration of major $PM_{2.5}$ components (Milw, 02 ~ 09)

	Seasons	2002	2003	2004	2005	2006	2007	2008	2009
PM2.5	Winter	14.1034	12.1643	13.1400	19.4370	12.9680	16.0259	14.2517	15.1267
	Spring	11.0714	10.9655	11.7200	11.8645	10.8880	12.1032	9.1968	9.2138
	Summer	15.0548	13.6567	9.9032	15.9207	14.2677	13.0742	10.5967	8.8571
	Fall	14.2533	12.5036	11.8833	14.4276	12.6833	12.7103	10.6000	9.7000
NH4	Winter	1.9576	1.5813	1.8505	3.1432	1.9640	2.5946	2.1781	2.3562
	Spring	1.6517	1.5313	1.5430	1.7846	1.6442	1.6759	1.4039	1.0963
	Summer	1.6553	1.4460	0.8609	1.9556	1.3082	1.5073	0.9614	0.6779
	Fall	2.0073	1.6264	1.5363	1.9210	1.4489	1.7532	1.2255	1.2522
NO3	Winter	4.9130	3.6341	4.3245	7.0726	4.0417	5.7352	4.4091	5.3052
	Spring	2.9952	2.9592	2.9776	3.3338	2.5709	2.7390	2.3459	1.6198
	Summer	1.4441	1.0714	0.8892	1.0807	0.8391	1.1845	0.8391	0.5732
	Fall	3.0257	2.5944	2.1734	2.0135	2.3997	2.3379	1.7281	2.0792
SO4	Winter	2.0645	1.7762	1.9868	4.0164	2.2463	2.0816	2.3145	2.1599
	Spring	2.5868	2.3869	2.3579	2.6241	2.7054	2.5403	2.1061	1.6477
	Summer	4.0302	3.6941	2.1421	5.4406	3.4784	3.3665	2.2920	1.6071
	Fall	3.6491	2.9055	2.9910	3.9909	2.2760	2.9678	2.2158	2.0544
EC	Winter	0.4234	0.4466	0.4352	0.5711	0.4209	0.5092	0.4657	0.5850
	Spring	0.3811	0.3510	0.4434	0.4286	0.4011	0.4903	0.3045	0.3285
	Summer	0.4855	0.5436	0.4754	0.5647	0.5679	0.5704	0.5336	0.3993
	Fall	0.6363	0.6279	0.5877	0.6944	0.6195	0.6573	0.6452	0.4925
OC	Winter	3.7797	3.3214	3.0530	3.7033	2.8036	3.4252	2.9383	5.7690
	Spring	2.7864	3.5424	3.0932	3.1781	2.9608	3.2523	2.8697	3.0041
	Summer	5.5119	5.1627	3.8845	4.7972	4.7474	4.6229	5.0227	4.4061
	Fall	4.0277	3.9507	3.8047	3.6934	3.7670	3.7003	4.1110	3.4223

Table AA2.5. Yearly seasonal mean concentration of major $PM_{2.5}$ components (Wauk, 02 ~ 09)

	Seasons	2002	2003	2004	2005	2006	2007	2008	2009
PM2.5	Winter	14.1034	12.1643	13.1400	19.4370	12.9680	16.0259	14.2517	15.1267
	Spring	11.0714	10.9655	11.7200	11.8645	10.8880	12.1032	9.1968	9.2138
	Summer	15.0548	13.6567	9.9032	15.9207	14.2677	13.0742	10.5967	8.8571
	Fall	14.2533	12.5036	11.8833	14.4276	12.6833	12.7103	10.6000	9.7000
NH4	Winter	1.9576	1.5813	1.8505	3.1432	1.9640	2.5946	2.1781	2.3562
	Spring	1.6517	1.5313	1.5430	1.7846	1.6442	1.6759	1.4039	1.0963
	Summer	1.6553	1.4460	0.8609	1.9556	1.3082	1.5073	0.9614	0.6779
	Fall	2.0073	1.6264	1.5363	1.9210	1.4489	1.7532	1.2255	1.2522
NO3	Winter	4.9130	3.6341	4.3245	7.0726	4.0417	5.7352	4.4091	5.3052
	Spring	2.9952	2.9592	2.9776	3.3338	2.5709	2.7390	2.3459	1.6198
	Summer	1.4441	1.0714	0.8892	1.0807	0.8391	1.1845	0.8391	0.5732
	Fall	3.0257	2.5944	2.1734	2.0135	2.3997	2.3379	1.7281	2.0792
SO4	Winter	2.0645	1.7762	1.9868	4.0164	2.2463	2.0816	2.3145	2.1599

	Spring	2.5868	2.3869	2.3579	2.6241	2.7054	2.5403	2.1061	1.6477
	Summer	4.0302	3.6941	2.1421	5.4406	3.4784	3.3665	2.2920	1.6071
	Fall	3.6491	2.9055	2.9910	3.9909	2.2760	2.9678	2.2158	2.0544
EC	Winter	0.4234	0.4466	0.4352	0.5711	0.4209	0.5092	0.4657	0.5850
	Spring	0.3811	0.3510	0.4434	0.4286	0.4011	0.4903	0.3045	0.3285
	Summer	0.4855	0.5436	0.4754	0.5647	0.5679	0.5704	0.5336	0.3993
	Fall	0.6363	0.6279	0.5877	0.6944	0.6195	0.6573	0.6452	0.4925
OC	Winter	3.7797	3.3214	3.0530	3.7033	2.8036	3.4252	2.9383	5.7690
	Spring	2.7864	3.5424	3.0932	3.1781	2.9608	3.2523	2.8697	3.0041
	Summer	5.5119	5.1627	3.8845	4.7972	4.7474	4.6229	5.0227	4.4061
	Fall	4.0277	3.9507	3.8047	3.6934	3.7670	3.7003	4.1110	3.4223

Table AA2.6. Yearly seasonal mean concentration of major $PM_{2.5}$ components (Mayv, 02 ~ 09)

	Season	**2002**	**2003**	**2004**	**2005**	**2006**	**2007**	**2008**	**2009**
PM2.5	Winter	12.2828	9.5414	12.1357	15.8138	10.8586	13.7000	13.2464	16.1000
	Spring	9.6107	11.9129	10.8346	10.3433	11.9207	11.0767	10.1069	7.5731
	Summer	13.2700	10.5103	7.9931	15.0654	11.8207	10.8100	9.3448	7.2320
	Fall	11.3500	10.4034	9.7500	10.5767	9.8733	10.9931	10.3071	9.0727
NH4	Winter	1.7959	1.3811	1.9297	2.6921	1.6642	2.0746	2.0519	2.6538
	Spring	1.5167	1.8605	1.6358	1.7074	1.3949	1.6056	1.6537	1.0445
	Summer	1.6084	1.1613	0.8885	1.7571	1.4169	1.2527	0.9449	0.7670
	Fall	1.7450	1.5576	1.4070	1.6662	1.4033	1.5930	1.3787	1.4546
NO3	Winter	4.7170	3.3893	4.5556	6.3437	3.7551	4.9780	4.6277	6.3044
	Spring	2.8439	3.7721	2.8549	3.1548	2.2386	2.5805	2.8003	1.7340
	Summer	1.5494	1.0691	0.9015	1.0631	1.0993	0.8726	0.8987	0.6542
	Fall	2.9525	2.3974	2.2255	2.0226	2.6262	2.2403	1.9131	1.3949
SO4	Winter	1.8374	1.4947	2.0020	2.6091	1.8171	1.9816	2.0515	2.2768
	Spring	2.3346	2.6941	2.4570	2.4502	2.2769	2.3830	2.2575	1.7548
	Summer	3.5563	2.7517	2.0085	4.6582	3.1531	2.7783	2.0390	1.7281
	Fall	3.1298	2.8646	2.5997	3.2369	1.8653	2.6691	2.3557	2.9280
EC	Winter	0.2224	0.2394	0.2498	0.2897	0.2438	0.2811	0.3071	0.3161
	Spring	0.1987	0.2158	0.2373	0.2536	0.2162	0.3575	0.2345	0.1979
	Summer	0.2163	0.2509	0.2207	0.2726	0.3055	0.3049	0.2989	0.2507
	Fall	0.2848	0.3099	0.2917	0.3420	0.3850	0.3897	0.3636	0.3581
OC	Winter	2.6076	2.1576	2.0557	2.4148	1.9730	2.1354	2.3618	3.1881
	Spring	2.4271	2.6097	2.1965	2.2313	2.2334	2.7063	2.5161	2.3469
	Summer	4.6033	3.4783	2.8645	3.6396	3.9110	3.6047	3.3769	3.3628
	Fall	3.2810	2.5828	2.3236	2.7920	2.4700	2.6862	3.6650	2.9027

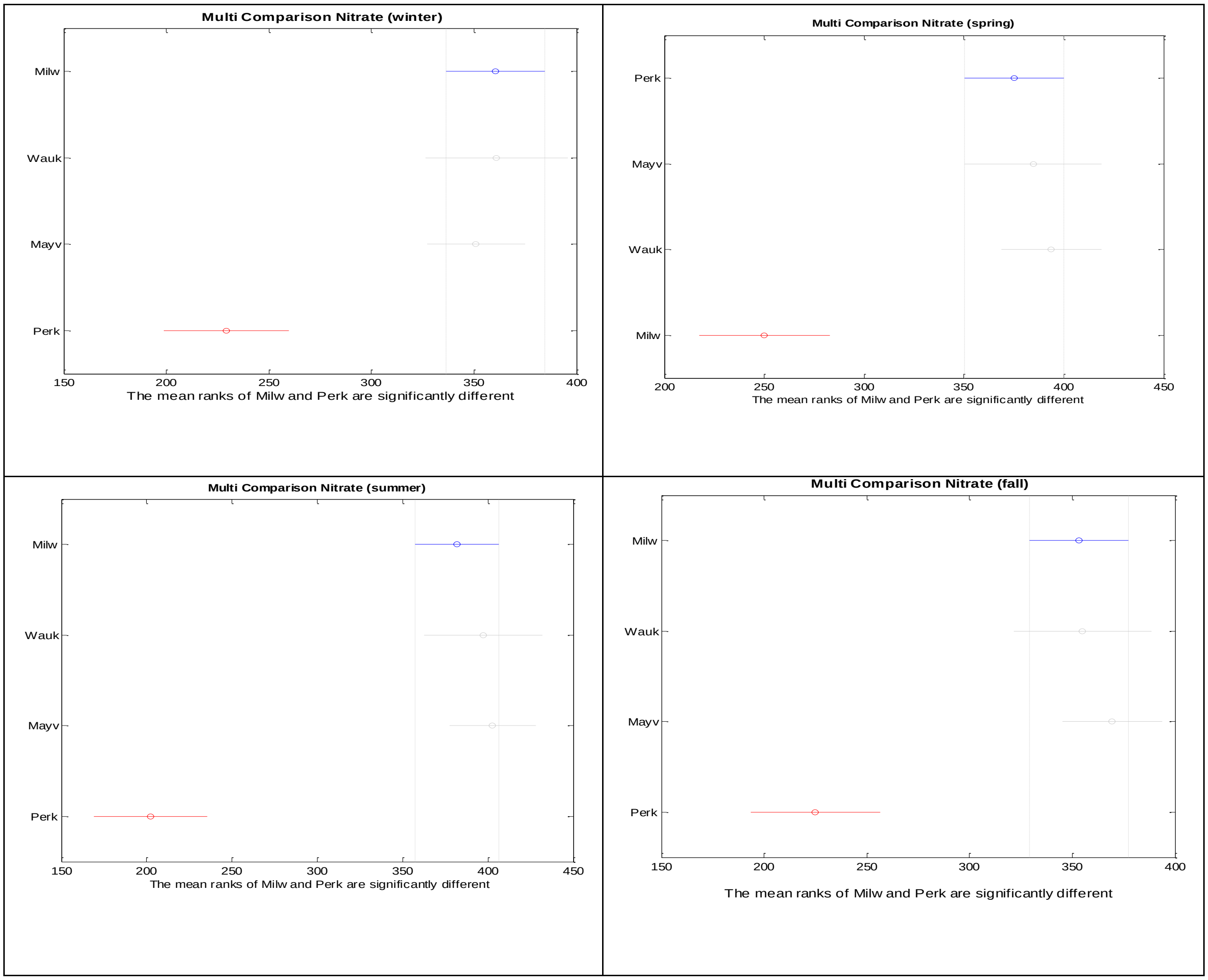
Table AA2.7. Yearly seasonal mean concentration of major $PM_{2.5}$ components (Perk, 02 ~ 09)

	Season	**2002**	**2003**	**2004**	**2005**	**2006**	**2007**	**2008**	**2009**
PM2.5	Winter	8.1759	8.3385	7.3538	7.3875	7.2533	7.1667	5.3733	6.1667
	Spring	7.0467	8.3400	6.5500	8.9400	9.2067	9.3563	7.8938	6.8357
	Summer	11.1517	10.3625	7.1333	12.5667	14.1143	9.2429	8.1733	5.6333
	Fall	7.9429	7.1000	8.8333	10.3267	8.0375	10.1538	11.4333	10.5800
NH4	Winter	1.0438	1.0300	0.8268	0.6748	0.8101	0.5888	0.5253	0.9202
	Spring	0.8810	0.8922	0.8201	1.3381	0.9502	0.8530	1.2157	0.7661
	Summer	0.9247	0.6730	0.4400	1.3120	0.4908	0.7155	0.9136	0.3098
	Fall	1.0751	0.9473	1.2245	1.5105	1.0718	1.3818	1.5851	1.5063
NO3	Winter	1.6693	1.3372	1.4033	1.0433	1.5113	0.9363	0.5757	1.1958
	Spring	1.5187	1.4146	1.3240	2.4038	1.2274	1.2283	2.0087	1.2031
	Summer	0.5606	0.3486	0.3256	0.5664	0.1856	0.3945	0.3848	0.2715
	Fall	2.8636	2.1135	2.3999	3.5556	2.2122	3.3160	3.5014	3.3541
SO4	Winter	2.0871	2.3241	1.6750	1.4409	1.3299	1.1787	1.2675	1.6412
	Spring	1.9674	1.8508	1.5181	2.1758	1.9683	1.6105	2.0043	1.4654
	Summer	2.5596	2.2367	1.3800	3.8906	1.4051	2.0241	2.5178	0.8886
	Fall	1.3709	1.3747	1.8809	1.7529	1.4818	1.5192	1.8275	1.7525
EC	Winter	0.1683	0.1720	0.2301	0.2203	0.2796	0.2563	0.2174	0.2030
	Spring	0.1363	0.1250	0.1758	0.2323	0.1616	0.2333	0.1606	0.1995
	Summer	0.1793	0.1779	0.1744	0.1841	0.1735	0.1879	0.2286	0.1656
	Fall	0.1479	0.1640	0.2178	0.2573	0.1905	0.2721	0.2739	0.2989
OC	Winter	2.7459	2.2783	1.9966	2.3598	2.4220	2.2467	2.5133	2.3688
	Spring	2.6252	2.2543	1.7351	2.1173	2.2184	2.1424	2.1644	2.0336
	Summer	4.1119	4.3313	2.8293	3.7393	3.8800	3.4679	3.3960	3.1600
	Fall	2.1782	1.8800	2.2680	2.2138	1.8241	2.1658	3.0333	2.6590

Table AA2.8. Long-term seasonal composition of major $PM_{2.5}$ components and trace metals

	Season	nh4	no3	so4	ec	oc	S	MMO	al	ca	si	fe	k
Milw	Winter	0.1505	0.3373	0.1589	0.0327	0.2415	0.0495	0.026	0.0011	0.0023	0.0029	0.0049	0.0035
	Spring	0.1416	0.2479	0.2172	0.036	0.2838	0.0698	0.0425	0.002	0.0033	0.0062	0.0068	0.004
	Summer	0.1024	0.0784	0.2569	0.0409	0.3759	0.0884	0.047	0.0027	0.0038	0.0066	0.0074	0.0096
	Fall	0.1297	0.1866	0.234	0.0512	0.312	0.078	0.0416	0.0016	0.0035	0.0046	0.0079	0.0045
Wauk	Winter	0.1293	0.3089	0.1414	0.0314	0.2395	0.0467	0.0394	0.0011	0.0023	0.0056	0.0078	0.0037
	Spring	0.1198	0.2244	0.1892	0.0371	0.2853	0.0584	0.0628	0.0025	0.0036	0.0106	0.01	0.0042
	Summer	0.0861	0.0699	0.2256	0.0476	0.3535	0.0757	0.07	0.0026	0.0038	0.0122	0.011	0.0095
	Fall	0.1097	0.1779	0.196	0.0523	0.3057	0.063	0.0734	0.0019	0.0041	0.0125	0.0127	0.0049
Chiw	Winter	0.155	0.3626	0.1818	0.0264	0.2235	0.058	0.0224	0.0009	0.0023	0.0032	0.0033	0.0039
	Spring	0.1429	0.2677	0.233	0.0276	0.2452	0.0749	0.0373	0.0019	0.0034	0.006	0.0049	0.0043
	Summer	0.1094	0.0701	0.3212	0.0278	0.2897	0.1039	0.042	0.003	0.0031	0.0065	0.0055	0.0049
	Fall	0.1328	0.1606	0.2914	0.0332	0.2551	0.0971	0.0302	0.0013	0.0031	0.0041	0.0048	0.0045
Mayv	Winter	0.1561	0.3718	0.1561	0.0208	0.1814	0.0511	0.0175	0.0012	0.002	0.0023	0.0022	0.0045
	Spring	0.1491	0.2644	0.223	0.0229	0.2305	0.0711	0.0311	0.0018	0.0022	0.0061	0.0032	0.0038
	Summer	0.1139	0.0948	0.2629	0.0246	0.3354	0.0898	0.0314	0.0023	0.0026	0.0054	0.0033	0.0048
	Fall	0.1475	0.2208	0.2587	0.0326	0.2722	0.0851	0.0279	0.0016	0.0033	0.0043	0.0033	0.0042
Perk	Winter	0.1381	0.3165	0.175	0.0236	0.2465	0.0568	0.0212	0.0014	0.0024	0.0035	0.0021	0.0052
	Spring	0.1207	0.1944	0.2318	0.0219	0.2787	0.0733	0.0409	0.0027	0.003	0.0084	0.0036	0.0045
	Summer	0.0751	0.0403	0.2185	0.0185	0.3692	0.0738	0.0394	0.0024	0.0031	0.0081	0.0033	0.0044
	Fall	0.1137	0.1729	0.2286	0.0296	0.3337	0.0759	0.0327	0.0021	0.0034	0.0061	0.0028	0.0047

1. Nitrate


Multi Comparison Nitrate (winter)

Multi Comparison Nitrate (spring)

Multi Comparison Nitrate (summer)

Multi Comparison Nitrate (fall)

Figure AA.1. K-Wanalysis for significant changes of Seasonal Nitrate

2. OC

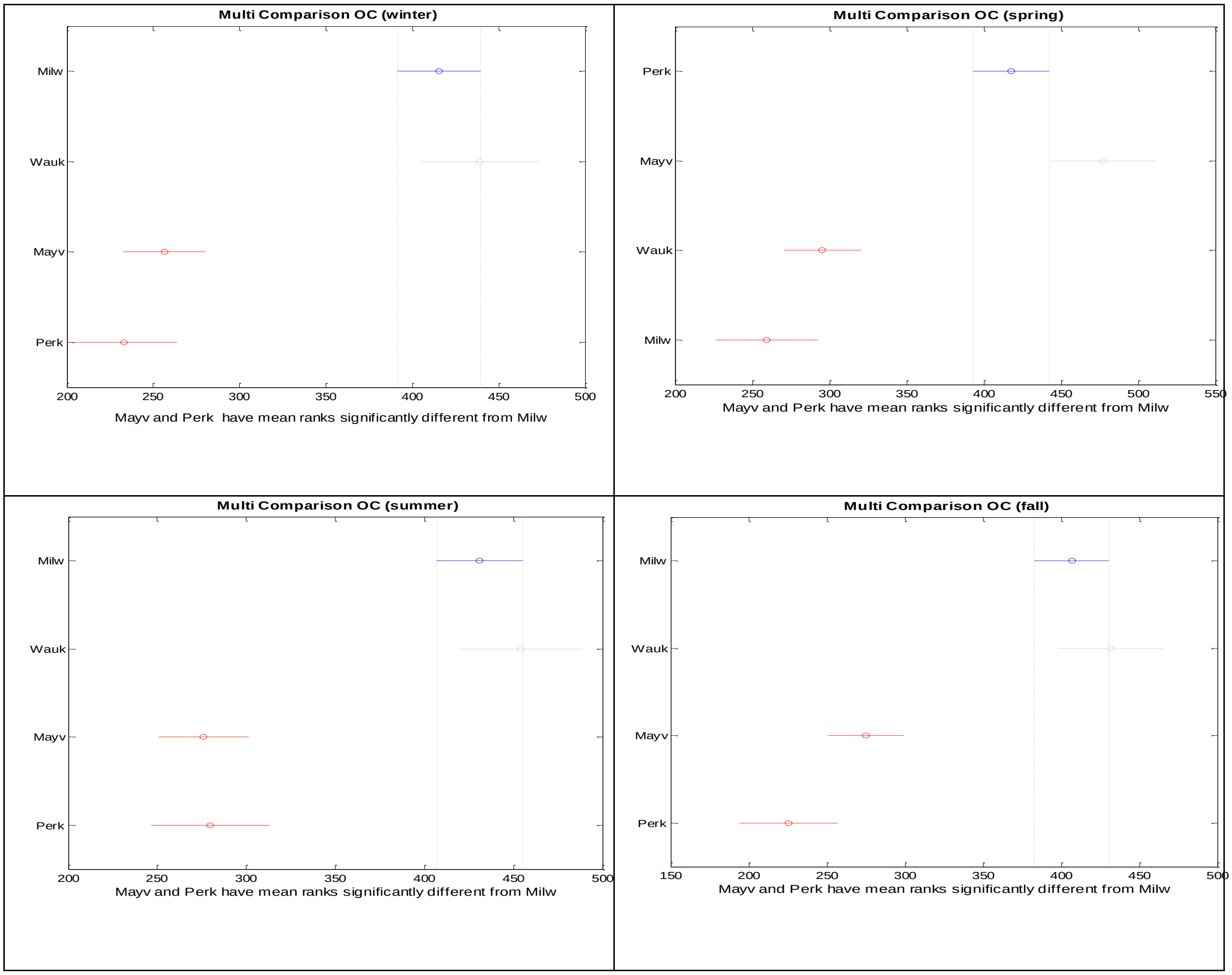


Figure AA.2 K-Wanalysis for significant changes of Seasonal OC

3. EC

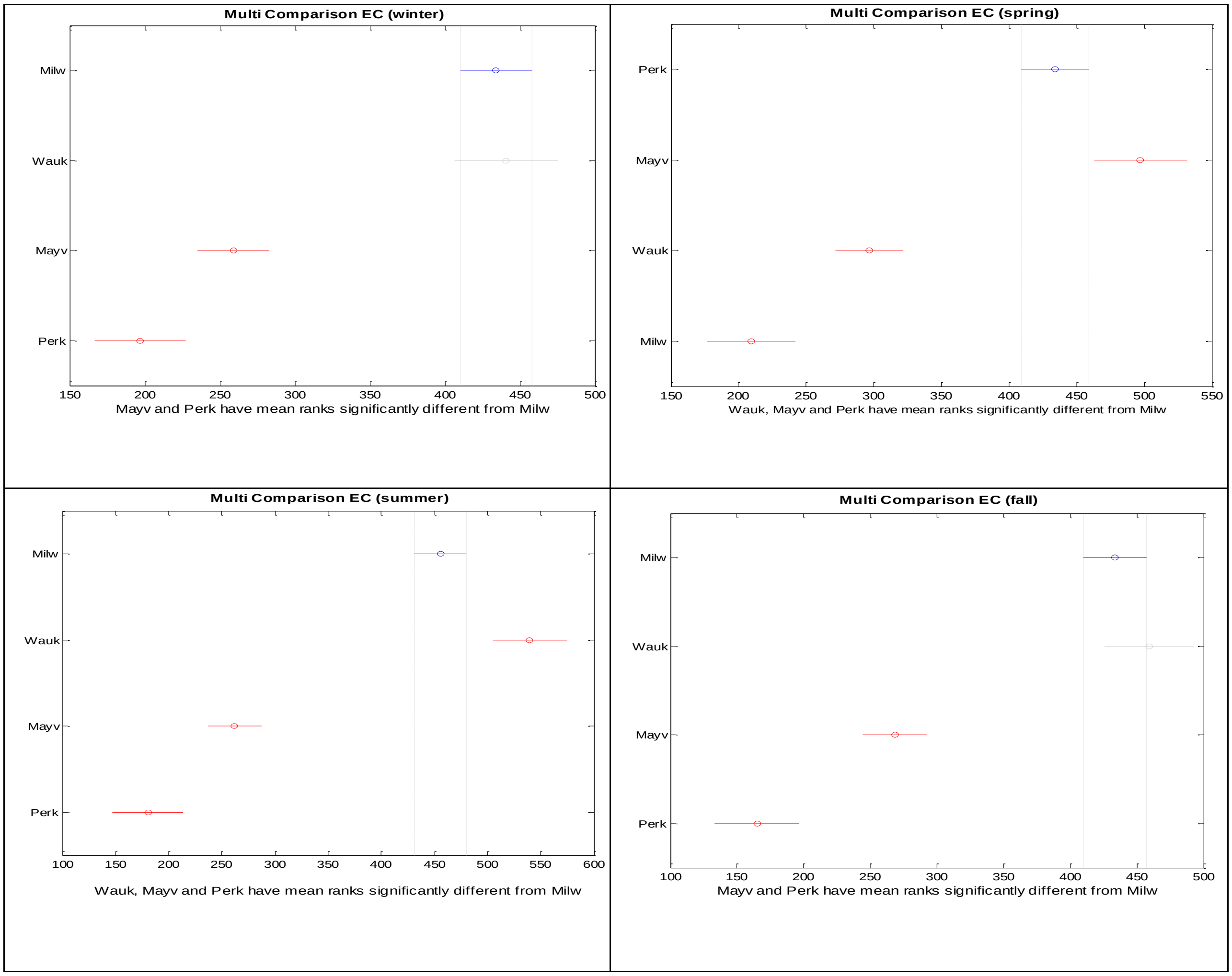


Figure AA.3 K-Wanalysis for significant changes of Seasonal EC

7.1.2. **Emission Inventory**

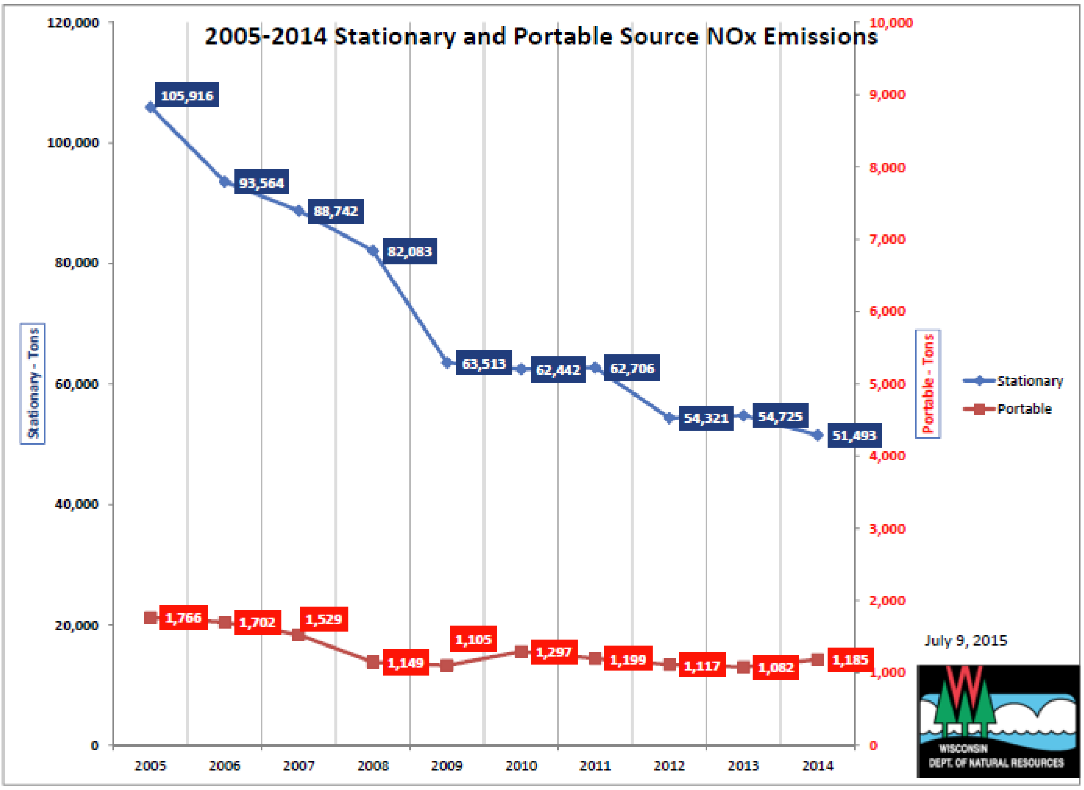


Figure AA.4 Wisconsin Nitrate Emission Inventory (2002 to 2014)

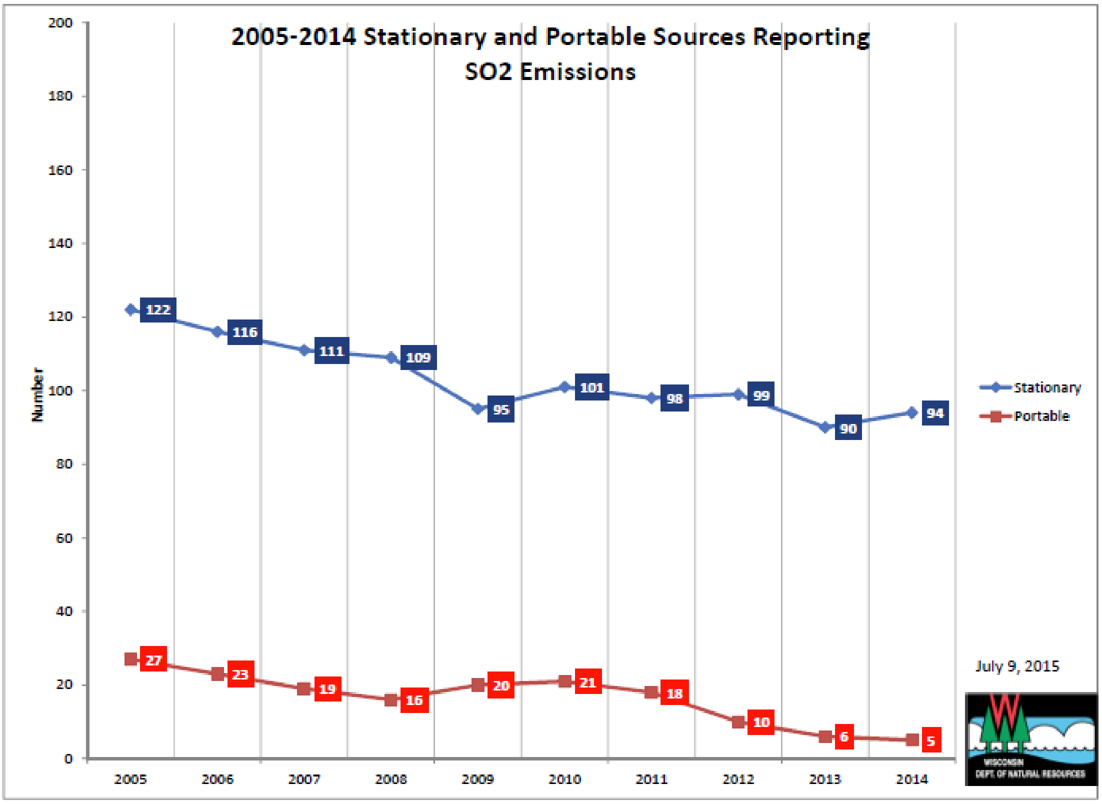


Figure AA.5 Wisconsin Sulfate Emission Inventory (2002 to 2014)

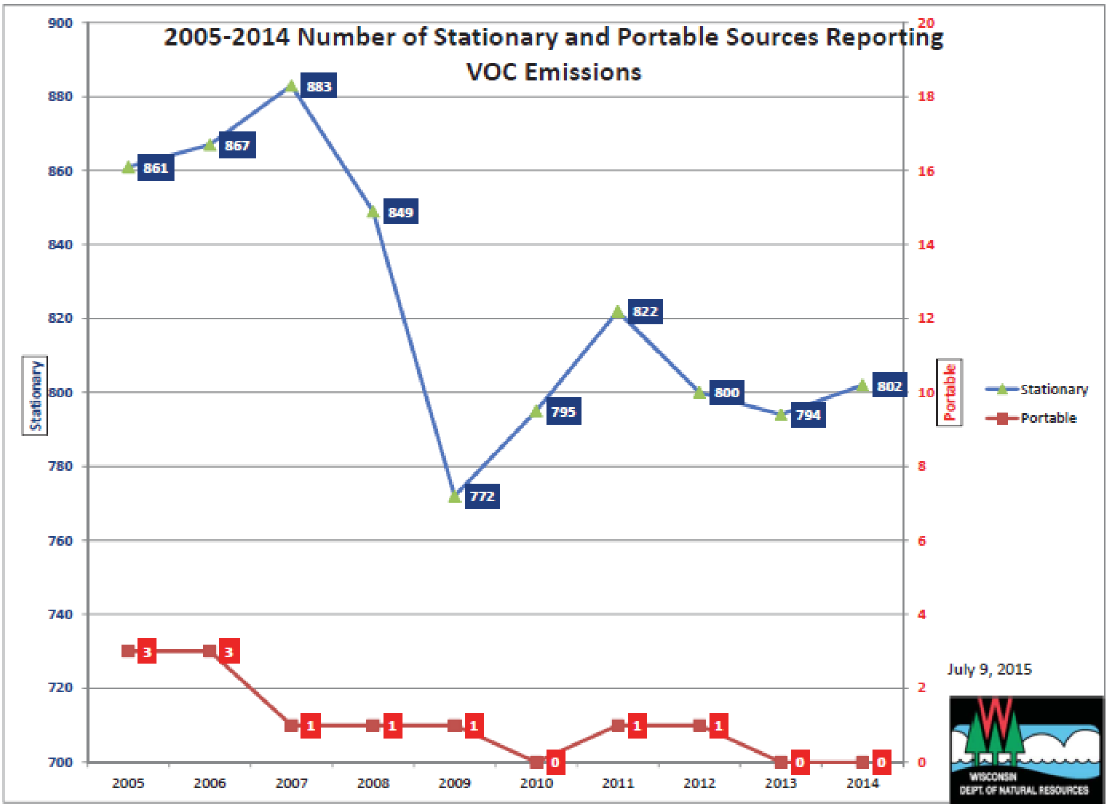


Figure AA.6 Wisconsin VOC Eimssion Inventory (2002 to 2014)

7.1.3. **Meteorology Data**

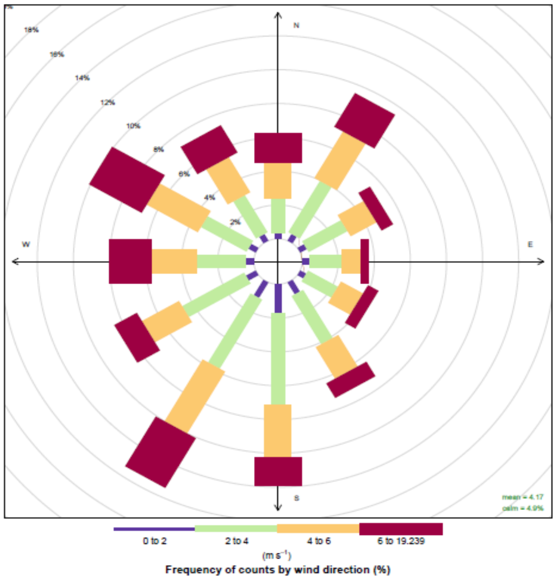


Figure 7.1. Mayv

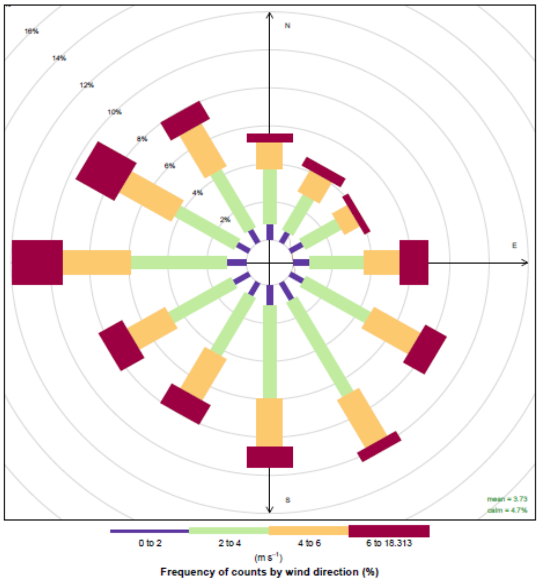


Figure 7.2. Perk

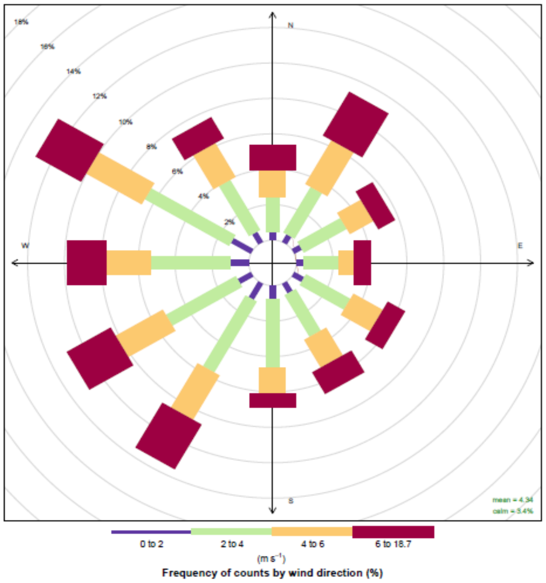


Figure 7.3. Milw

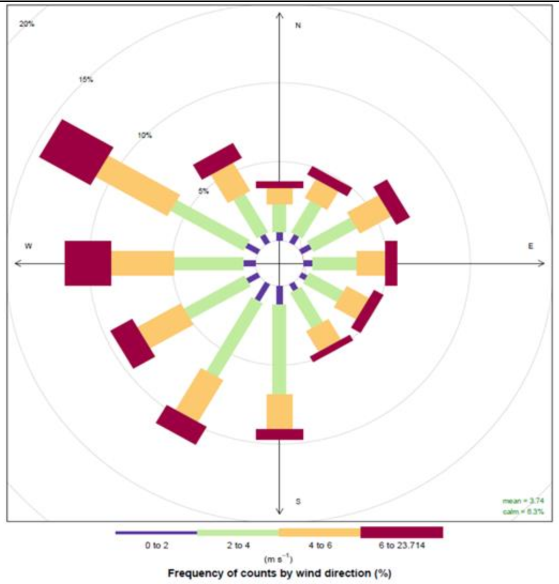


Figure 7.4. Wauk

Figure AA.7 Wind Roses at Mayv, Perk, Milw and Wauk, Wisconsin

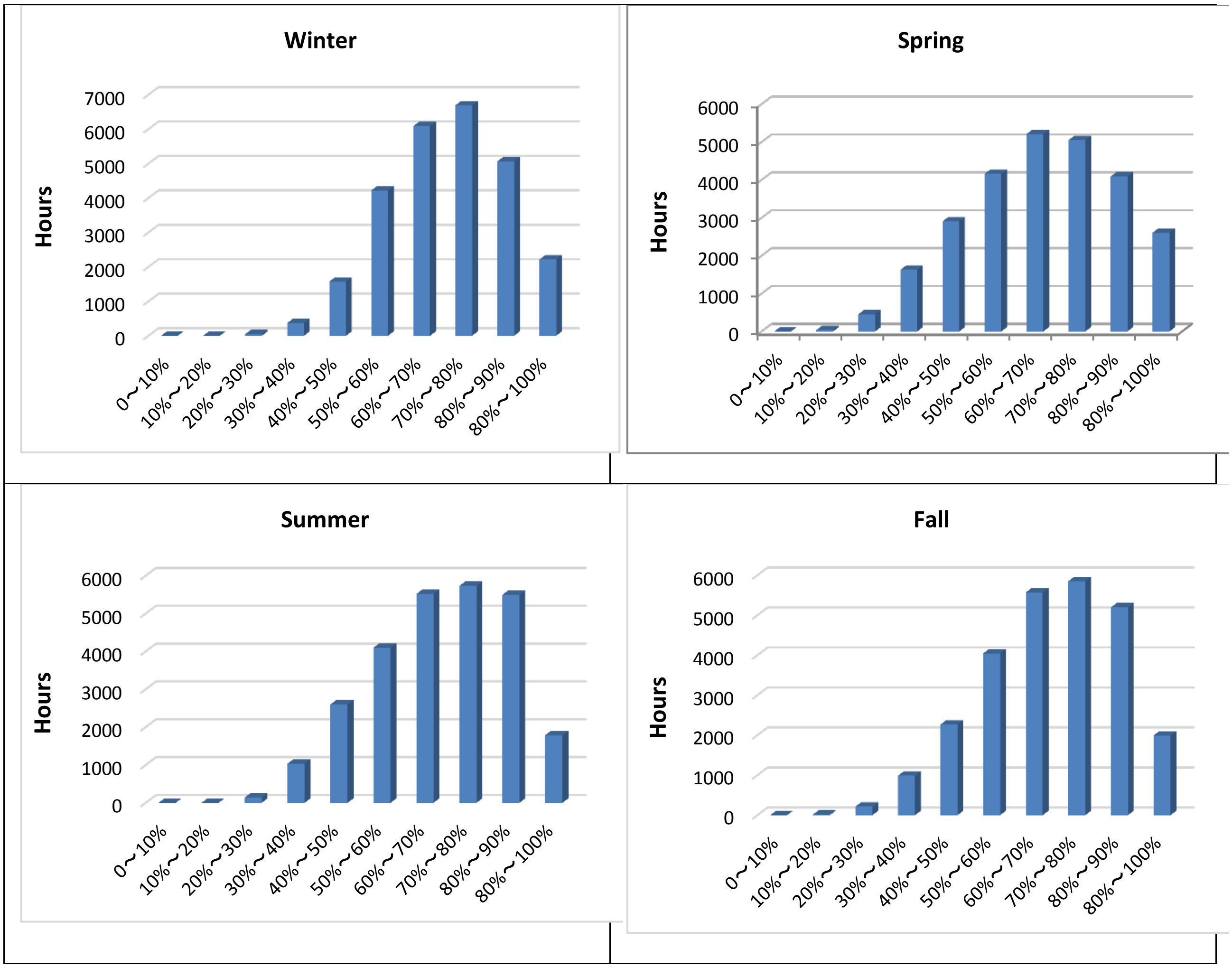


Figure AA.8 RH Distribution – Milwaukee

Table AA2.9 Seasonal RH _ Milwaukee

RH	Winter	Winter%	Spring	Spring%	Summer	Summer%	Fall	Fall%	Total
0～10%	0	0	0	0	0	0	0	0	0
10%～20%	0	0	37	0.0014	0	0	12	0.0005	49
20%～30%	46	0.0018	455	0.0174	137	0.0052	214	0.0082	852
30%～40%	368	0.0140	1627	0.0623	1036	0.0392	988	0.0378	4019
40%～50%	1572	0.0599	2904	0.1111	2599	0.0985	2268	0.0868	9343
50%～60%	4219	0.1607	4156	0.1590	4097	0.1552	4044	0.1547	16516
60%～70%	6088	0.2318	5210	0.1994	5517	0.2090	5569	0.2131	22384
70%～80%	6689	0.2547	5049	0.1932	5729	0.2170	5851	0.2239	23318
80%～90%	5065	0.1929	4088	0.1564	5494	0.2081	5195	0.1988	19842
80%～100%	2214	0.0843	2608	0.0998	1789	0.0678	1992	0.0762	8603

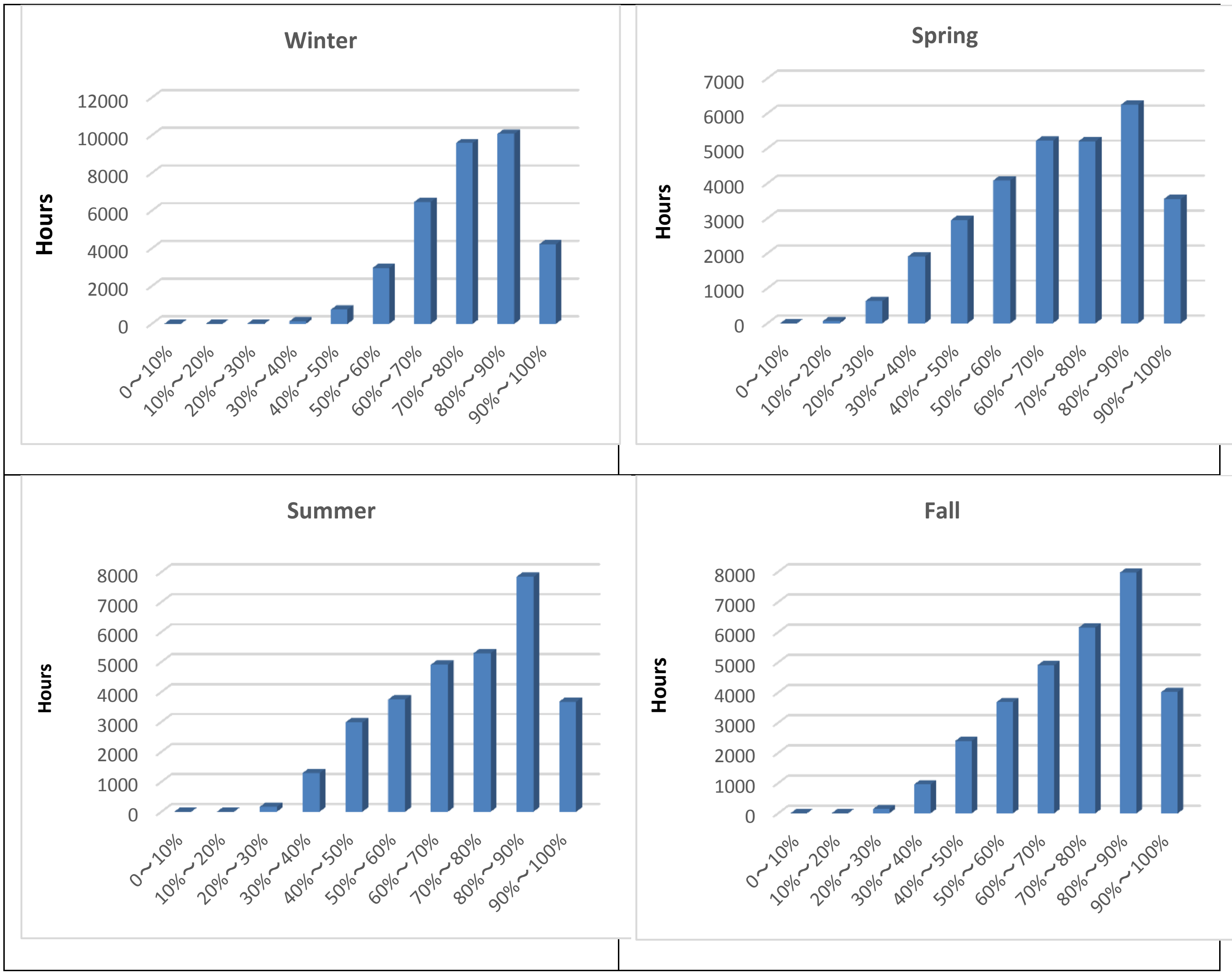


Figure AA.9 RH Distribution – Mayville

Table AA2.10 Seasonal RH _ Milwaukee

RH	Winter	Winter%	Spring	Spring%	Summer	Summer%	Fall	Fall%	Total
0～10%	0	0	0	0	0	0	0	0	0
10%～20%	0	0	60	0.0020	3	0.0001	3	0.0001	66
20%～30%	18	0.0005	635	0.0213	163	0.0055	138	0.0046	954
30%～40%	133	0.0039	1912	0.0641	1291	0.0432	957	0.0316	4293
40%～50%	759	0.0222	2942	0.0986	2978	0.0997	2398	0.0793	9077
50%～60%	2965	0.0866	4084	0.1368	3743	0.1253	3683	0.1218	14475
60%～70%	6470	0.1890	5215	0.1747	4904	0.1641	4910	0.1624	21499
70%～80%	9588	0.2801	5202	0.1743	5291	0.1771	6156	0.2036	26237
80%～90%	10080	0.2944	6251	0.2094	7836	0.2622	7975	0.2637	32142
90%～100%	4222	0.1233	3550	0.1189	3671	0.1229	4017	0.1329	15460

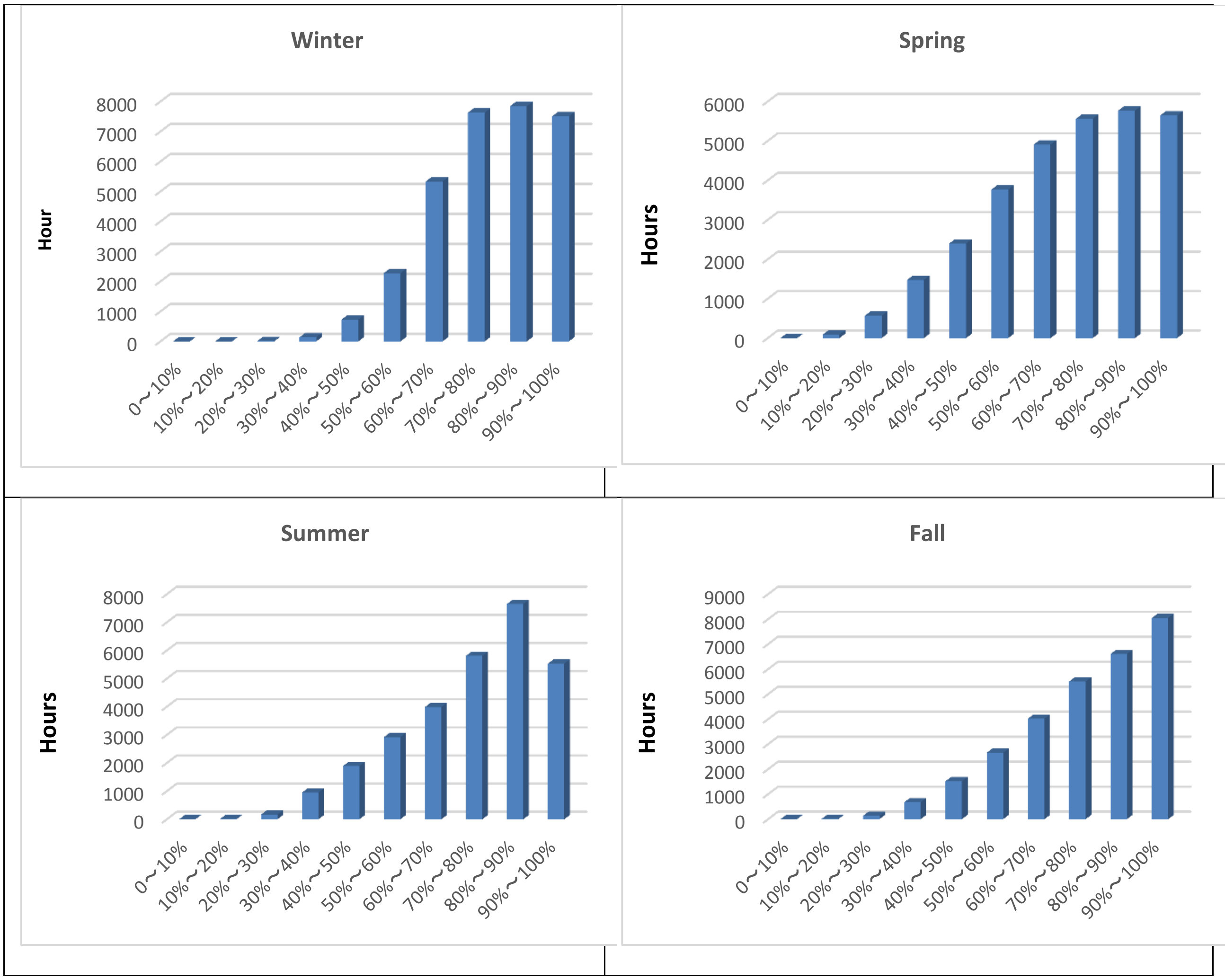


Figure AA.10 RH Distribution – Waukesha

Table AA2.11 Seasonal RH _ Waukesha

RH	winter	Winter%	spring	Spring%	Summer	Summer%	Fall	Fall%	Total
0～10%	0	0	0	0	0	0	0	0	0
10%～20%	0	0	86	0.0029	11	0.0004	15	0.0005	112
20%～30%	12	0.0004	567	0.0188	167	0.0058	133	0.0046	879
30%～40%	134	0.0043	1475	0.0489	950	0.0329	677	0.0232	3236
40%～50%	729	0.0232	2398	0.0795	1892	0.0654	1517	0.0520	6536
50%～60%	2273	0.0723	3767	0.1249	2919	0.1010	2655	0.0910	11614
60%～70%	5334	0.1696	4907	0.1626	3988	0.1379	4022	0.1379	18251
70%～80%	7628	0.2425	5558	0.1842	5807	0.2008	5509	0.1888	24502
80%～90%	7842	0.2493	5766	0.1911	7649	0.2645	6604	0.2264	27861
90%～100%	7505	0.2386	5646	0.1871	5531	0.1913	8041	0.2756	26723

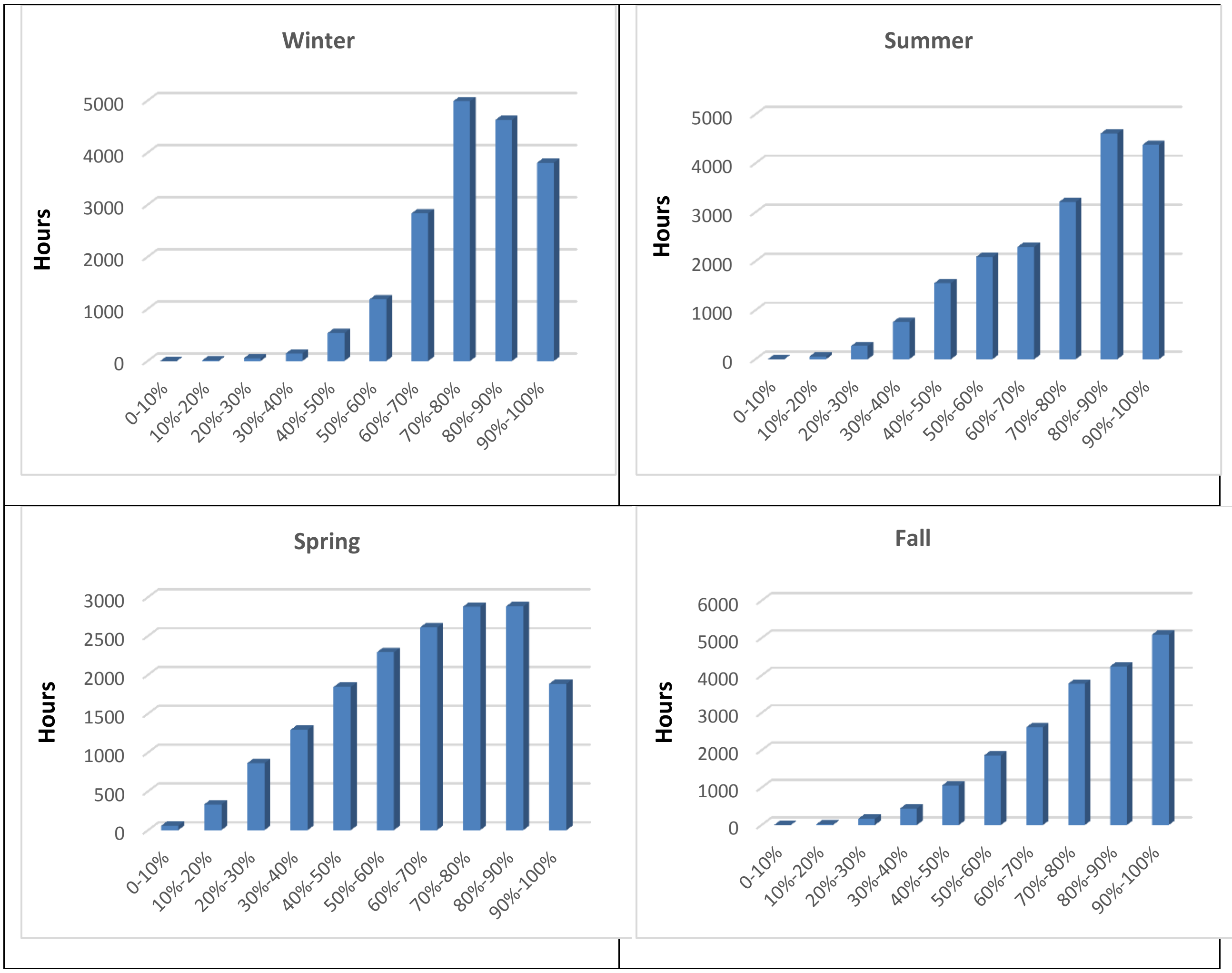


Figure AA.11 RH Distribution – Perkinstown

Table AA2.12 Seasonal RH _ Perkinstown

	Winter	Winter%	Spring	Spring%	Summer	Summer%	Fall	Fall%	Tatal
0-10%	0	0	55	0.0033	0	0	2	0.0001	57
10%-20%	10	0.0005	331	0.0196	56	0.0029	15	0.0008	412
20%-30%	55	0.0030	862	0.0509	269	0.0140	164	0.0085	1350
30%-40%	145	0.0080	1290	0.0762	758	0.0394	443	0.0230	2636
40%-50%	537	0.0295	1843	0.1089	1554	0.0809	1058	0.0549	4992
50%-60%	1184	0.0651	2289	0.1353	2086	0.1086	1860	0.0966	7419
60%-70%	2834	0.1558	2608	0.1541	2294	0.1194	2610	0.1355	10346
70%-80%	4990	0.2743	2876	0.1700	3212	0.1672	3778	0.1961	14856
80%-90%	4627	0.2544	2881	0.1703	4611	0.2400	4242	0.2202	16361
90%-100%	3808	0.2093	1885	0.1114	4376	0.2277	5092	0.2643	15161

7.2. Appendix B

7.2.1. Acidity Parameters

Table AB4.1 A Summary of Acidity Parameters _ Mayville

Parameters	Winter	Spring	Summer	Fall	Whole year
SO_4^{2-}(μg m^{-3})	0.0203±0.0124	0.0208±0.0131	0.0197±0.0266	0.0183±0.0260	0.0197±0.0223
NO_3^- (μg m^{-3})	0.0700±0.0480	0.0345±0.0362	0.0111±0.0111	0.0235±0.0326	0.0235±0.0377
NH_4^+(μg m^{-3})	0.0954±0.0660	0.0721±0.0576	0.0460±0.0571	0.0588±0.0681	0.0626±0.0639
Sum of anions (μg m^{-3})	0.1062±0.0649	0.0810±0.0571	0.0538±0.0599	0.0681±0.0694	0.0728±0.0651
$PM_{2.5}$(μg m^{-3})	11.80±6.971	8.700±5.855	8.700±5.800	7.700±6.415	8.900±6.286
$(NH_4^+)_{mea}/(NH_4^+)_{neu}$	0.9104±0.1080	0.8983±0.0916	0.8652±0.1251	0.8814±0.1118	0.8832±0.1127
$(NO_3^-)/(SO_4^{2-})$	1.473±1.028	0.8068±0.5162	0.2671±0.2102	0.6147±0.6392	0.5681±0.7577
$(NH_4^+)/(SO_4^{2-})$	2.245±1.054	1.611±0.5338	1.082±0.2327	1.370±0.5983	1.325±0.7434
$[H^+]_{AR,}$ (nmol m^{-3})	0.0102±0.0062	0.0104±0.0066	0.0098±0.0133	0.0091±0.0130	0.0098±0.0111
$[H^+]_{AER,}$ (nmol m^{-3})	0.0095±0.0063	0.0077±0.0055	0.0070±0.0069	0.0073±0.0067	0.0076±0.0065
$[H^+]_{in-situ}$, (nmol m$^{-)}$	0.0025±0.0035	0.0013±0.0024	0.0008±0.0018	0.0013±0.0033	0.0013±0.0028
Aerosol H_2O (μg m^{-3})	0.5955±0.6126	0.2834±0.6008	0.1403±0.3292	0.2396±0.6548	0.2470±0.5717
pH	2.618±0.5004	2.837±0.5398	2.985±0.6171	2.799±0.5862	2.825±0.5880

Note: $(NH_4^+)_{mea}/(NH_4^+)_{neu}$, $(NO_3^-)/(SO_4^{2-})$ and $(NH_4^+)/(SO_4^{2-})$ are molar ratio

Table AB4.2 A Summary of Acidity Parameters _ Waukesha

Parameters	Winter	Spring	Summer	Fall	Whole year
SO_4^{2-}(μg m^{-3})	0.0220±0.0092	0.0162±0.0134	0.0189±0.0311	0.0167±0.0271	0.0189±0.0241
NO_3^- (μg m^{-3})	0.0677±0.0442	0.0247±0.0341	0.0102±0.0132	0.0207±0.0319	0.0197±0.0361
NH_4^+(μg m^{-3})	0.1026±0.0552	0.0429±0.0578	0.0362±0.0649	0.0527±0.0688	0.0530±0.0643
Sum of anions (μg m^{-3})	0.1145±0.0568	0.0558±0.0590	0.0494±0.0700	0.0679±0.0712	0.0650±0.0672
$PM_{2.5}$(μg m^{-3})	15.30±7.721	10.15±5.141	10.35±6.804	10.85±8.271	11.20±7.221
$(NH_4^+)_{mea}/(NH_4^+)_{neu}$	0.8796±0.1344	0.7893±0.1711	0.7633±0.1462	0.8437±0.1688	0.8134±0.1581
$(NO_3^-)/(SO_4^{2-})$	1.446±0.9025	0.7847±0.4090	0.2708±0.2084	0.6593±0.5977	0.5634±0.6944
$(NH_4^+)/(SO_4^{2-})$	2.063±0.9349	1.351±0.5054	0.9630±0.2386	1.241±0.5710	1.164±0.7087
$[H^+]_{AR,}$ (nmol m^{-3})	0.0110±0.0046	0.0081±0.0067	0.0095±0.0156	0.0083±0.0136	0.0095±0.0120
$[H^+]_{AER,}$ (nmol m^{-3})	0.0110±0.0091	0.0105±0.0081	0.0113±0.0091	0.0103±0.0079	0.0110±0.0086
$[H^+]_{in-situ}$, (nmol m$^{-3)}$	0.0047±0.0049	0.0027±0.0051	0.0031±0.0037	0.0033±0.0045	0.0033±0.0045
Aerosol H_2O (μg m^{-3})	0.7759±0.7774	0.2507±2.504	0.2527±0.6074	0.3549±2.581	0.3494±1.815
pH	2.426±0.5201	2.416±0.4486	2.551±0.4993	2.564±0.6020	2.504±0.5242

Note: $(NH_4^+)_{mea}/(NH_4^+)_{neu}$, $(NO_3^-)/(SO_4^{2-})$ and $(NH_4^+)/(SO_4^{2-})$ are molar ratio

Table AB4.3 A Summary of Acidity Parameters _ Perkingstown

Parameters	Winter	Spring	Summer	Fall	Whole year
SO_4^{2-}(μg m^{-3})	0.0167±0.0083	0.0142±0.0198	0.0118±0.0268	0.0111±0.0140	0.0125±0.0198
NO_3^- (μg m^{-3})	0.0264±0.0329	0.0142±0.0221	0.0037±0.0072	0.0050±0.0217	0.0057±0.0228
NH_4^+(μg m^{-3})	0.0404±0.0433	0.0302±0.0402	0.0177±0.0561	0.0211±0.0392	0.0243±0.0468
Sum of anions (μg m^{-3})	0.0540±0.0428	0.0448±0.0490	0.0281±0.0593	0.0283±0.0411	0.0356±0.0498
$PM_{2.5}$(μg m^{-3})	7.300±4.144	5.050±7.945	7.650±8.049	4.900±5.731	6.600±6.829
$(NH_4^+)_{mea}/(NH_4^+)_{neu}$	0.7596±0.1213	0.7339±0.1651	0.7383±0.2650	0.7354±0.2163	0.7419±0.2212
$(NO_3^-)/(SO_4^{2-})$	0.7216±1.036	0.4267±0.4848	0.1537±0.1085	0.2291±0.5482	0.2283±0.6415
$(NH_4^+)/(SO_4^{2-})$	1.486±1.010	1.133±0.5773	0.8276±0.2999	0.9016±0.6550	0.9189±0.7068
$[H^+]_{AR,}$ (nmol m^{-3})	0.0083±0.0042	0.0067±0.0064	0.0056±0.0134	0.0056±0.0070	0.0061±0.0095
$[H^+]_{AER,}$ (nmol m^{-3})	0.0095±0.0041	0.0087±0.0048	0.0070±0.0067	0.0064±0.0043	0.0072±0.0054
$[H^+]_{in-situ}$, (nmol m^{-3})	0.0039±0.0028	0.0026±0.0021	0.0022±0.0028	0.0019±0.0019	0.0024±0.0025
Aerosol H_2O (μg m^{-3})	0.3360±4.345	0.1620±0.9916	0.0765±2.356	0.1250±1.235	0.1544±2.433
pH	2.496±0.3177	2.450±0.4629	2.560±0.7127	2.684±0.3984	2.564±0.5284

Note: $(NH_4^+)_{mea}/(NH_4^+)_{neu}$, $(NO_3^-)/(SO_4^{2-})$ and $(NH_4^+)/(SO_4^{2-})$ are molar ratio

Table AB4.4 The Statistics of Atmospheric Acidity Parameters _ Milwaukee

	Winter	Spring	Summer	Fall	Whole year
$[H^+]_{In\text{-}Situ,}$ (nmol m^{-3})					
Mean	0.0021±0.0034	0.0015±0.0034	0.0015±0.003	0.0015±0.002	0.0015±0.0029
median	0.0032	0.0029	0.0024	0.0021	0.0026
95th	0.0066	0.0070	0.0046	0.0043	0.0057
75th	0.0042	0.0039	0.0028	0.0028	0.0032
25th	0.0010	0.0008	0.0007	0.0008	0.0008
10th	0.0006	0.0003	0.0004	0.0006	0.0004
$[H^+]_{AER,}$ (nmol m^{-3})					
Mean	0.0076±0.0063	0.0079±0.007	0.009±0.0093	0.0084±0.0061	0.0083±0.0077
median	0.0093	0.0101	0.0122	0.0098	0.0107
95th	0.0169	0.0209	0.0219	0.0175	0.0201
75th	0.0124	0.0128	0.0159	0.0114	0.0139
25th	0.0054	0.0053	0.0058	0.0060	0.0057
10th	0.0024	0.0024	0.0043	0.0041	0.0036
$[H^+]_{AR,}$ (nmol m^{-3})					
Mean	0.0122±0.0062	0.0103±0.0071	0.0111±0.0153	0.0111±0.0137	0.0111±0.0125
median	0.0128	0.0117	0.0163	0.0156	0.0146
95th	0.0183	0.0218	0.0344	0.0347	0.0314
75th	0.0163	0.0148	0.0216	0.0207	0.0181
25th	0.0089	0.0065	0.0064	0.0057	0.0063
10th	0.0054	0.0045	0.0030	0.0048	0.0041
NH_4^+ meas / NH_4^+ neu					
Mean	0.9067±0.1004	0.8693±0.1137	0.8182±0.1452	0.8634±0.1157	0.853±0.1301
median	0.8899	0.8400	0.7818	0.8422	0.8263
95th	0.9874	0.9711	0.9339	0.9625	0.9657
75th	0.9682	0.9266	0.8774	0.9388	0.9243
25th	0.8379	0.7706	0.7154	0.7689	0.7585
10th	0.7769	0.6704	0.5759	0.6769	0.6466
NH_4^+/SO_4^{2-}					
Mean	2.21±0.8398	1.47±0.5305	0.982±0.2473	1.32±0.5889	1.2±0.6572
median	2.2246	1.5482	1.0049	1.4613	1.4211
95th	3.1526	2.2964	1.2992	2.1839	2.3108
75th	2.7805	1.8428	1.1328	1.8063	1.7109
25th	1.5334	1.1474	0.8676	1.0497	0.9686
10th	1.2274	0.9207	0.7162	0.8995	0.8398

Table AB4.5 The Statistics of Atmospheric Acidity Parameters _ Milwaukee

	Winter	Spring	Summer	Fall	Whole year
6). $[H^+]_{In\text{-}Situ,}$ (nmol m^{-3})					
Mean	0.0025±0.0035	0.0013±0.0024	0.0008±0.0018	0.0013±0.0032	0.0013±0.0028
median	0.0038	0.0022	0.0016	0.0025	0.0023
95th	0.0076	0.0048	0.0037	0.0059	0.0057
75th	0.0047	0.0027	0.0022	0.0029	0.0029
25th	0.0016	0.0006	0.0003	0.0006	0.0006
10th	0.0008	0.0004	0.0001	0.0003	0.0002
7). $[H^+]_{AER,}$ (nmol m^{-3})					
Mean	0.0095±0.0062	0.0077±0.0055	0.0070±0.0069	0.0073±0.0066	0.0076±0.0065
median	0.0106	0.0086	0.0083	0.0093	0.0090
95th	0.0180	0.0146	0.0161	0.0202	0.0176
75th	0.0138	0.0110	0.0109	0.0118	0.0118
25th	0.0063	0.0049	0.0034	0.0051	0.0047
10th	0.0041	0.0030	0.0018	0.0030	0.0023
8). $[H^+]_{AR,}$ (nmol m^{-3})					
Mean	0.0102±0.0062	0.0104±0.0065	0.0098±0.0132	0.0091±0.0129	0.0098±0.0111
median	0.0115	0.0120	0.0142	0.0136	0.0131
95th	0.0181	0.0209	0.0305	0.0298	0.0247
75th	0.0138	0.0145	0.0182	0.0162	0.0163
25th	0.0076	0.0070	0.0060	0.0055	0.0064
10th	0.0057	0.0057	0.0037	0.0042	0.0045
9). NH_4^+ meas / NH_4^+ neu					
Mean	0.9104±0.1079	0.8983±0.0915	0.8652±0.125	0.8814±0.1118	0.8832±0.1127
median	0.8720	0.8743	0.8403	0.8485	0.8550
95th	0.9766	0.9720	0.9757	0.9699	0.9729
75th	0.9524	0.9470	0.9334	0.9331	0.9384
25th	0.8170	0.8170	0.7841	0.7919	0.7969
10th	0.7032	0.7316	0.6451	0.6751	0.6837
10). NH_4^+/SO_4^{2-}					
Mean	2.245±1.05	1.611±0.5337	1.082±0.2327	1.370±0.5982	1.325±0.7433
median	2.383	1.691	1.116	1.535	1.573
95th	3.660	2.370	1.381	2.382	2.568
75th	2.889	2.005	1.226	1.867	1.858
25th	1.528	1.331	0.9967	1.103	1.078
10th	1.180	1.125	0.8433	0.9603	0.9611

Table AB4.6 The Statistics of Atmospheric Acidity Parameters _ Milwaukee

	Winter	Spring	Summer	Fall	Whole year
11). $[H^+]_{In-Situ,}$ (nmol m^{-3})					
Mean	0.0047±0.0048	0.0027±0.0051	0.0031±0.0036	0.0033±0.0045	0.0033±0.0044
median	0.0059	0.0049	0.0042	0.0047	0.0048
95th	0.0123	0.0112	0.0089	0.0111	0.0111
75th	0.0086	0.0068	0.0053	0.0052	0.0066
25th	0.0024	0.0012	0.0017	0.0015	0.0017
10th	0.0009	0.0007	0.0007	0.0005	0.0006
12). $[H^+]_{AER,}$ (nmol m^{-3})					
Mean	0.0110±0.0091	0.0105±0.0081	0.0113±0.0091	0.0103±0.0078	0.0110±0.0085
median	0.0138	0.0126	0.0134	0.0122	0.0130
95th	0.0238	0.0213	0.0247	0.0230	0.0241
75th	0.0193	0.0175	0.0171	0.0178	0.0181
25th	0.0084	0.0060	0.0072	0.0067	0.0069
10th	0.0032	0.0054	0.0048	0.0035	0.0043
13). $[H^+]_{AR,}$ (nmol m^{-3})					
Mean	0.0110±0.0046	0.0081±0.0067	0.0095±0.0155	0.0083±0.0135	0.0095±0.012
median	0.0112	0.0102	0.0144	0.0142	0.0129
95th	0.0173	0.0182	0.0309	0.0360	0.0243
75th	0.0132	0.0138	0.0185	0.0192	0.0148
25th	0.0081	0.0057	0.0057	0.0053	0.0057
10th	0.0053	0.0039	0.0035	0.0037	0.0039
14). NH_4^+ meas / NH_4^+ neu					
Mean	0.8796±0.1344	0.7893±0.1711	0.7633±0.1462	0.8437±0.1687	0.8134±0.1581
median	0.8364	0.7683	0.7440	0.7872	0.7789
95th	0.9678	0.9530	0.9092	0.9523	0.9508
75th	0.9353	0.8890	0.8503	0.9049	0.9004
25th	0.7819	0.7146	0.6503	0.7264	0.6975
10th	0.6391	0.6007	0.5439	0.5692	0.5719
15). NH_4^+/SO_4^{2-}					
Mean	2.063±0.9349	1.351±0.5053	0.9630±0.2385	1.241±0.5709	1.164±0.7087
median	2.155	1.426	0.9816	1.371	1.409
95th	3.379	2.075	1.239	2.187	2.411
75th	2.745	1.763	1.071	1.731	1.745
25th	1.444	1.066	0.8420	0.9974	0.9365
10th	0.9266	0.8298	0.7405	0.7530	0.7989

Table AB4.7 The Statistics of Atmospheric Acidity Parameters _ Milwaukee

	Winter	Spring	Summer	Fall	Whole year
16). $[H^+]_{In\text{-}Situ,}$ (nmol m^{-3})					
Mean	0.0039±0.0028	0.0026±0.002	0.0022±0.0028	0.0019±0.0018	0.0024±0.0025
median	0.0045	0.0028	0.0029	0.0026	0.0031
95th	0.0075	0.0049	0.0060	0.0052	0.0065
75th	0.0064	0.0039	0.0039	0.0032	0.0041
25th	0.0027	0.0013	0.0011	0.0012	0.0013
10th	0.0012	0.0007	0.0004	0.0007	0.0007
17). $[H^+]_{AER,}$ (nmol m^{-3})					
Mean	0.0095±0.004	0.0087±0.0048	0.0070±0.0067	0.0064±0.0043	0.0072±0.0053
median	0.0097	0.0093	0.0094	0.0076	0.0088
95th	0.0153	0.0138	0.0184	0.0137	0.0157
75th	0.0125	0.0111	0.0121	0.0091	0.0115
25th	0.0063	0.0066	0.0048	0.0048	0.0052
10th	0.0049	0.0042	0.0028	0.0039	0.0034
18). $[H^+]_{AR,}$ (nmol m^{-3})					
Mean	0.0083±0.0041	0.0067±0.0064	0.0056±0.0134	0.0056±0.007	0.0061±0.0095
median	0.0082	0.0088	0.0114	0.0076	0.0092
95th	0.0134	0.0157	0.0269	0.0157	0.0182
75th	0.0104	0.0117	0.0154	0.0097	0.0111
25th	0.0049	0.0045	0.0025	0.0026	0.0033
10th	0.0035	0.0032	0.0017	0.0017	0.0019
19). NH_4^+ meas / NH_4^+ neu					
Mean	0.7596±0.1213	0.7339±0.1651	0.7383±0.2649	0.7354±0.2162	0.7419±0.2211
median	0.7915	0.7347	0.6457	0.6972	0.7002
95th	0.9548	0.9127	0.9043	0.9315	0.9359
75th	0.9123	0.8733	0.8447	0.8777	0.8664
25th	0.7066	0.6209	0.5116	0.5758	0.5893
10th	0.6347	0.5329	0.1764	0.4366	0.4151
20). NH_4^+/SO_4^{2-}					
Mean	1.486±1.01	1.133±0.5772	0.8276±0.2998	0.9016±0.655	0.9189±0.7068
median	1.720	1.174	0.7469	1.074	1.082
95th	3.133	1.813	1.055	2.102	2.005
75th	2.056	1.324	0.9642	1.101	1.163
25th	0.9953	0.7682	0.5979	0.6852	0.7012
10th	0.7864	0.6490	0.2654	0.4895	0.4762

7.2.1. **The Trends of Aerosol Acidity Observed at Wisconsin**

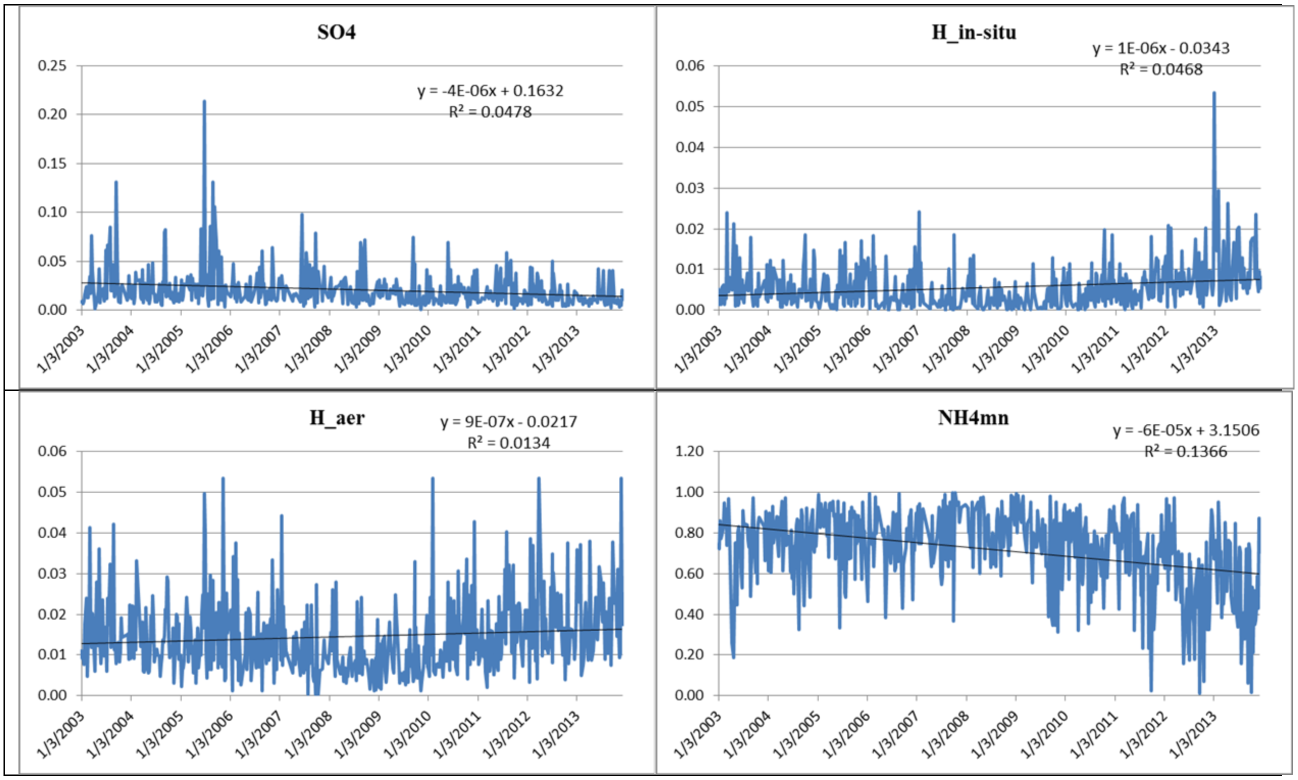


Figure AB4.1 The Trend of Aerosol Acidity in Waukesha

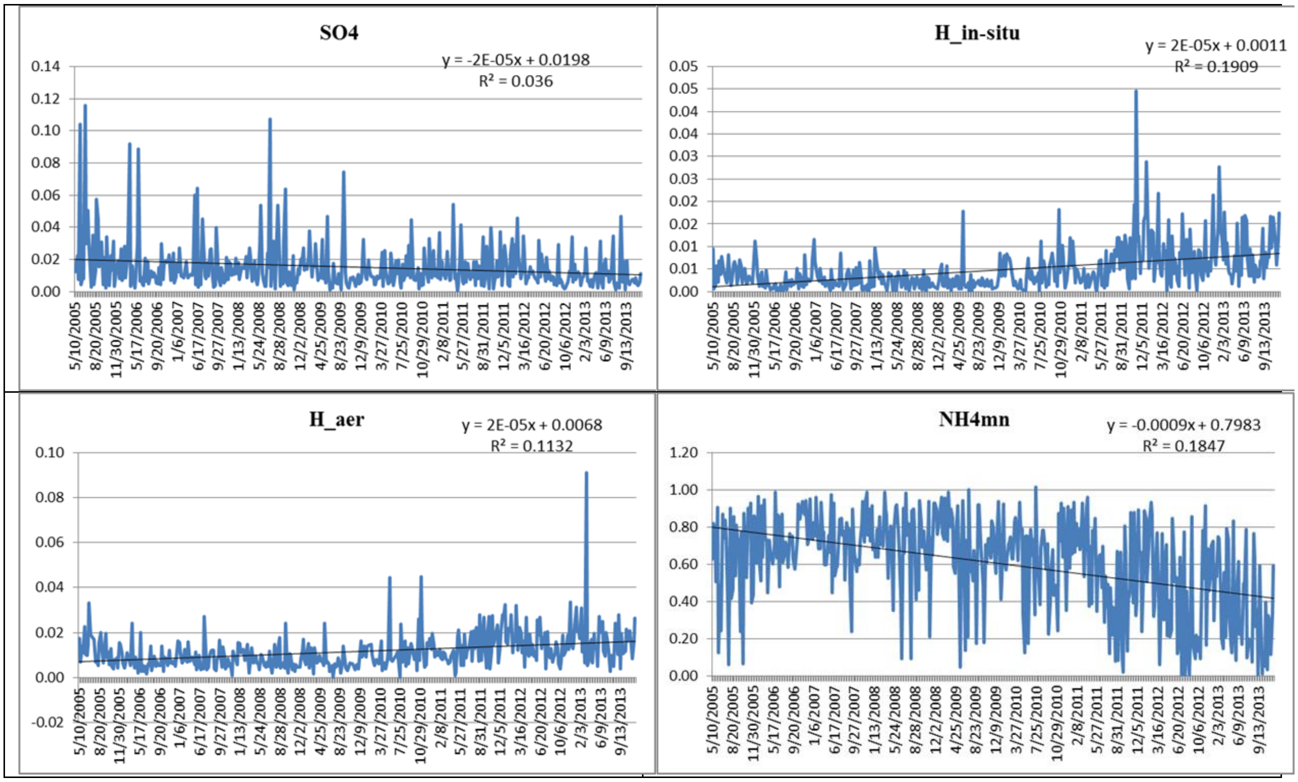


Figure AB4.2 The Trend of Aerosol Acidity in Perkinstown

7.2.2. **The Correlations Related to Aerosol Acidity**

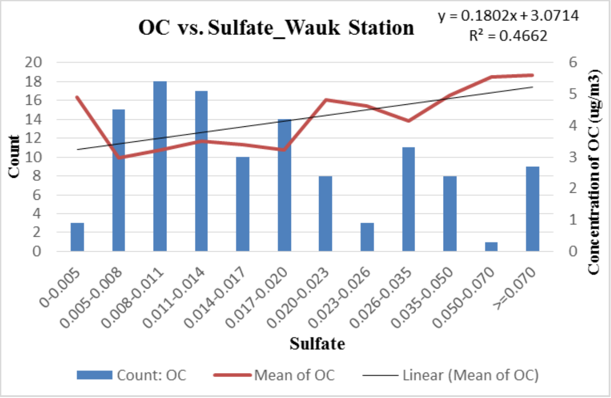
7.2.2.1. **OC vs Sulfate**

1. Waukesha Station

Figures AB7.3-1 and AB7.3-2 show how ambient concentration of OC corresponds to the different concentration of sulfate in Waukesha area. The linear regression results are:

AP, 234, >60%, All season, $y = 0.1802x + 3.0714$, $R^2 = 0.4662$

AR, 255, >60%, All season, $y = 0.1841x + 2.6678$, $R^2 = 0.6667$



4.3-1 Wauk <1.5, 117, >60%, All season

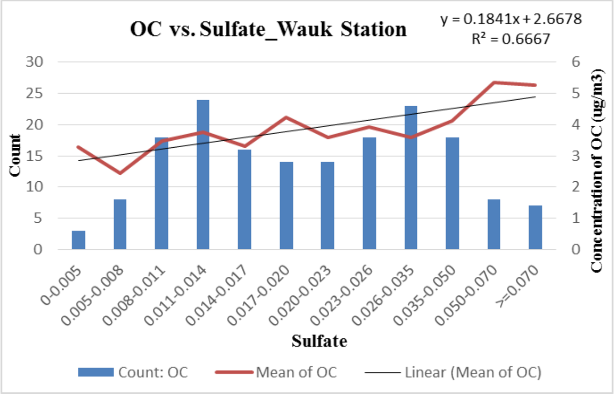


Figure 4.3-2 Wauk >1.5, 171, >60%, All season

Figure AB7.3 OC vs Sulfate _ Wauk

The regression results indicate when the concentration of sulfate increass, the concentration of OC increases too. The correlation under AR conditions is stronger than that under AP conditions.

2. Mayville Station

Figures AB7.4-1 and AB7.4-2 show how amboent concentration of OC corresponds to the different concentration of sulfate in Mayville region. The linear regression results are:

AP, 171, >60%, All season, $y = 0.1615x + 1.7565$, $R^2 = 0.7603$

AR, 430, >60%, All season, $y = 0.1792x + 1.5781$, $R^2 = 0.6844$

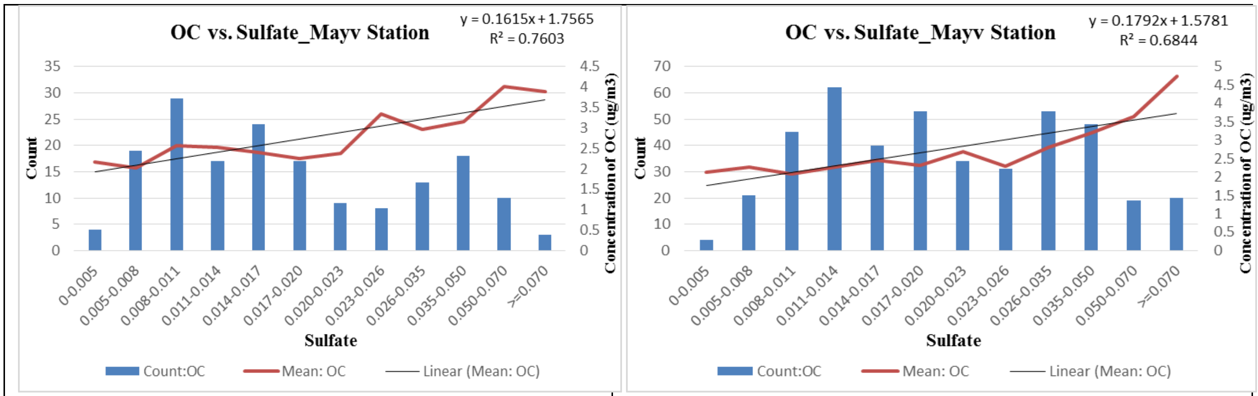


Figure 4.4-1. Mayv <1.5, 171, >60%, All season

Figure 4.4-2. Mayv >1.5, 430, >60%, All season

Figure AB7.4 OC vs Sulfate _ Mayv

The regression results indicate that there are significant positive correlations between ambient concentration of OC and concentration of sulfate, under both AP and AR conditions in Mayville area.

3. Perkinstown Station

Figures AB7.5-1 and AB7.5-2 show how atmospheric concentration of OC corresponds to the variations of concentration of sulfate in Perkinstown area. The linear regression results are:

AP, 271, >60%, All season, $y = 0.2534x + 1.6203$, $R^2 = 0.7347$

AR, 131, >60%, All season, $y = 0.0378x + 2.7331$, $R^2 = 0.0226$

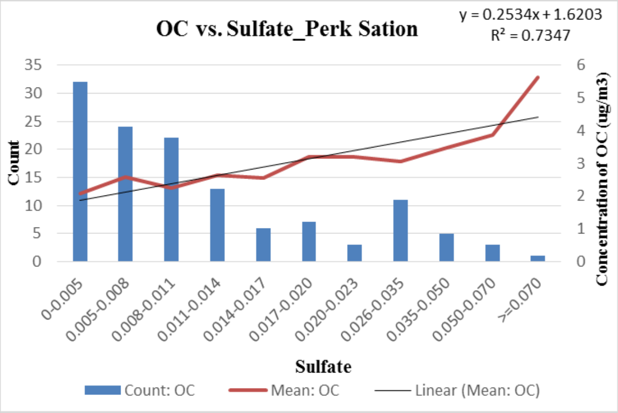


Figure 4.5-1. Perk <1.5, 271, >60%, All season

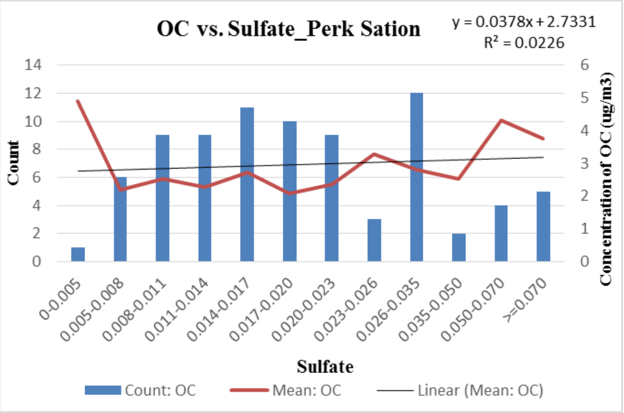


Figure 4.5-2. Perk >1.5, 131, >60%, All season

Figure AB7.5 OC vs Sulfate _ Perk

The regression results indicate a significant positive correlations between ambient concentration of OC and sulfate only under AP condition in Perkinstown area.

7.2.2.2. **OC vs. H_aer**

2 Mayville Station

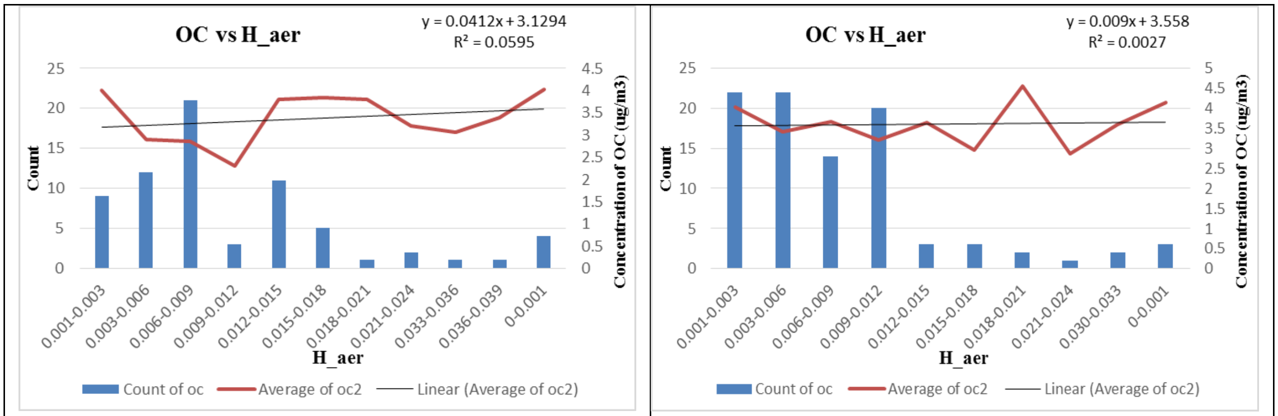


Fig 4.6-1. Summer, RH > 60%, <1.5, #=70

Fig. 4.6-2. Summer, RH > 60%, >1.5, #=92

Figure AB7.6. OC vs H_aer _Mayv (summer)

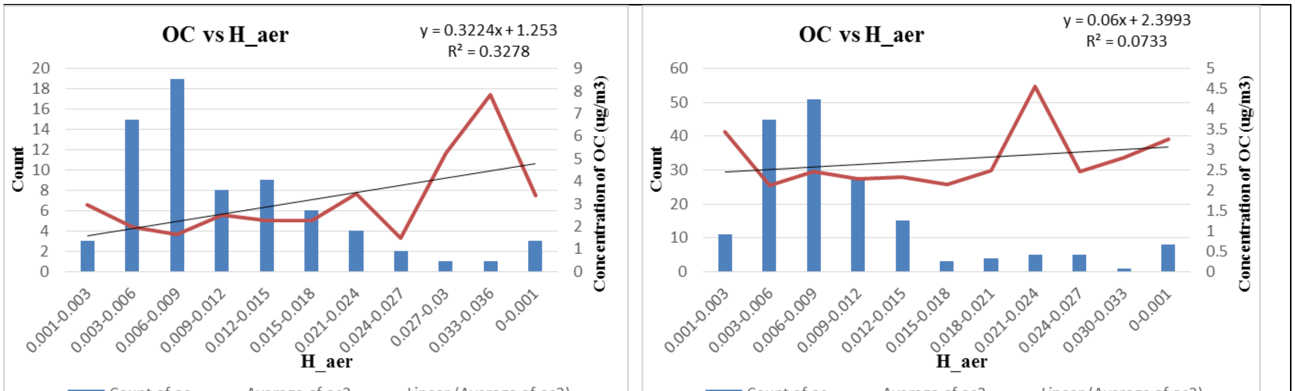


Fig. 4.7-1. Spring and Fall, RH > 60%,<1.5, #=71

Fig.4.7-2. Spring and Fall, RH > 60%, >1.5, #=176

Figure AB7.7 OC vs H_aer _Mayv (Spring)

Figures AB7.6 and AB7.7 demonstrate how atmospheric OC concentration corresponds to the variations in atmospheric aerosol acidity (strong acid, $[H^+]_{AER}$) in Mayville region. Comparing concentration of OC vs $[H^+]_{AER}$ bin plot under AP conditions with that under AR conditions, we find that, for all seasons, $[H^+]_{AER}$ has a bigger impact on OC concentration under AP conditions and the higher the acidity, the higher the concentration of OC is. For example, the slopes of the linear regression for summer data are 0.0412 for AP conditions verses 0.009 for AR conditions; and 0.3224 for AP conditions verses 0.06 for AR conditions for spring and fall data.

3 Perkinstown Station

Figures AB7.8 and AB7.9 demonstrated how atmospheric concentration of OC corresponds to the variations of atmospheric aerosol acidity (strong acid, $[H^+]_{AER}$) in Perkinstown area.

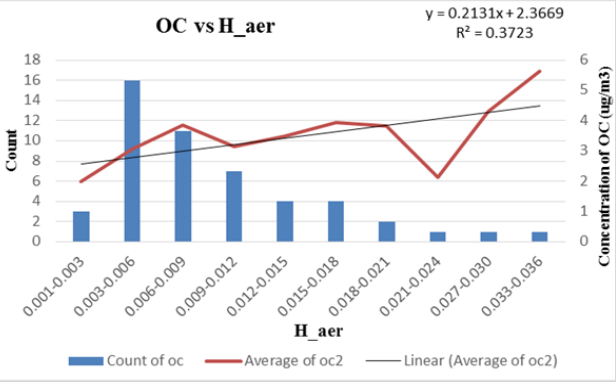


Figure 4.8-1 Summer, <1.5, >60%, #=50

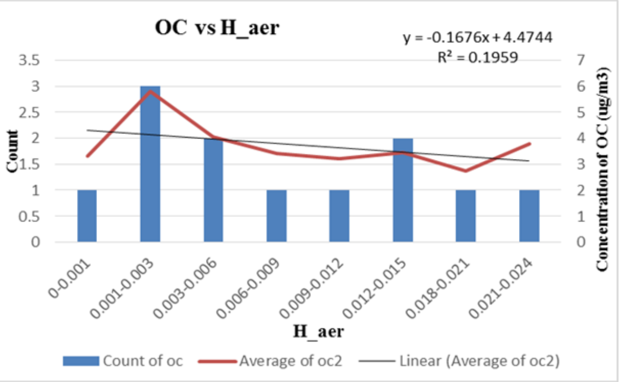


Figure 4.8-2. Summer, >1.5, >60%, #=12

Figure AB7.8 OC vs H_aer _Perk (summer)

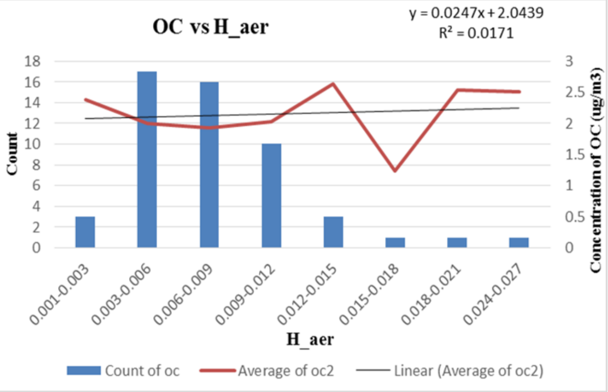


Figure 4.9-1. Spring and Fall, <1.5, >60%, #=52

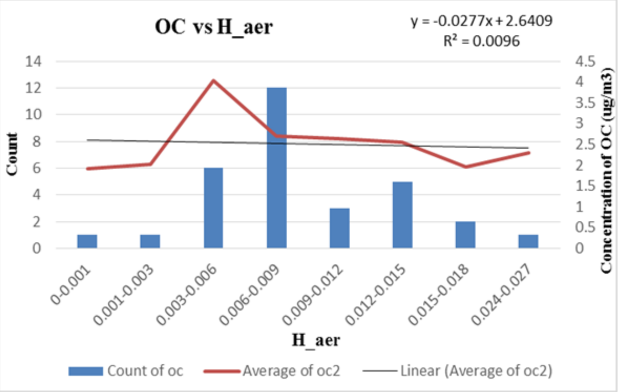


Figure 4.9-2. Spring and Fall, >1.5, >60%, #=31

Figure AB7.9 OC vs H_aer _ Perk (Spring)

$[H^+]_{AER}$ has a bigger impact to OC concentration under AP coPerknditions. The higher the acidity, the higher the concentration of OC is, especially in summer. The analysis for correlations between OC and $[H^+]_{AER}$ could not be performed due to the uncertainty caused by the small set of data (12) available.

7.2.2.3. **Aerosol acidity vs $PM_{2.5}$**

1. Mayville

Figure AB7.10 shows how summer atmospheric concentration of $PM_{2.5}$ relates to the variations of atmospheric aerosol acidity (strong acid, $[H^+]_{AER}$) in Mayville area.

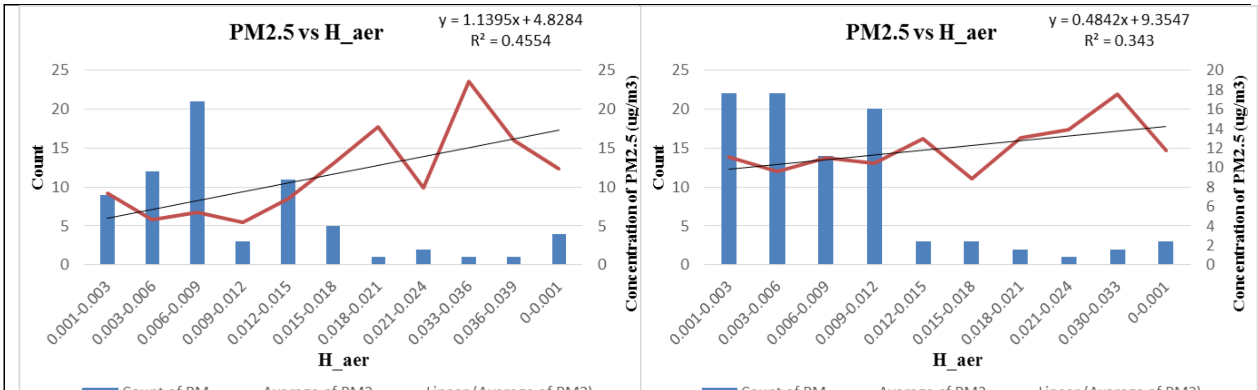


Figure 4.10-1. Summer, RH > 60%, <1.5, #=70	Figure 4.10-2. Summer, RH > 60%, >1.5, #=92

Figure AB7.10 $PM_{2.5}$ vs H_aer _Mayv

There is no good correlation between summer $PM_{2.5}$ and $[H^+]_{AER}$ in Mayville area.

Summer, RH > 60%, <1.5, #=70, $y = 1.1395x + 4.8284$, $R^2 = 0.4554$

Summer, RH > 60%, >1.5, #=92, $y = 0.4842x + 9.3547$, $R^2 = 0.343$

2. Waukesha

Figure AB7.11 demonstrated a significant correlation between summer atmospheric concentration of $PM_{2.5}$ and the variations of atmospheric aerosol acidity (strong acid, $[H^+]_{AER}$) in Waukesha area, under AP conditions.

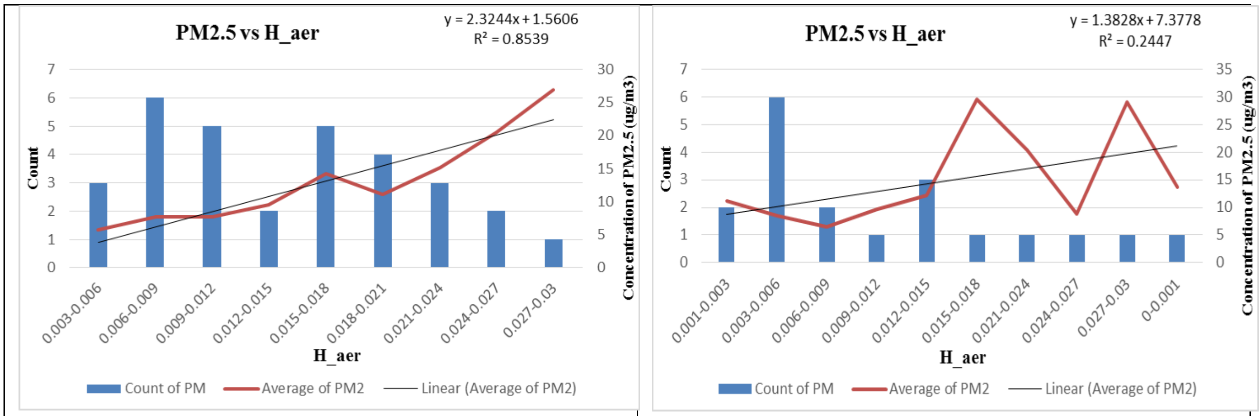


Figure 4.11-1. Summer, <1.5, >60%, #=31

Figure 4.11-2. Summer, >1.5, >60%, #=19

Figure AB7.11 $PM_{2.5}$ vs H_aer _Wauk

Summer, <1.5, >60%, #=31, $y = 2.3244x + 1.5606$, $R^2 = 0.8539$

Summer, >1.5, >60%, #=19, $y = 1.3828x + 7.3778$, $R^2 = 0.2447$

Figure AB7.12 demonstrated how summer atmospheric concentration of $PM_{2.5}$ corresponds to the variations of atmospheric aerosol acidity (strong acid, $[H^+]_{AER}$) in Perkinstown area.

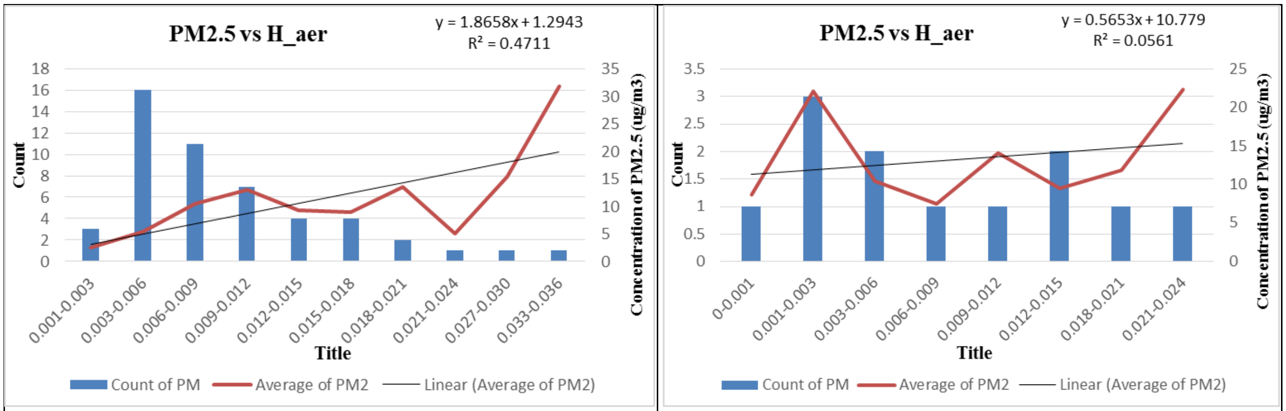


Figure 4.12-1

Figure 4.12-2

Figure AB7.12 $PM_{2.5}$ vs H_aer _Perk

There is no good correlation between summer $PM_{2.5}$ and $[H^+]_{AER}$ in Perkinstown area.

Summer, RH > 60%, <1.5, #=50, $y = 1.8658x + 1.2943$, $R^2 = 0.4711$

Summer, RH > 60%, >1.5, #=12, $y = 0.5653x + 10.779$, $R^2 = 0.0561$