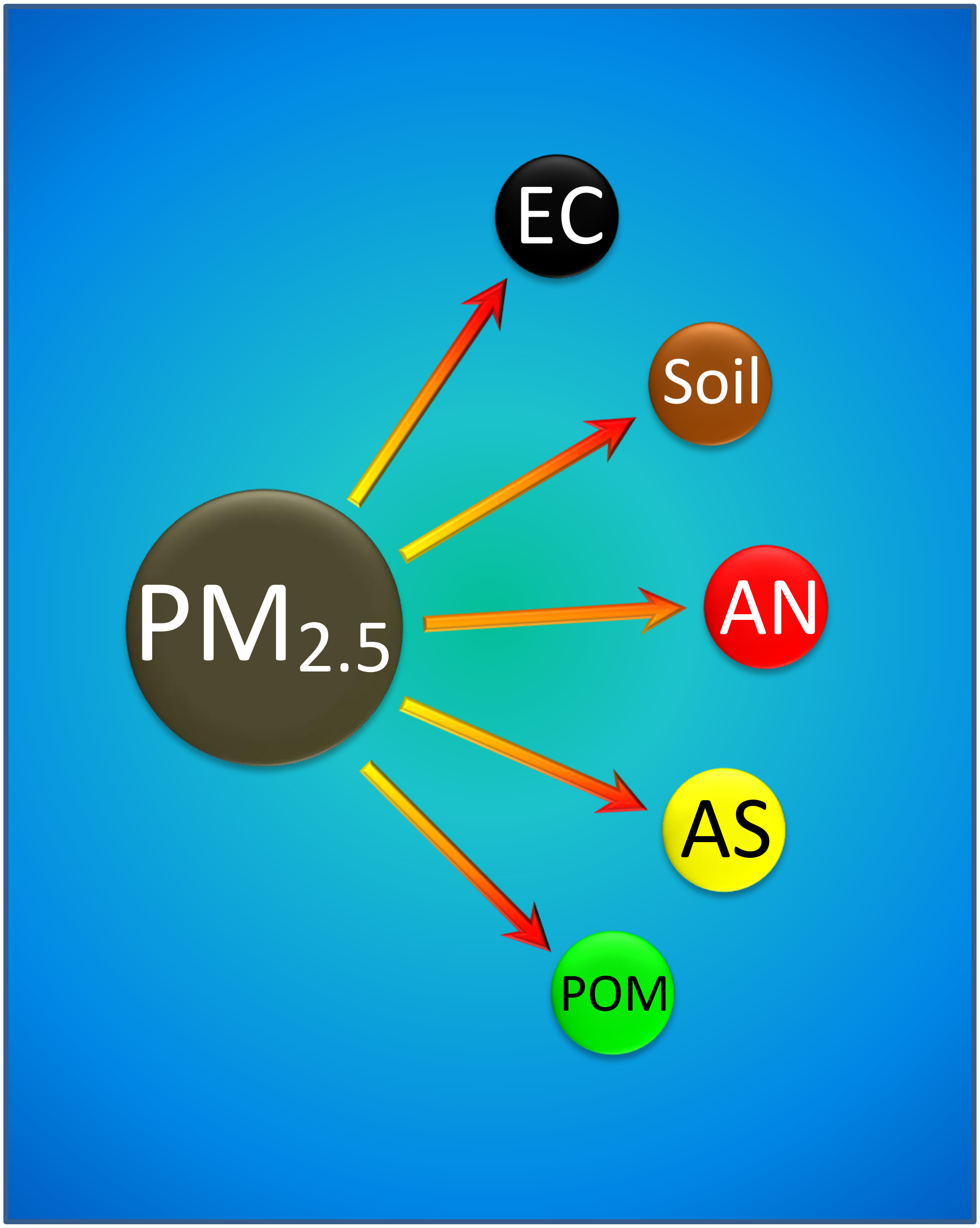
# $PM_{2.5}$ Chemical Speciation Data in Iowa

## Analysis for 2010 - 2014



# Table of Contents

Introduction ........ 2

Discussion........ 3

Measurement Locations ........ 3

Data & Charts........ 3

Comparability with the Federal Reference Method ........ 10

Case Studies ........ 12

References ........ 13

# Introduction

Fine particulate matter ($PM_{2.5}$) is made up of many individual constituents that can vary by time of year. When one of those constituents' concentration increases an exceedance of the 24-hour $PM_{2.5}$ NAAQS becomes more likely.

Iowa's main regional components typically consist of airborne soil particles (soil), elemental carbon (EC), ammonium sulfate (AS), ammonium nitrate (AN) and particulate organic matter (POM). Other compounds unique to areas near sources may be more prominent in some areas, but they typically dissipate quickly outside of the pollutant source's area of influence. This information in this section can be found in the latest report under the Interagency Monitoring of Protected Visual Environments (IMPROVE).[1] Equations can be found on a table located in Section 2, Page 3.

Soil is derived from a summation of basic elements of aluminum (Al), silicon (Si), calcium (Ca), iron (Fe) and titanium (Ti) after each is multiplied by a constant that represents the conversion to the mass of the typical compound each is a part of such that:

$$Soil = 2.2(Al) + 2.49(Si) + 1.63(Ca) + 2.42(Fe) + 1.94(Ti)$$

AN is found by multiplying measured nitrate ($NO_3$) values in the air by a constant to represent the typical mass of water and ammonia in the molecule. It is approximated as:

$$AN = 1.29(NO_3)$$

AS is derived by multiplying measured sulfate ($SO_4$) values by a constant to represent the typical mass of water and ammonia in the molecule. It is approximated as:

$$AS = 1.375(SO_4)$$

POM is calculated by a similar correction to account for components of a typical organic carbon molecule. It is approximated as:

$$POM = 1.8([Organic\ Carbon] - 0.3)$$

The above calculated values are summed with EC to produce RCFM. Once this value is known, fractional analysis of a given day's $PM_{2.5}$ can be performed.

$$RCFM = Soil + AN + AS + POM + EC$$

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[1] Spatial and Seasonal Patterns and Temporal Variability of Haze and its Constituents in the United States: Report V, June 2011. http://vista.cira.colostate.edu/improve/Publications/Reports/2011/PDF/IMPROVE_V_FullReport.pdf

## Discussion

In recent history many of the regional exceedances of the 24-hour $PM_{2.5}$ NAAQS have been attributable to large increases in AN during the winter season. This is largely due to situations that promote higher near-surface relative humidity levels. This can be brought on by stagnant air masses, melting snow and warm, moisture-laden air flowing over cold ground.[2] [3]

The increased relative humidity provides an aqueous pathway for AN to develop from vehicle emissions and other sources of combustion. Those emissions and AN particles will typically remain suspended over an area until winds from a direction with relatively low $PM_{2.5}$ concentrations (typically the northwest) arrive to sweep the pollution out of the area.

## Measurement Locations

Speciated $PM_{2.5}$ is currently measured at five locations in Iowa. Locations as of December 31, 2014 consist of the Public Health in Cedar Rapids, the Health Department in Des Moines, Viking Lake State Park, Lake Sugema and the NCORE monitoring site at Jefferson School in Davenport.

EPA funding for the chemical speciation monitoring sites in Des Moines and Cedar Rapids was discontinued at the conclusion of calendar year 2014 following a network analysis that showed they were not high value sites in the national network. Therefore the supplemental speciation data set from these two sites ended on December 31, 2014. The $PM_{2.5}$ speciation site in Davenport will remain.

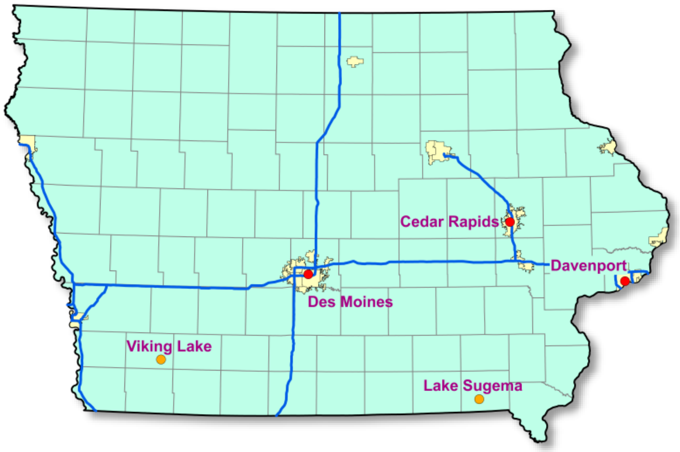

Figure 1. Map showing relative locations of the three Chemical Speciation Network (red dots) and IMPROVE (orange dots) sites in Iowa as of December 2014.

## Data & Charts

Charts are shown below that denote typical $PM_{2.5}$ components for Des Moines, Cedar Rapids, Davenport, Viking Lake State Park and Lake Sugema. Two instances of $PM_{2.5}$ levels that exceeded the 24-NAAQS are also included for comparison. In these exceedances the increased level of AN is very prominent.

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[2] Wintertime fine particle events in Wisconsin during the 2009 LADCO Winter Nitrate Study: http://epa.gov/scram001/adhoc/Spak2012.pdf

[3] LACDO Winter Nitrate Study: Phase I and II: http://www.ladco.org/reports/pm25/winter_nitrate/index.php

Data for Cedar Rapids is split between two sites. From January 1, 2010 through December 31, 2011 the speciation data was collected from the now decommissioned Army Reserve site. On January 1, 2012, the speciation data samples began being collected from the Public Health site.

Lake Sugema and Viking Lake are part of the Interagency Monitoring of Protected Visual Environments (IMPROVE) project. Its goal is to document, alleviate and prevent future visibility loss in national parks. For this report, the data is only current through 2013. The 2014 IMPROVE data will not be available until August 2015.

Figure 2 demonstrates the average monthly concentrations for the various measured components of $PM_{2.5}$ in Iowa metropolitan areas. The chart demonstrates a degree of month-to-month consistency for soil, EC, and AS. Parameters such as AN and POM can vary considerably especially AN which sees average concentrations increase by several micrograms per cubic meter ($\mu g/m^3$) during cool and cold season months.

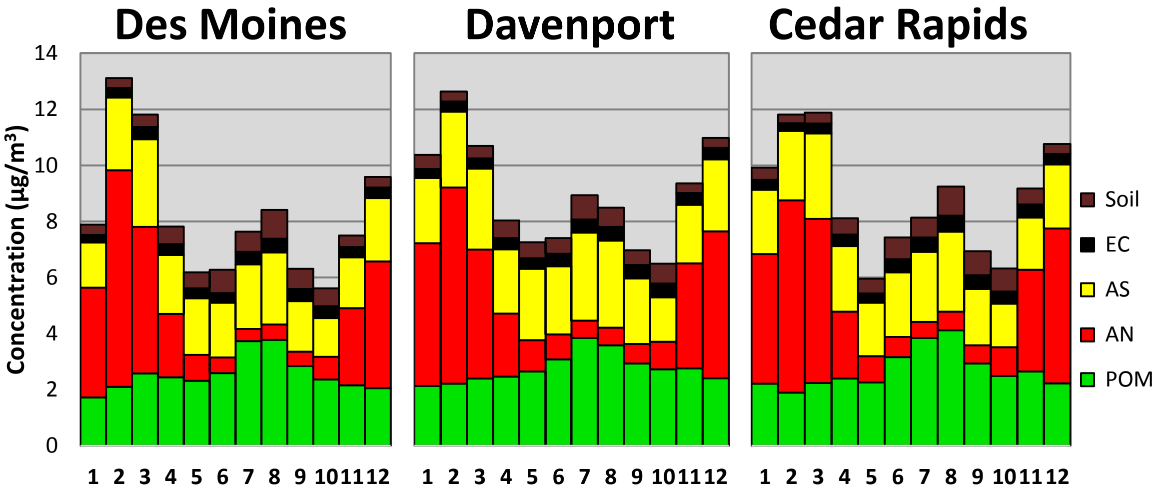

Figure 2. Monthly average (2010-2014) $PM_{2.5}$ speciation concentrations for Des Moines, Davenport and Cedar Rapids.

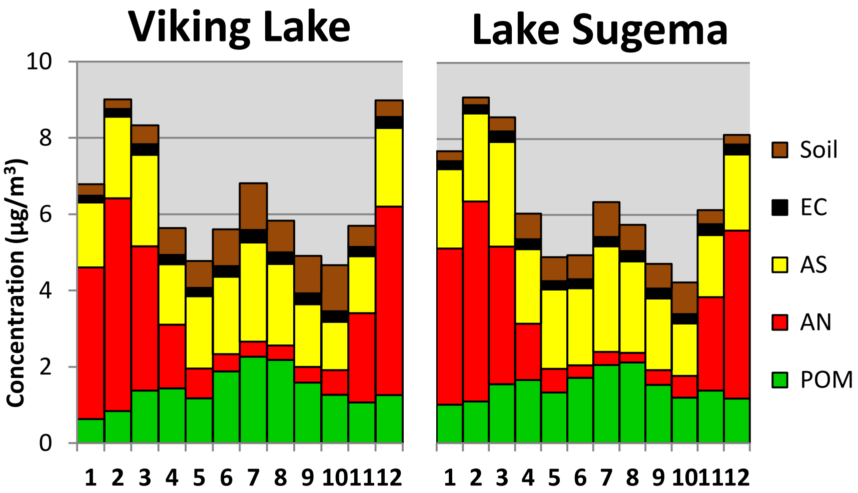

Figure 3. Monthly average (2010-2013) $PM_{2.5}$ speciation concentrations for the IMPROVE sites at Viking Lake State Park and Lake Sugema.

Figure 3 displays the monthly average concentrations for the two IMPROVE sites located at Viking Lake State Park and Lake Sugema. These are considered regional background sites, but still follow similar patters as the urban sites in Des Moines, Davenport and Cedar Rapids despite seeing lower overall concentrations. At the IMPROVE sites POM tends to reach a peak during the warm season while AN peaks in the cool season.

Figure 4a,b,c,d,e shows the average monthly percentage for the various measured components of $PM_{2.5}$ in Iowa. The two most variable percentages come from POM which peaks during the growing season and AN which peaks during the cool and cold seasons. This pattern is consistent for both urban and IMPROVE sites in Iowa.

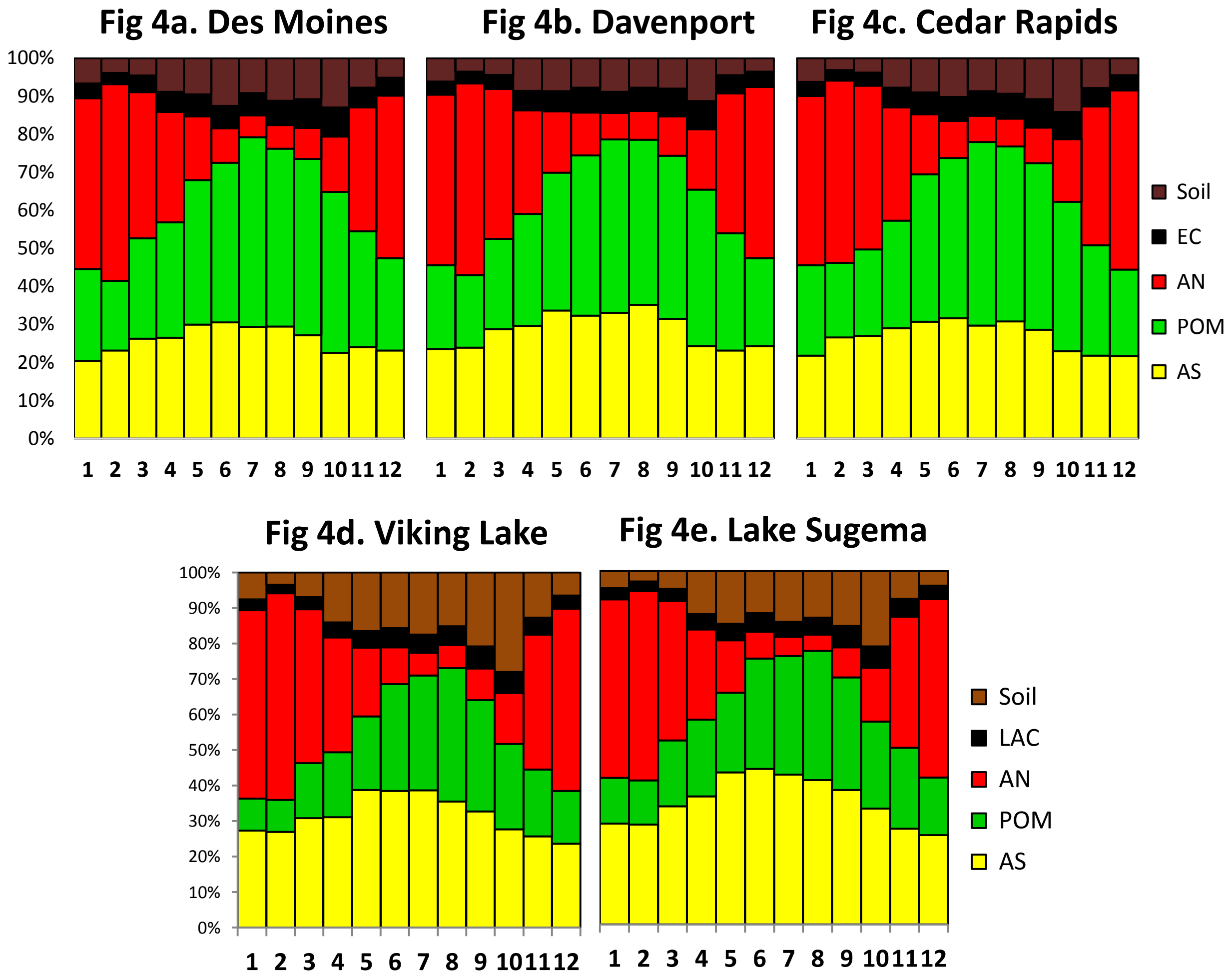
Fig 4a. Des Moines

Fig 4b. Davenport

Fig 4c. Cedar Rapids

Fig 4d. Viking Lake

Fig 4e. Lake Sugema

Figure 4a,b,c,d,e. Monthly average $PM_{2.5}$ speciation percentage. Data for Figures 4a,b,c covers 2010-2014. Data for Figures 4d,e spans 2010-2013.

There has been a certain degree of yearly variability in the average concentrations. From 2010 to the conclusion of 2013 AN levels have dropped. Figures 5a,b,c demonstrate the average monthly concentrations broken down by year. For Des Moines and Davenport the peak year for AN in this dataset was 2010. From that point on it declined with the lowest average concentrations for the cold season coming during the winter of 2011-2012 (Dec 2011 – Mar 2012). The overall drop is likely attributable to lower emissions, but some year-to-year variability can be attributed to snowfall and associated snowmelt. The winter of 2011-2012 was particularly dry and preceded the drought of 2012. Past studies by the Lake Michigan Air Directors Consortium (LADCO) has found snowmelt to be a contributor to elevated levels of $PM_{2.5}$ and AN.[4] [5] Monthly nitrate levels in Cedar Rapids and Davenport increased relative to the previous two years in the early months of 2014.

Figure 5a. Des Moines Monthly Average $PM_{2.5}$ Speciation by Year

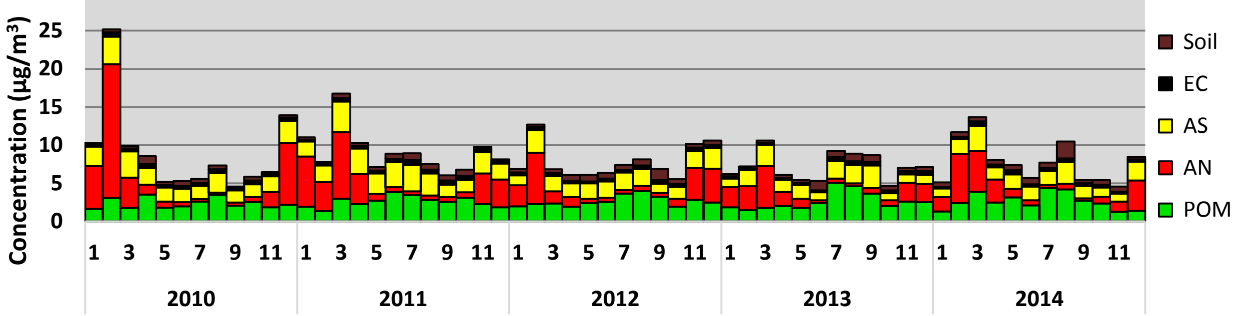

Figure 5b. Davenport Monthly Average $PM_{2.5}$ Speciation by Year

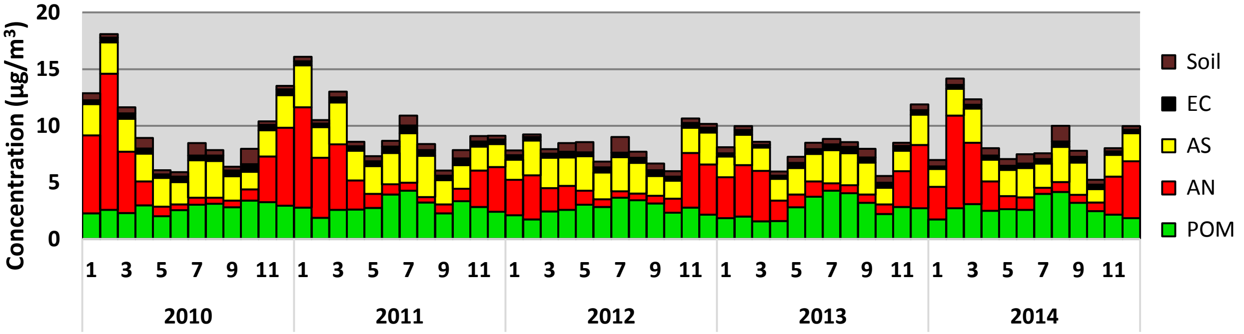

Figure 5c. Cedar Rapids Monthly Average $PM_{2.5}$ Speciation by Year

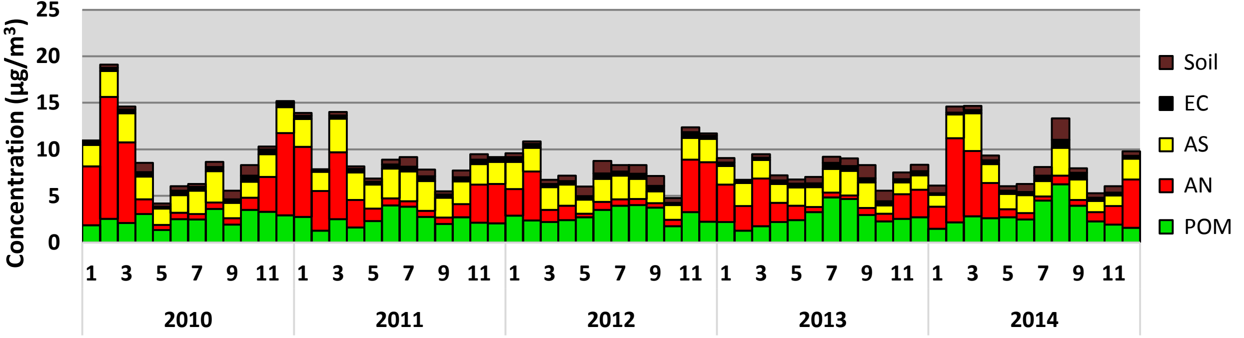

Figure 5a,b,c. Charts showing monthly average $PM_{2.5}$ speciation component concentrations separated by year.

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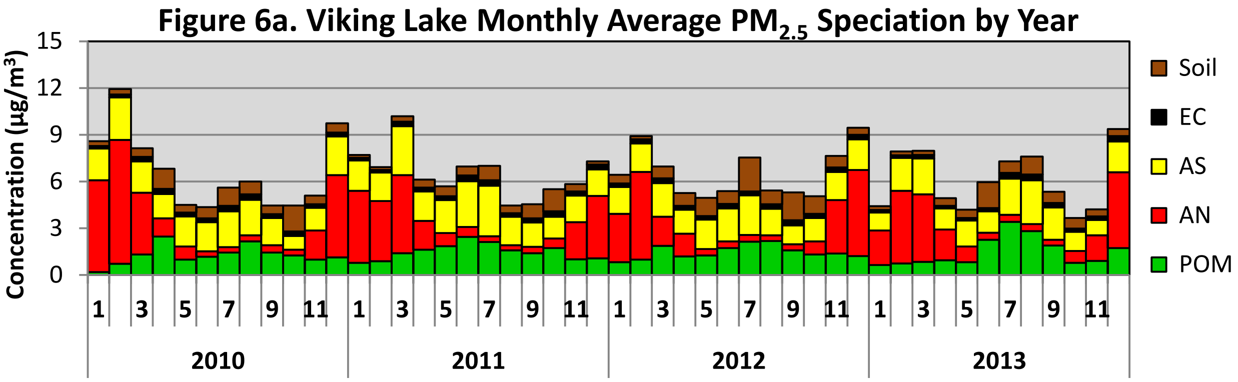
[4] Wintertime fine particle events in Wisconsin during the 2009 LADCO Winter Nitrate Study: http://epa.gov/scram001/adhoc/Spak2012.pdf

[5] LACDO Winter Nitrate Study: Phase I and II: http://www.ladco.org/reports/pm25/winter_nitrate/index.php



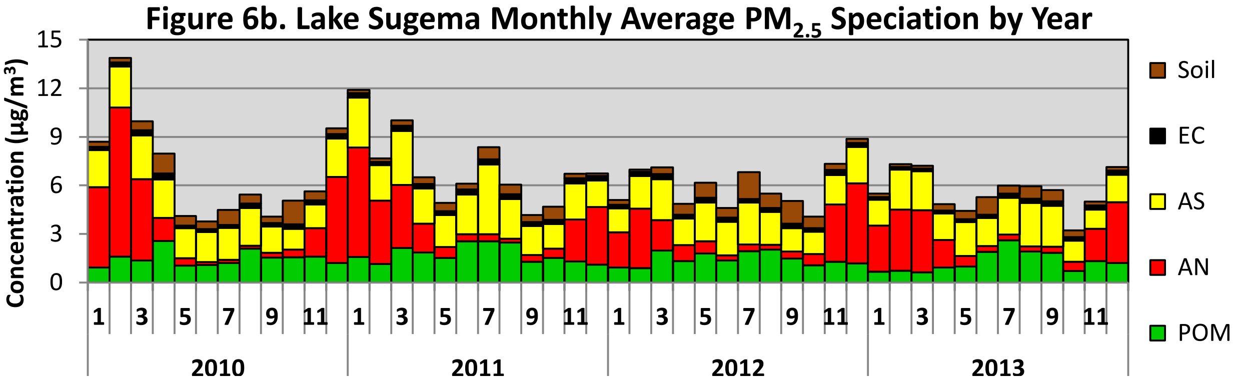


Figure 6a,b. Charts showing monthly average $PM_{2.5}$ speciation component concentrations separated by year.

Figure 6a,b shows a similar monthly breakdown by year for the rural IMPROVE sites. The seasonal variability of AN is present along with a general decline in concentrations.

Daily sampling concentrations (Figures 7a,b,c) can vary widely over an area. Winds originating from the west and northwest can easily dilute pollution levels, but once those subside concentrations generally begin to rise again. Overall they tend to follow trends established above. Concentrations of POM reach relative highs during the warm growing season and AN levels peak during the cool and cold winter months.

Figure 7a. Des Moines Daily PM$_{2.5}$ Speciation

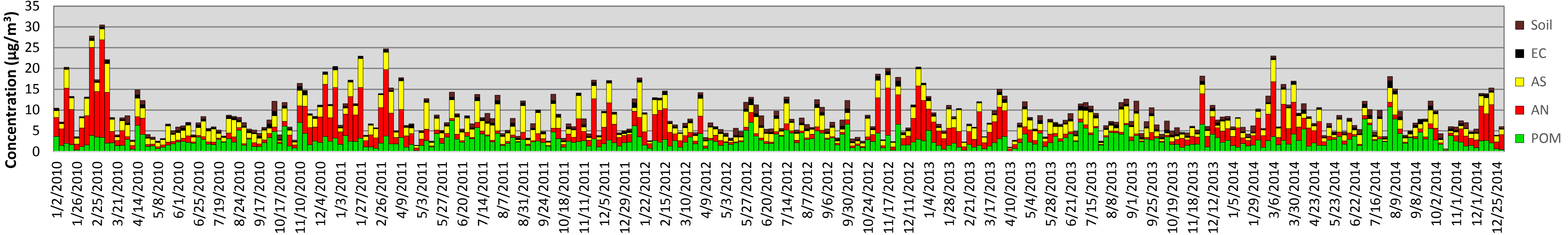


Figure 7b. Davenport Daily PM$_{2.5}$ Speciation

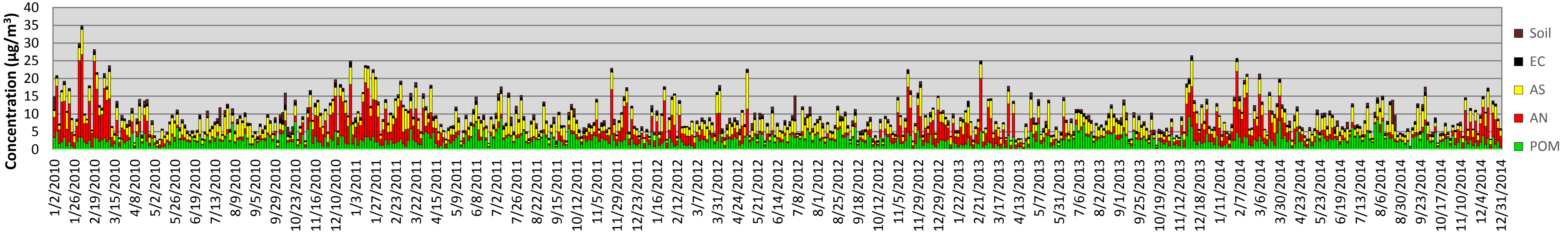
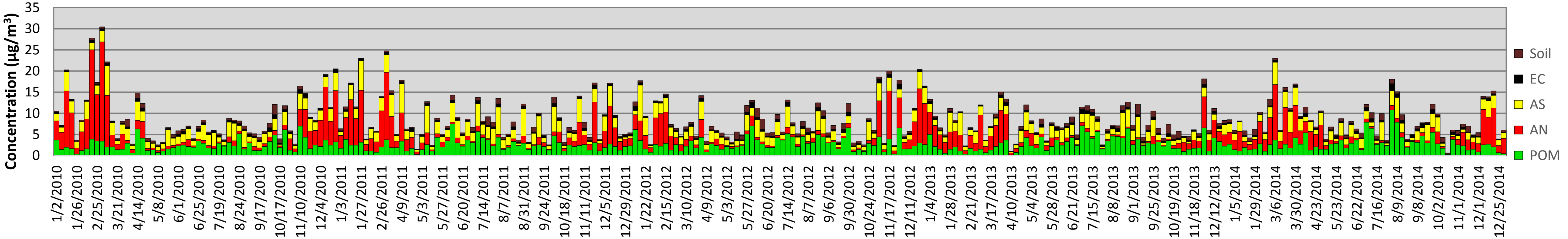


Figure 7c. Cedar Rapids Daily PM$_{2.5}$ Speciation



Figures 7a,b,c. Graphs displaying the daily PM$_{2.5}$ speciation data. Previously discussed trends of POM and AN reaching relative peaks during the growing season and winter months respectively are apparent. The most prominent of those trends is AN peaking in during winter months.

**Figure 8a. Viking Lake Daily PM$_{2.5}$ Speciation**

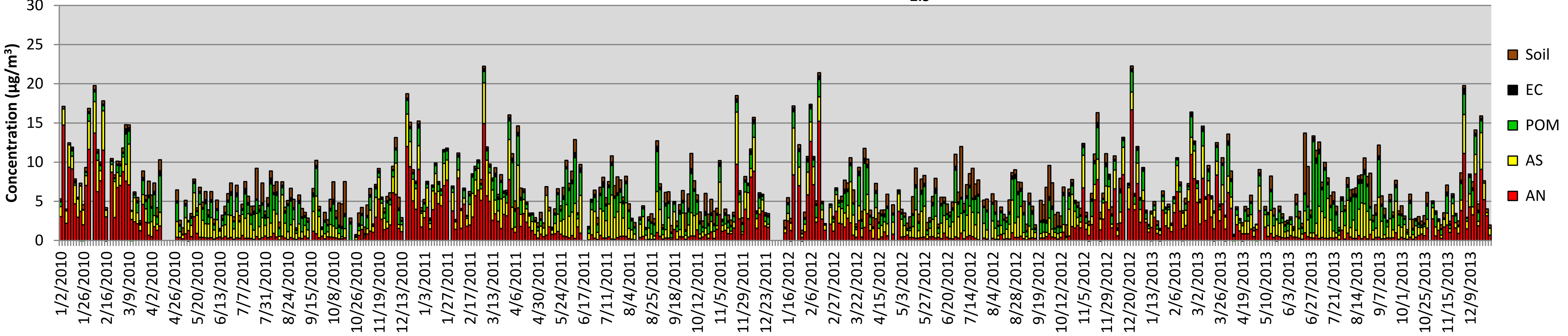
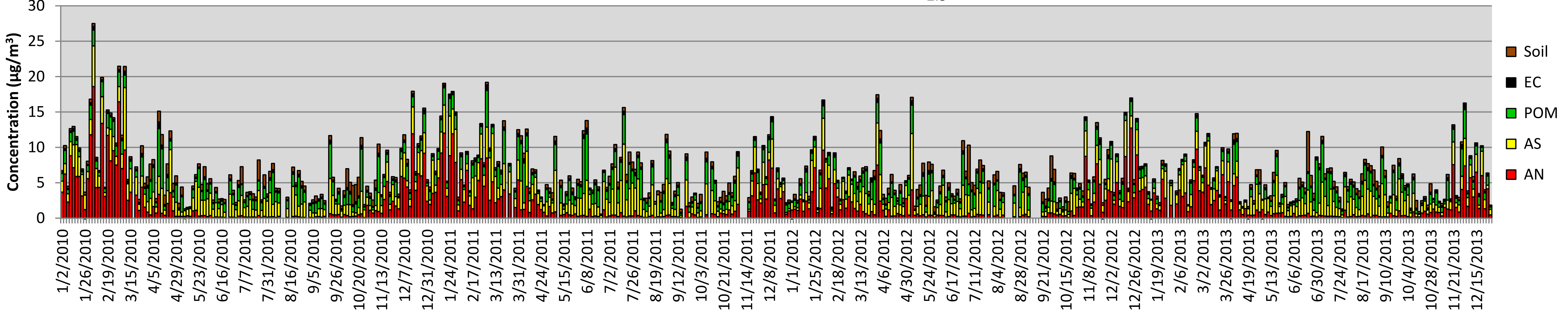


**Figure 8b. Lake Sugema Daily PM$_{2.5}$ Speciation**



Figures 8a,b. Graphs displaying the daily PM$_{2.5}$ speciation data. Previously discussed trends of POM and AN reaching relative peaks during the growing season and winter months respectively are apparent. The most prominent of those trends is AN peaking in during winter months.

IMPROVE daily $PM_{2.5}$ speciation concentrations (Figure 8a,b) reflect the same trends as the urban sites. Nitrate tends to peak in the cool season while POM reaches a relative high in the warm season. Other pollutants remain fairly steady.

## Comparability with the Federal Reference Method

The available speciation data was then compared to data outputted by the $PM_{2.5}$ monitors used for attainment of the National Ambient Air Quality Standards that use the Federal Reference Method (FRM) for measuring $PM_{2.5}$. This comparison was performed using the RCFM (Figures 9a,b,c).

In this study RCFM concentrations tended to be lower than the FRM despite a high degree of correlation. This can be attributed to several factors.

During sampling, the Teflon filter in the FRM sampler can lose nitrate and other volatile relative humidity sensitive species. Acidic particulate retained on the filter can also retain excess water. These known sampling artifacts affect the gravimetric mass obtained from the FRM filter analysis.

In contrast, a speciation sampler is a multiple channel instrument that captures a Teflon, nylon and quartz filter for each sampling event. The use of nylon and quartz filter media improves the capture efficiency for nitrate and organic particulate, respectively. However, the RCFM mass is based on reconstruction equations that assume its constituents (soil, EC, AN, POM and AS) can be found by multiplying elements (obtained by chemical analysis of the various filters) by an empirically-derived constant and summing the calculated members. This approach loses accuracy if the actual chemical composition of the collected particulate and associated constants differs from the assumed chemical composition of the particulate that is incorporated in constants in the reconstruction equations. In addition, the RCFM equation does not account for the mass of water retained on the Teflon filter of the speciation sampler.

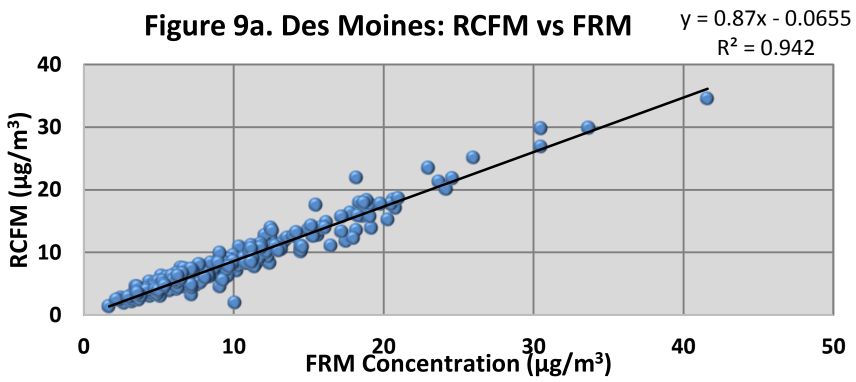


**Figure 9a. Des Moines: RCFM vs FRM**

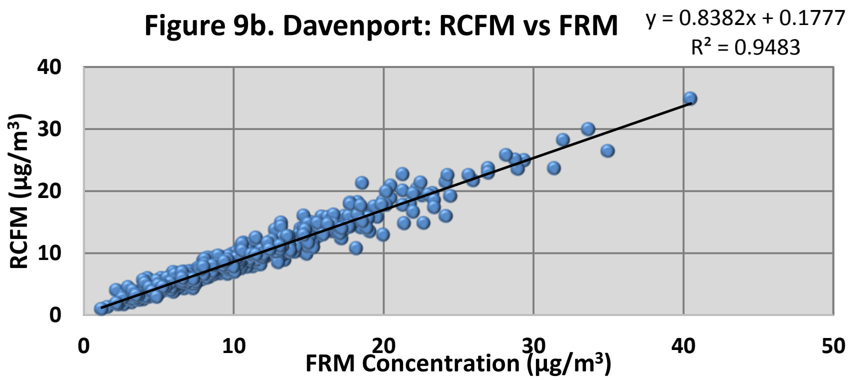


Figure 9b. Davenport: RCFM vs FRM

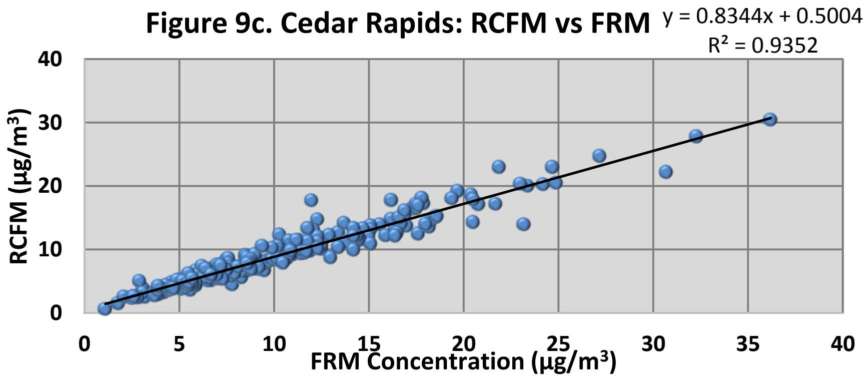


Figure 9c. Cedar Rapids: RCFM vs FRM

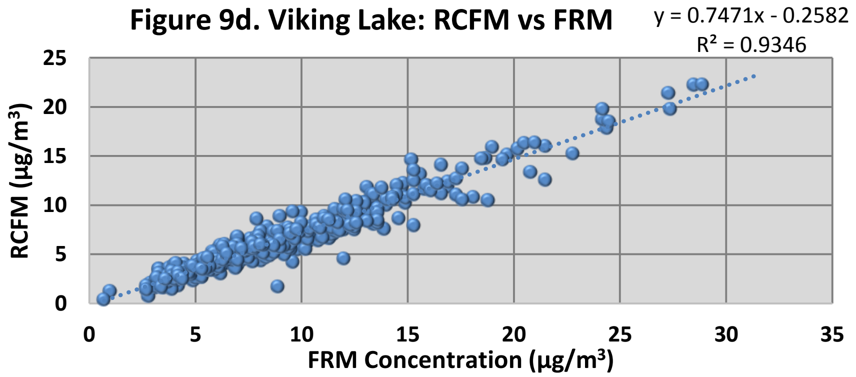


Figure 9d. Viking Lake: RCFM vs FRM

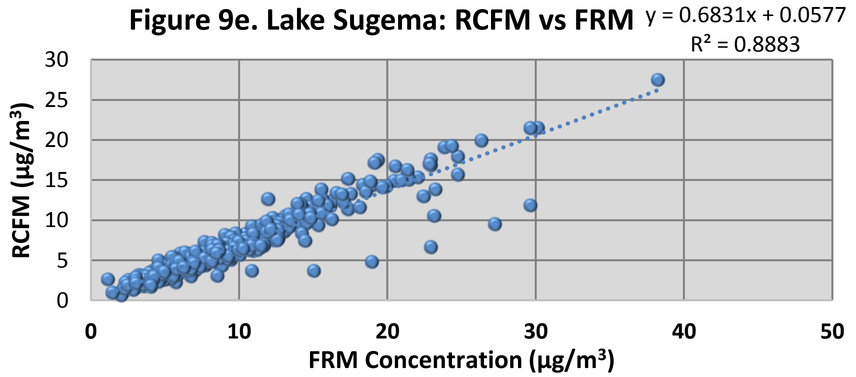


Figure 9e. Lake Sugema: RCFM vs FRM

Figures 9a,b,c,d,e. Scatter plots with regression equations for RCFM vs FRM data. Slopes exceed 0.8, intercepts are less than 0.5 and $R^2$ values exceed 0.92 with the exception of Lake Sugema. This implies the data is well-correlated. Data for Figures 9a,b,c is 2010-2014. Data for figures 9d,c is 2010-2013.

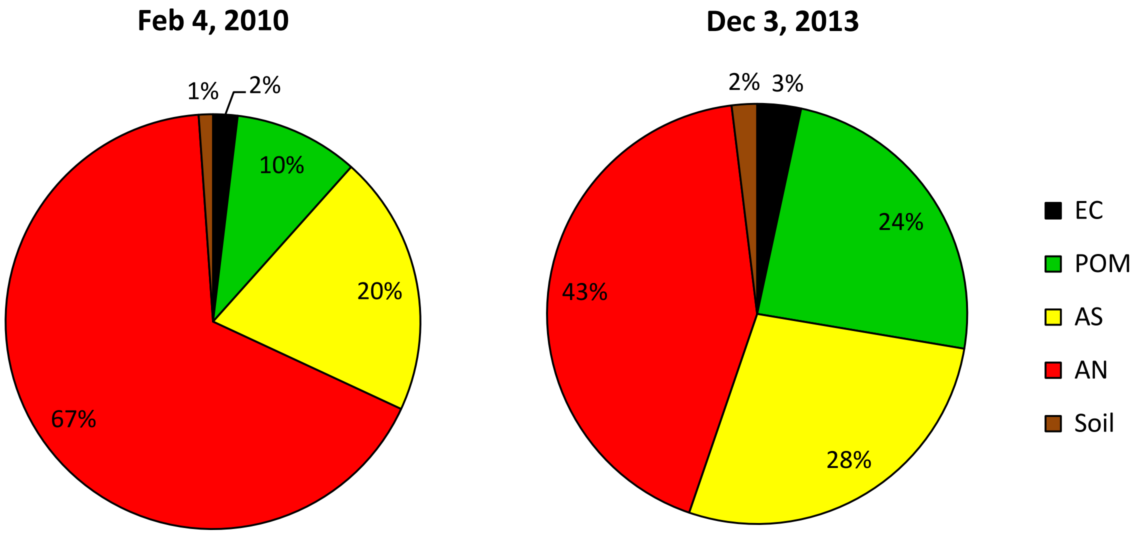
## Case Studies

An exceedance of the 24-hour NAAQS occurs when a FRM $PM_{2.5}$ monitor reads in excess of 35.5 µg/$m^3$. Exceedances tend to be more common in the cool season months for non-source oriented monitors. An investigation into the speciation data during these episodes can yield clues pertaining to the origins of the particle pollution.

On February 4, 2010 and December 3, 2013 exceedances of the 24-hour NAAQS were recorded on days in which the speciation monitor in Davenport was taking a sample (Figures 10a,b). AN comprised most of the speciated data which is consistent with previous analysis.

A major difference between the two events is the percentage that AN accounted for relative to AS, POM, EC and soil. On February 4, 2010 AN comprised 67% of the $PM_{2.5}$ mass. That ratio is substantially more than from December 3, 2013 in which AN accounted for 43% of the $PM_{2.5}$ mass.

This reduction may be indicative that regional control strategies to reduce other pollutants are aiding in the reduction of AN.



Figures 10a,b. Pie charts representing the percentage mass of each measured component of $PM_{2.5}$ in Davenport on the listed dates. In both exceedances of the 24-hour NAAQS, AN comprised most of the mass followed by AS and POM.

# References

Wintertime fine particle events in Wisconsin during the 2009 LADCO Winter Nitrate Study:
http://epa.gov/scram001/adhoc/Spak2012.pdf

LACDO Winter Nitrate Study: Phase I and II:
http://www.ladco.org/reports/pm25/winter_nitrate/index.php

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