Appendix 3

An Analysis of Characteristics and Precursors to Ambient $PM_{2.5}$ Levels in Southeastern Wisconsin for Purposes of Designing Emission Inventories for Inclusion in a Request for Redesignation to Attainment $PM_{2.5}$ Nonattainment Counties of Milwaukee, Waukesha and Racine

Bureau of Air Management
Wisconsin Department of Natural Resources
August 2011

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1 Purpose of Report

The purpose of this report is to provide a technical demonstration to identify certain long-term (2001 through 2009, 2010) characteristics, distributions and profiles in measured fine particulates (i.e. those particles with an aerodynamic diameters less than 2.5 microns [“$PM_{2.5}$”]) and some of their precursors in southeastern Wisconsin.

Evaluating these long-term behaviors and features of $PM_{2.5}$ and precursors in southeastern Wisconsin will help in assessing which (if any) additional emission inventories need to be constructed as part of the Wisconsin Department of Natural Resources (WDNR)’s request for the redesignation to attainment for $PM_{2.5}$ nonattainment counties in southeastern Wisconsin as part of the state implementation plan (SIP) for $PM_{2.5}$.

2 Overview: $PM_{2.5}$ nonattainment designations and request to redesignate to attainment

On November 13, 2009 (74 **FR** 58688) the U.S. Environmental Protection Agency (EPA) designated the Wisconsin counties of Milwaukee, Racine and Waukesha (Figure 1) as being in nonattainment of the year 2006 24-hour $PM_{2.5}$ National Ambient Air Quality Standard (NAAQS). This designation was part of the U.S. EPA’s national rulemaking in which numerous other regions in the country were also designated as not attaining a $PM_{2.5}$ NAAQS.

This rulemaking, which was done in accordance with Section 107(d) of the Federal Clean Air Act (CAA), was based upon the Agency’s review of $PM_{2.5}$ measurements collected during the three year period 2006-2008.

The $PM_{2.5}$ measurements collected at monitoring sites in Milwaukee and Waukesha Counties during 2008-2010 show that all sites have attained all $PM_{2.5}$ NAAQS during this three year period. There never has been any $PM_{2.5}$ monitoring conducted in Racine County.

Consequently, the Wisconsin Department of Natural Resources (WDNR) is in the process of drafting a request that the U.S. EPA redesignate Milwaukee, Racine and Waukesha Counties (Figure 1) as attaining the year 2006 24-hour $PM_{2.5}$ NAAQS.

The U.S. EPA has established guidance and requirements that any state must follow in submitting a redesignation request.

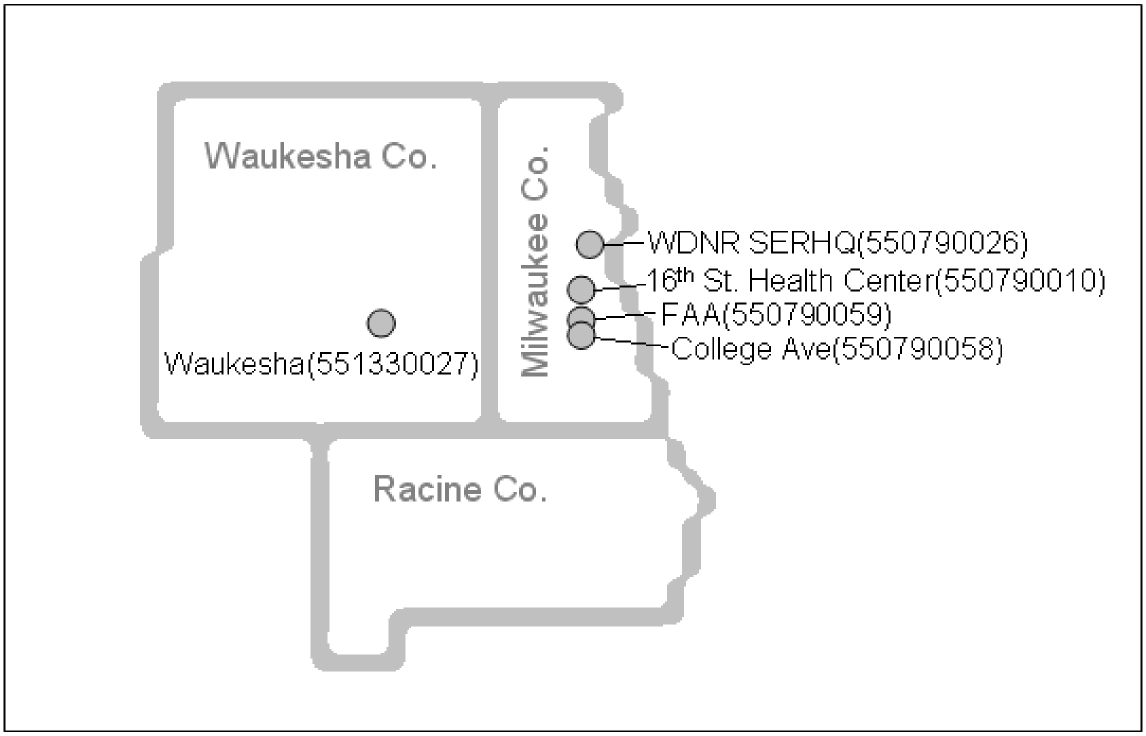
Under section 172(c)(3) of the federal Clean Air Act (CAA), any state seeking a redesignation to attainment is required to submit a comprehensive, accurate and current inventory of actual (base year / attainment year) emissions. Additionally, under section 175A of the CAA, the state must submit a maintenance plan that demonstrates continued attainment for at least 10 years after approval of a redesignation. This maintenance plan must include a maintenance inventory.

Eight years after the redesignation, a revised maintenance plan for the next ten years must be submitted to the U.S. EPA. In order to address the possibility of future NAAQS violations, the maintenance plan must contain contingency measures.

Figure 1

Wisconsin Nonattainment Counties
And FRM $PM_{2.5}$ Monitoring Sites
(Milwaukee, Waukesha and Racine)

2006 24-Hour $PM_{2.5}$ NAAQS



3 Overview: Requirements on evaluating concentration levels of $PM_{2.5}$ and gaseous $PM_{2.5}$ precursors for $PM_{2.5}$ SIP revisions (e.g., redesignation requests)

On April 25, 2007 the U.S. EPA promulgated many requirements and guidance notes regarding provisions for implementation of $PM_{2.5}$ NAAQS – as part of the Agency's Clean Air Fine Particle Implementation Rule (72 **FR** 50586). These requirements are codified in 40 **CFR** 51 subpart Z ("provisions for implementation of $PM_{2.5}$ NAAQS").

Among these $PM_{2.5}$ SIP requirements is addressing pollutants contributing to $PM_{2.5}$ concentrations. Section 40 CFR 51.1002(c) requires that

> "The State implementation plan [SIP] must identify and evaluate sources of $PM_{2.5}$ direct emissions and $PM_{2.5}$ attainment plan precursors in accordance with §§ 51.1009 and 51.1010. After January 1, 2011, for purposes of establishing emissions limits under 51.1009 and 51.1010, States must establish such limits taking into consideration the condensable fraction of direct $PM_{2.5}$ emissions"
>
> "(1) The State must address sulfur dioxide [SO_2] as a $PM_{2.5}$ attainment plan precursor and evaluate sources of SO_2 emissions in the State for control measures."

> “(2)-(4) The State must address any of the following gaseous precursors: NOx [oxides of nitrogen], volatile organic compounds [VOCs], and ammonia [NH_3] as $PM_{2.5}$ attainment plan precursors and evaluate their emission sources in the State for control measures, unless the State and the U.S. EPA provide an appropriate technical demonstration for a specific area showing that these emissions from sources in the State do not significantly contribute to $PM_{2.5}$ concentrations in the nonattainment area.”
>
> “(5) The State must submit a demonstration to reverse any presumption in this rule for a $PM_{2.5}$ precursor with respect to a particular nonattainment area, if the administrative record related to development of its SIP shows that the presumption is not technically justified for that area.”

4 Data analysis overview

Addressing the requirements listed in 40 CFR 51.1002(c)(2) and (3) forms the heart of this study -- as they pertain to the WDNR drafting a request that the U.S. EPA redesignate Milwaukee, Racine and Waukesha Counties to attainment of the year 2006 24-hour $PM_{2.5}$ NAAQS. Specifically, for the long-term (2001-2009) period in Wisconsin’s $PM_{2.5}$ nonattainment counties - this analysis looks at the characteristics and distributions of the following pollutants:

a) $PM_{2.5}$ (measured according to EPA’s federal reference method [FRM]),

b) Major speciated $PM_{2.5}$ ions, and

c) The gaseous $PM_{2.5}$ precursors VOCs and NOx - how their concentration levels relate to the targeted $PM_{2.5}$ ions and FRM $PM_{2.5}$.

Meteorological conditions are known to greatly influence ambient levels of $PM_{2.5}$, especially those formed as secondary particles from gaseous precursors (Damburg 2007, LADCO 2009). Consequently, some of the graphical assessments illustrate how varying profiles of several meteorological metrics (e.g., average daily temperature, average daily relative humidity) relate to $PM_{2.5}$ levels.

The results of these analyses will provide a technical demonstration that helps answer the following questions regarding emission inventories for this redesignation request:

a) How should the emissions inventories be configured on a temporal basis? Based on annual activity levels? Or targeted to those portion(s) of the calendar when the ambient $PM_{2.5}$ levels are most dominant?

b) Which gaseous precursor(s) demonstrate to make contributions to secondary (condensable) $PM_{2.5}$ levels that are sufficiently large such that their emissions must be taken into account as part of the $PM_{2.5}$ SIP?

With regards to part (b) – this assessment will address the influence of the $PM_{2.5}$ precursor pollutants VOCs and NOx. There are little, if any ambient ammonia (NH_3) measurement data available for southeastern Wisconsin. Consequently, NH_3 is not evaluated for this study.

5 Measurement data

The geographical focus of this study of $PM_{2.5}$ and $PM_{2.5}$ precursor measurements for purposes of assessing which emission inventories need to be constructed is the $PM_{2.5}$ nonattainment area in Wisconsin (i.e., the Counties of Milwaukee, Waukesha and Racine [Figure 1]). Note, there have never been any measurements of any $PM_{2.5}$ and $PM_{2.5}$ precursors collected in Racine County.

5.1 FRM $PM_{2.5}$ data

One of the questions that need answering in this study is how the emissions inventories should be configured on a temporal basis. Should the emissions be established for annual activities and throughputs? Or should they be derived for the calendar season of greatest $PM_{2.5}$ impact? (e.g., winter months). In order to evaluate this question all of the validated 24 hour, filter-based FRM $PM_{2.5}$ measurements collected in both Milwaukee and Waukesha Counties during January 1999 – December 2010 were analyzed. The WDNR commenced FRM $PM_{2.5}$ monitoring in Wisconsin in January 1999.

At varying times during January 1999 – December 2010 the WDNR has operated a total of 7 FRM $PM_{2.5}$ monitoring sites in Milwaukee County, as follows:

Site Name	Site ID #
16th St. Health Center	550790010 (a)
DNR SER HQ	550790026 (a)
Virginia St. Fire Station	550790043
Craig School	550790050
County Zoo	550790051
College Ave.	550790058 (a)
Fed Aviation Adm. Bldg	550790059
Wells St. Fire Station	550790099

(a) Active site as of July 2011. All other monitoring sites have been discontinued.

The WDNR, during the same 12 year period, maintained two FRM $PM_{2.5}$ monitoring sites in Waukesha County:

Site Name	Site ID #
Cleveland Ave	551330027(a)
Barstow St	551330034

(a) Active site as of July 2011. The Barstow site has been discontinued.

5.2 Speciated $PM_{2.5}$ data

Since 2001 the WDNR , at the Milwaukee-DNR SERHQ and Waukesha-Cleveland sites, has also collected a second series of 24-hour, filter-based $PM_{2.5}$ mass samples using a different instrument and filter system from the FRM equipment. (i.e., the Speciation Air Sampling System [SASS]). In turn, these SASS $PM_{2.5}$ mass samples have been laboratory-analyzed for many different types of $PM_{2.5}$ species that comprise the total $PM_{2.5}$ mass..

Based upon the lab analysis of the $PM_{2.5}$ mass collected on these speciation filters, the large majority of $PM_{2.5}$ mass has been identified as pertaining to four $PM_{2.5}$ species, as follows:

- Sulfates (SO_4), most which are formed from the atmospheric chemical processes involving the gaseous $PM_{2.5}$ precursor sulfur dioxide (SO_2).

- Organic carbon (OC), most which is formed from the atmospheric chemical processes involving heavier volatile organic compounds (VOCs) – largely in the aromatics species group.

- Nitrates (NO_3), most which are formed from the atmospheric chemical processes involving the gaseous $PM_{2.5}$ precursor oxides of nitrogen (NOx).

The U.S. EPA guidance for $PM_{2.5}$ SIPs already requires that the states need to compile and assess SO_2 emission inventories for their contribution to $PM_{2.5}$ levels (mostly via SO_4).

However, the U.S. EPA requirements state that it is also necessary to evaluate how both the $PM_{2.5}$ precursors VOCs and NOx may influence $PM_{2.5}$ levels in the Wisconsin $PM_{2.5}$ nonattainment area in order to determine if either / both of these $PM_{2.5}$ precursors need to have emission inventories compiled. To assess the degree of this influence, it is necessary to relate the OC $PM_{2.5}$ levels to VOC concentrations and also compare NO_3 $PM_{2.5}$ concentrations to NOx levels.

The data sets of both VOC and NOx measurements collected in southeastern Wisconsin that were analyzed for these comparisons are described in the following two sections.

5.3 VOC measurement data

The purpose of evaluating VOC measurements as they relate to $PM_{2.5}$ concentrations is that one of the largest $PM_{2.5}$ component species is organic carbon (OC) (Wis DNR, 2003). Some OC $PM_{2.5}$ is formed as a primary pollutant directly emitted into the atmosphere.

However, the large majority of OC $PM_{2.5}$ is formed in the atmosphere as a secondary organic aerosol (SOA) (Grosjean and Seinfeld, 1989). The ability of a given VOC species to produce these condensable SOA products depends on its atmospheric abundance, reactivity, oxidant availability and volatility of its products (NARSTO, 2001). Of note is that the large majority of VOC species do not form SOA under atmospheric conditions due to the typically high vapor pressure of their products.

The SOA particles are formed mostly as a result of certain atmospheric chemistry processes involving a synthesis of sunlight, heat and moisture which transform some of the heavier (i.e., lower vapor pressure) VOCs (mostly from the aromatics group) to yield condensable particulates (Grosjean and Seinfeld, 1989).

Consequently, the two categories of ambient VOC concentrations that are analyzed in this $PM_{2.5}$ study are total VOCs (i.e., total nonmethane organic carbon [TNMOCs]) and the aromatic species.

The only ambient speciated VOC measurement data collected in Wisconsin's $PM_{2.5}$ nonattainment area have been at the Milwaukee DNR SERHQ site, located approximately 2 miles north of the Milwaukee downtown and 2 miles east of Lake Michigan (Figure 1).

There have been two types of speciated VOC measurement data collected at the SER site:

a) Lab analysis of integrated 24 hour air samples collected in stainless steel canisters – once every 6th calendar day, year around. The "VOC canister" data base used in this study is for the period 2001 – 2009.

b) Continuous analysis of ambient air streamed into an automated gas chromatograph ("autoGC") during the months of June-July-August for the years 2001-2007. The VOC concentrations derived from this continuous sampling were synthesized into hourly averaged and then into calendar day (24-hour) levels.

The WDNR Air Monitoring Section has evaluated how "canister" and "autoGC" 24-hour averaged VOC measurements compare for same day sampling. Their findings concluded that the overall differences between the two VOC measurement methods were sufficiently minimal. Consequently, the WDNR ruled that both VOC data bases could be used interchangeably in the same analysis.

Consequently, the data base of validated 24-hour VOC (i.e., TNMOC, aromatic species) established for this study was derived as of 1) VOC concentrations from for all canister-based samples (year-around collection), and 2) the 24-hour averaged VOC data from the autoGC on those dates that were not already witness to canister sampling.

This resulting data base of 24-hour averaged TNMOC and aromatic VOCs concentrations is used in comparison with the same day 24-hour FRM and OC $PM_{2.5}$ measurements at Milwaukee-SER during 2001-2009.

5.4 NOx measurement data

The purpose of evaluating NOx measurements as they relate to $PM_{2.5}$ concentrations is that one of the largest $PM_{2.5}$ component species is nitrate (NO_3). Some nitrates are formed as a primary pollutant directly emitted into the atmosphere.

However, the large majority of NO_3 $PM_{2.5}$ is formed in the atmosphere as secondary fine particulates (Damberg, 2007).

The only ambient NOx measurement data collected in Wisconsin's $PM_{2.5}$ nonattainment area have been at the Milwaukee DNR SERHQ site. The NOx data base used in this study consist of 24-hour (calendar day) averaged values that have been aggregated from validated hourly-averaged NOx.

This resulting data base of 24-hour averaged NOx concentrations is used in comparison with the same day 24-hour FRM and NO_3 $PM_{2.5}$ measurements at Milwaukee-SER during 2001-2009.

5.5 Meteorological data

The concentration levels of $PM_{2.5}$ and its major precursors can be greatly influenced by varying meteorological conditions (LADCO, 2009). Consequently, there are graphs constructed for this study that profile changes in FRM $PM_{2.5}$, OC and NO_3 $PM_{2.5}$ and their precursor concentrations.

The source of all meteorological data employed in this study was the weather measurements taken at the National Weather Service (NWS) station located at Milwaukee Mitchell Field Airport ("MKE"). The MKE site is located approximately 3 miles west of Lake Michigan and approximately 10 miles directly south of the WDNR monitoring site at the Milwaukee-DNR SERHQ office.

Many of the graphs that contain air pollution data from Milwaukee-SER site also display MKE meteorological data. Both the SER and MKE sites are approximately the same distance west of the Lake Michigan, which can greatly modify weather patterns on the east side of Milwaukee. Consequently, it is believed that the MKE meteorological data are adequately representative of the meteorology at the SER site.

The MKE NWS meteorological data were used because they are more complete and subject to more quality assurance than the meteorological measurements taken at Milwaukee-DNR SERHQ.

6 Evaluating characteristics of $PM_{2.5}$ in Milwaukee and Waukesha Counties

6.1 Month of year distributions - average FRM $PM_{2.5}$ concentrations

Figures 2 and 3 display county-wide, collective month-of-year metrics - both the average daily FRM $PM_{2.5}$ concentrations and the percentage of daily FRM $PM_{2.5}$ concentrations greater than 30 ug/m3 for all validated

FRM $PM_{2.5}$ monitoring conducted during January 1999 – December 2010 in Milwaukee and Waukesha Counties, respectively.

Both graphs display the same general patterns. Those patterns are that the highest monthly average $PM_{2.5}$ levels and the greatest occurrence of high site-$PM_{2.5}$ days (i.e., defined as > 30ug/m3) during January 1999 – December 2010 are noticeably skewed to the colder months of November – March. Using Milwaukee County $PM_{2.5}$ data, the collective average month-of-year $PM_{2.5}$ concentration for November – March (15.0 ug/m3) is 26% higher than for the remaining seven months (11.8 ug/m3). Furthermore, the collective average percentage rate of high $PM_{2.5}$ days for November – March (6.68%) is more than twice the rate of high $PM_{2.5}$ site-days during the other seven months (2.97%).

There is a weak secondary maximum in these $PM_{2.5}$ statistics during July-August. The graphs show that the lowest monthly $PM_{2.5}$ levels typically occur during the meteorologically transitional spring (March-April) and autumn (September-October) seasons. For Waukesha County - a very similar evaluation of annual distribution in FRM $PM_{2.5}$ can be derived from applying the same metrics.

Figures 2 and 3 reveal that both the long-term (1999-2010) $PM_{2.5}$ levels are highest and the exceedances of the 24-hour $PM_{2.5}$ NAAQS are most likely during the colder months of December – February in southeastern Wisconsin. These characteristics suggest that the focus of $PM_{2.5}$ SIP work, including emissions inventory development might be most effective if directed towards $PM_{2.5}$-related activity levels and throughput during December-February.

Reid, et.al. (2011) have already compiled winter time emissions inventories (“average January weekday”, years 2005 and 2008) for the pollutants NOx, VOCs and carbon monoxide (CO) for several sites in the upper Midwest, including the vicinity of the Milwaukee DNR SERHQ site. These emission inventories were constructed from inventory components developed by the Lake Michigan Air Directors Consortium (LADCO). Of note is that summertime emissions inventories were also compiled as part of this study.

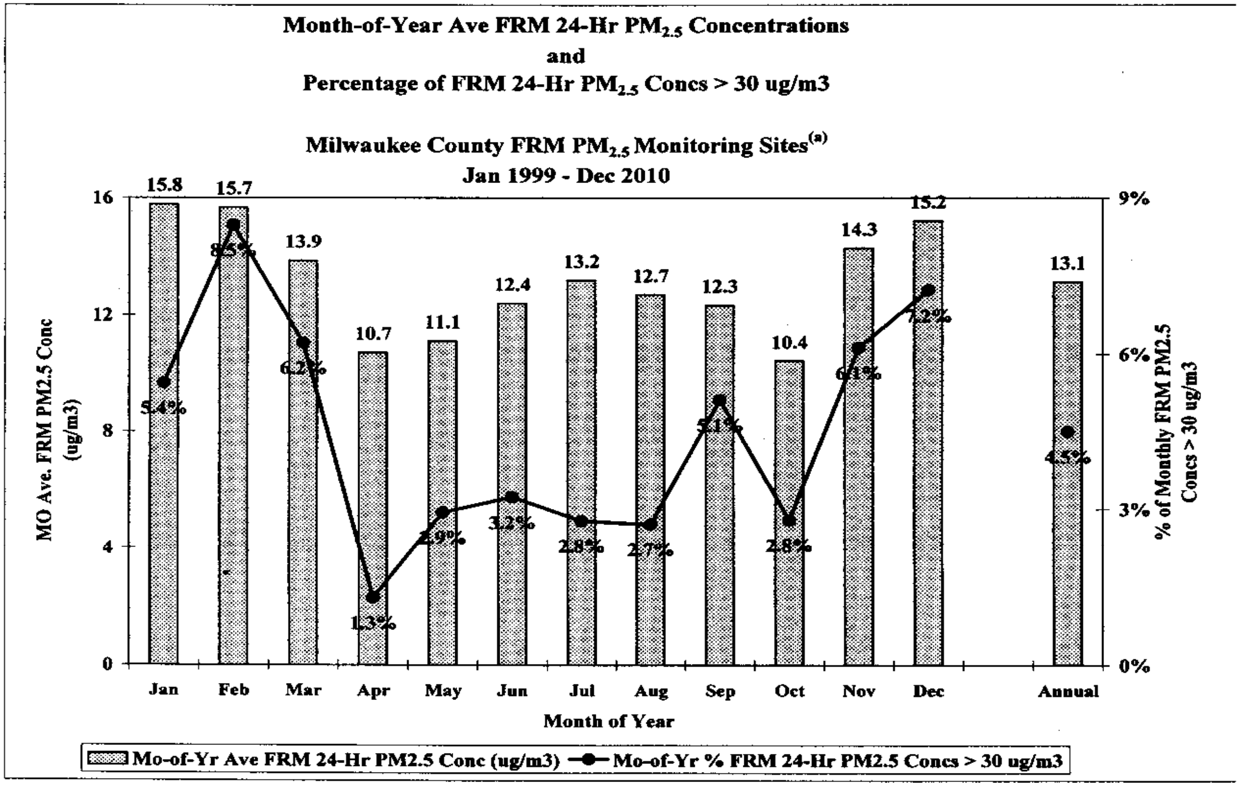
6.2 Month of Year – Average speciated $PM_{2.5}$ concentrations

Figures 4 is similar to Figure 2 in that it displays collective month-of-year average daily $PM_{2.5}$ concentrations collected in Milwaukee during the past decade. However, Figures 4, as well as Figure 5, is derived from the 24-hour speciated $PM_{2.5}$ measurements collected at the Milwaukee-SER site during January 2001 (when speciation $PM_{2.5}$ monitoring started) through December 2009. Figures 4 and 5 show composite month-of-year stacked bar graphs of the daily average concentrations and percentage fractions of FRM values, respectively for the four major $PM_{2.5}$ species (organic carbon [OC], nitrate [NO_3], sulfate [SO_4] and ammonium [NH_4]) that together comprise 90%+ of the $PM_{2.5}$ mass collected on filters in Wisconsin.

These graphs show that OC is generally the single largest speciated $PM_{2.5}$ component, expressing a slight bias towards higher values during the warmer months of June – August. Furthermore, Figure 5 reveals that the OC comprises almost half the total $PM_{2.5}$ mass during May-August. Damberg (2007) notes that OC exhibits higher mass in the summer when photochemical activity is highest (i.e., peak solar radiation and temperature). This results in generating sizable amounts of secondary organic aerosols (SOA) from the heavier volatile organic compounds (VOCs) that have lower vapor pressures. These VOCs are classified as aromatics (e.g., toluene, xylene). Man-made sources of aromatic gases include mobile sources, petrochemical manufacturing and solvents (Damberg, 2007).

The next largest overall $PM_{2.5}$ constituent is nitrate (NO_3), at least when this pollutant is significantly highest during the colder months. According to Husar (1999) and Blanchard and Tanenbaum (2003), the formation of NO_3 $PM_{2.5}$ is favored by the availability of gaseous ammonia (NH_3) and nitric acid (HNO_3) along with low temperatures, and high relative humidity. Figures 4 and 5 corroborate that nitrate’s properties of being semi-volatile and not stable in higher temperatures lead to NO_3 levels that are typically higher during winter months and significantly lower in summer (Husar, 1999).

Figure 2

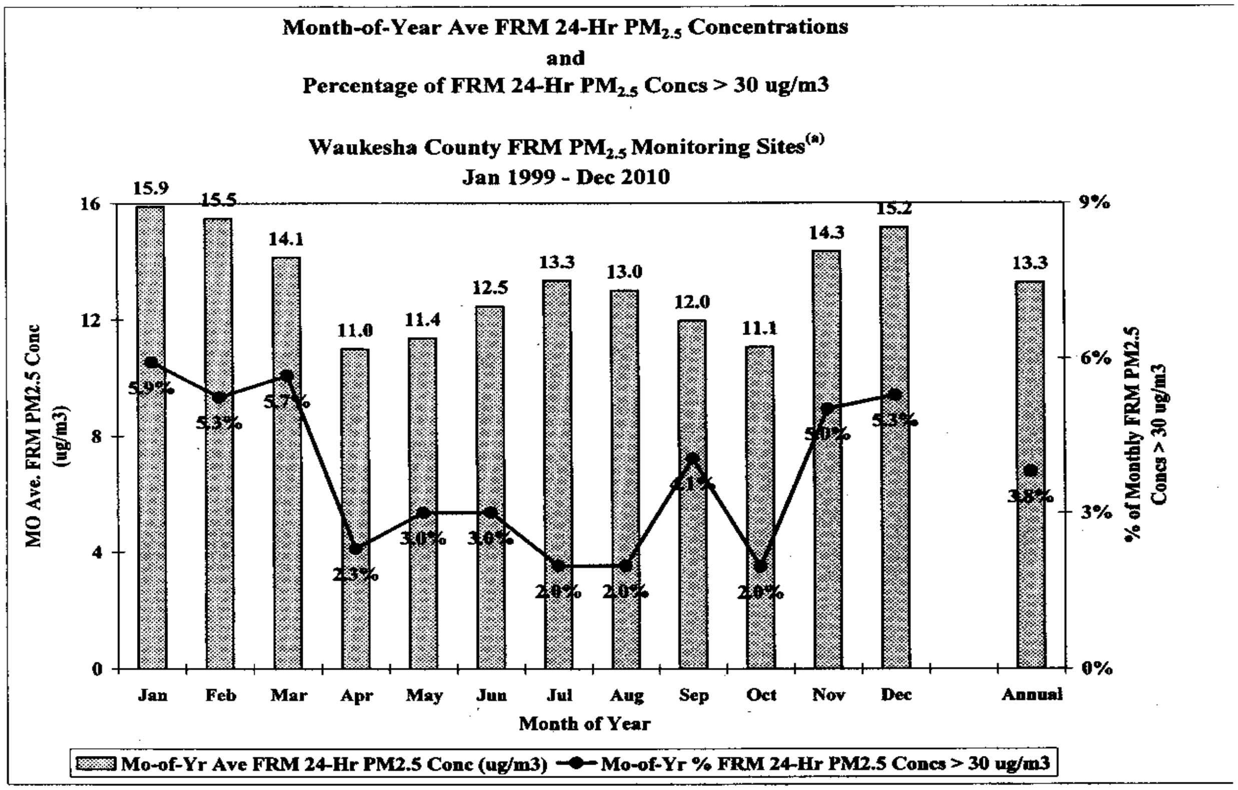

Month-of-Year Ave FRM 24-Hr $PM_{2.5}$ Concentrations and Percentage of FRM 24-Hr $PM_{2.5}$ Concs > 30 ug/m3

Milwaukee County FRM $PM_{2.5}$ Monitoring Sites[(a)]

Jan 1999 - Dec 2010

(a) The WDNR operated seven FRM $PM_{2.5}$ monitoring sites in Milwaukee County during Jan 1999 - Dec 2010 -- collecting a total of 9065 validated FRM 24-Hr $PM_{2.5}$ samples.

Figure 3


Month-of-Year Ave FRM 24-Hr $PM_{2.5}$ Concentrations and Percentage of FRM 24-Hr $PM_{2.5}$ Concs > 30 ug/m3

Waukesha County FRM $PM_{2.5}$ Monitoring Sites[(a)]

Jan 1999 - Dec 2010

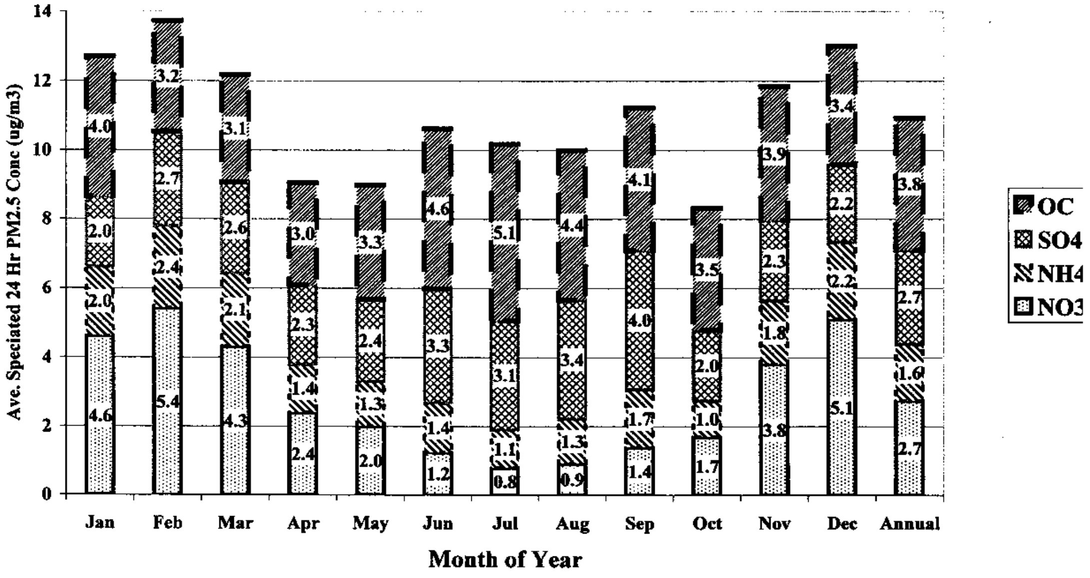
(a) The WDNR operated two FRM $PM_{2.5}$ monitoring sites in Waukesha County during Jan 1999 - Dec 2010 -- collecting a total of 2445 validated FRM 24-hr $PM_{2.5}$ samples.

Figure 4

Ave Month-Of-Yr Speciated 24 Hr $PM_{2.5}$ Concentrations

Nitrate (NO_3), Ammonium (NH_4), Sulfate (SO_4), Organic Carbon (OC)[(a)]

Milwaukee-DNR SERHQ (550790026)
989 Daily $PM_{2.5}$ Speciation Samples During Jan 01 - Dec 09

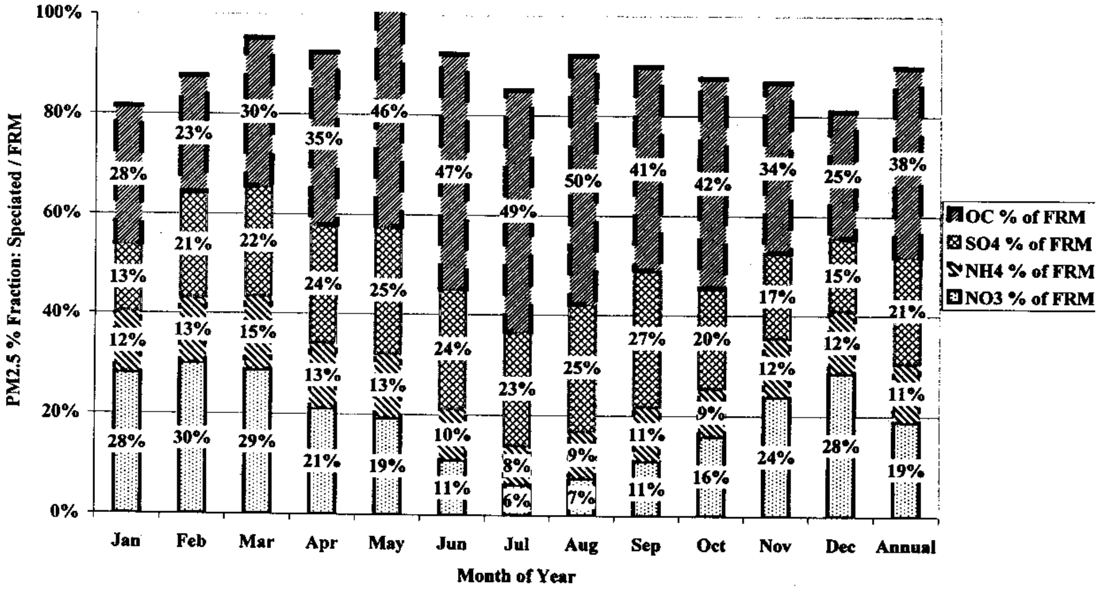


[(a)] All speciated PM 2.5 concentrations, including OC, are unadjusted from final validated values.

Figure 5

Ave Month-Of-Yr Speciated 24 Hr $PM_{2.5}$ Concentrations as Percentage of Same-Day FRM $PM_{2.5}$ Values

Nitrate (NO_3), Ammonium (NH_4), Sulfate (SO_4), Organic Carbon (OC)[(a)]
Milwaukee-DNR SERHQ (550790026)
989 Daily $PM_{2.5}$ Speciation / FRM Samples for Jan 01-Dec 09



[(a)] All speciated PM 2.5 concentrations, including OC, are unadjusted from the final validated values.

Overall, the 3rd largest overall $PM_{2.5}$ component is sulfate (SO_4). Figures 4 and 5 reveal that the distribution in sulfate's concentrations throughout a 12-month period is similar to OC in that its monthly average concentrations also peak during the summer months – only much more dramatically. Sulfate, like OC, is mostly formed as a secondary aerosol through oxidation (for sulfate through SO_2 – via either gas-phase photochemistry with the hydroxyl radical [OH^-]) in the presence of sunlight or aqueous-phase oxidation in presence of cloud droplets (Seinfeld and Pandis, 1998). The SO_4 production is substantially maximized during days of warm weather and high solar radiation (Husar, 1999).

Ammonium (NH_4) is the remaining major $PM_{2.5}$ constituent of any sizable mass. Ammonium is formed largely from the gaseous precursor ammonia (NH_3), which mostly comes from oxides of nitrogen (NOx) emissions being oxidized in the presence of the hydroxyl radical (OH^-) (Seinfeld and Pandis, 1998). Ammonium is actually part of the products when NH_3 reacts with either sulfuric acid (H_2SO_4) or nitric acid (HNO_3) to form either ammonium sulfate (NH_4SO_4) or ammonium nitrate (NH_4NO_3), respectively (Damberg, 2007). Ammonium sulfate formation is preferential under most conditions, though ammonium nitrate is favored by low temperature and high humidity.

Similar to NO_3, Figures 4 and 5 show that ambient NH_4 levels at Milwaukee SER exhibit a seasonal trend of the highest monthly values occurring during the colder months (November – March) and the lowest concentrations during the warmer period (April – October). However, the spread in the range of monthly NH_4 is much less than for NO_3.

6.3 Speciated $PM_{2.5}$ distributions vs. increasing ambient temperature

Figure 6 shows how NO_3, NH_4, SO_4 and OC $PM_{2.5}$ at Milwaukee DNR SERHQ varied with increasing daily average ambient temperature, as measured at Milwaukee Mitchell Airport's National Weather Service [NWS] office [MKE] during 2001-2009.

As expected, the average NO_3 profile exhibits a generally inverse relationship – substantially decreasing concentrations with increasing temperatures (i.e., a minimum of 0.6 ug/m3 at temperatures > 85 F). As noted by Stanier, et.al (2009) nitrate is semi-volatile secondary aerosol (formed from a highly complex set of processes involving nitric acid [HNO_3] and ammonium) that can evaporate in warmer environments.

However, it is noteworthy that the peak daily average NO_3 concentrations (mean: 5.6 ug/m3) were not during the coldest temperatures but in the 30-35 F range. This suggests that other factors (e.g., high relative humidity) may have played an important secondary role in nitrate formation. Husar (1999) makes reference to high humidity assisting NO_3 formation.

Ammonium (NH_4) levels were a bit more uniform with respect to increasing daily average temperature (i.e., ranging from 1.3 to 2.5 ug/m3). There also was no real NH_4 trend with respect to temperature. The peak NH_4 (2.5 ug/m3 for 80-85 F) was followed by a relatively low 1.5 ug/m3 for temperatures > 85 F.

Also as expected - the average SO_4 profile exhibits a generally direct correlation with ambient temperature. Sulfates are largely a product of both photochemical and in-cloud oxidation involving sulfur dioxide (SO_2) (US EPA, 2003). These processes are optimized during warmer weather periods.

There is a significant rise in SO_4 concentrations with increasing temperatures (i.e., a minimum of 1.3 ug/m3 at temperatures < 15 F, peaking at 6.6 ug/m3 for the 80-85 F bin). The distribution in OC vs. increasing temperatures generally followed a similar, but less dramatic trend to that for SO_4. Namely, OC levels averaged approximately 3.4 ug/mg for temperatures under 55 F and above 5.1 ug/m3 when daily average temperatures were > 75 F.

Figure 6

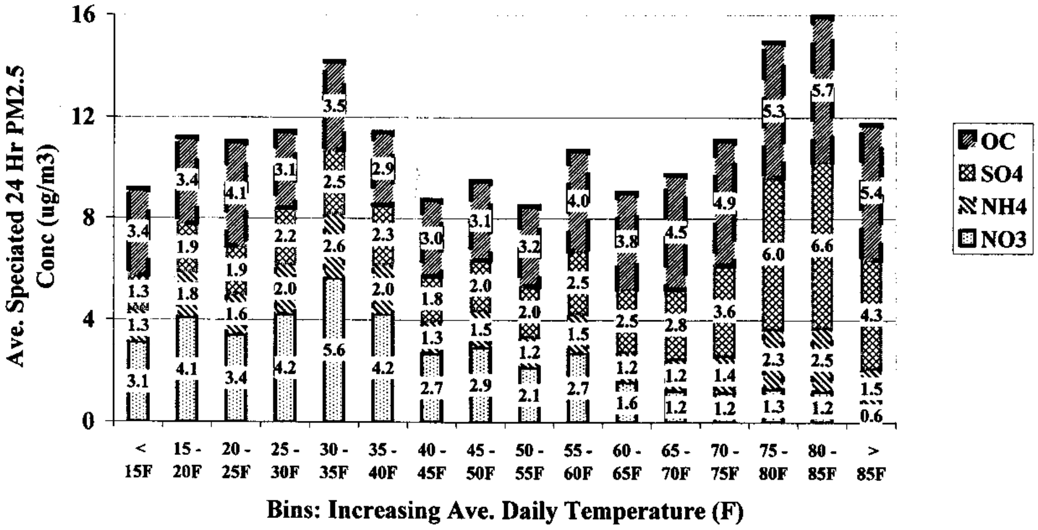
Ave Speciated 24 Hr $PM_{2.5}$ Concentrations

vs. Increasing Ave Daily Temperature[a]

Nitrate (NO_3), Ammonium (NH_4), Sulfate (SO_4), Organic Carbon (OC)[b]

Milwaukee-DNR SERHQ (550790026)

988 Daily $PM_{2.5}$ Speciation Samples During Jan 01 - Dec 09



[a] Meteorological data are from the Nat'l Weather Service (NWS) at Milwaukee Mitchell Airport.

[b] All speciated $PM_{2.5}$ values, including OC, are unadjusted from final validated concs.

Figure 7

Ave Speciated 24 Hr $PM_{2.5}$ Concs

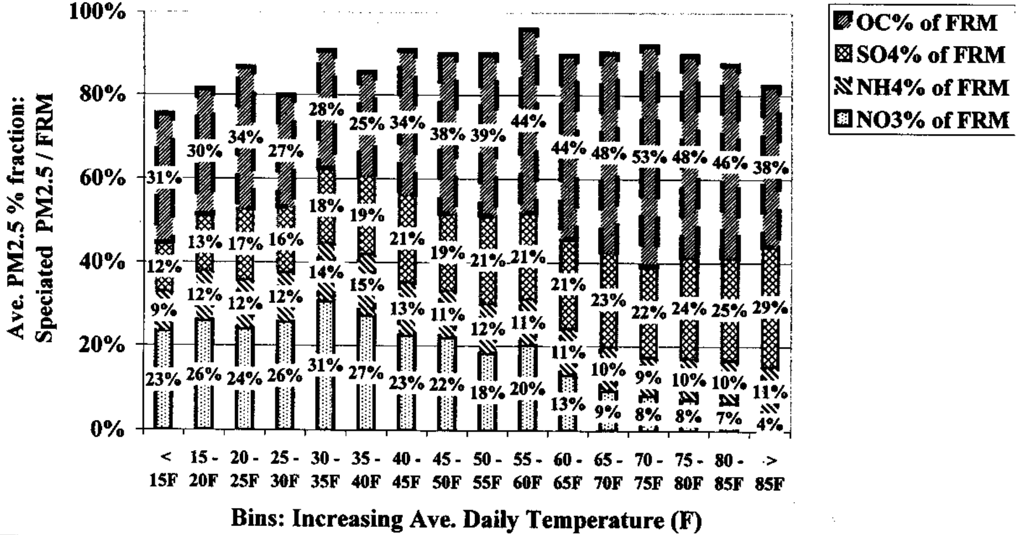
as Percentage of Same-Day FRM $PM_{2.5}$ Concs

vs. Increasing Ave Daily Temperature[a]

Nitrate (NO_3), Ammonium (NH_4), Sulfate (SO_4), Organic Carbon (OC)[b]

Milw-DNR SERHQ

988 Daily $PM_{2.5}$ Speciation Samples During Jan 01 - Dec 09



[a] Meteorological data are from the Nat'l Weather Service (NWS) at Milwaukee Mitchell Airport.

[b] All speciated $PM_{2.5}$ data, including OC, are unadjusted from final validated concs.

Figure 7 is similar to Figure 6 except that Milwaukee-SER $PM_{2.5}$ species' percentage fraction profiles of FRM $PM_{2.5}$ are normalized against bins of increasing MKE daily average temperatures. This graph generally validates most of the Figures 6 features. Namely, the profiles' percentage fractions for NO_3 and SO_4 $PM_{2.5}$ relative to increasing temperature largely follow the same for the speciated $PM_{2.5}$ concentrations (Figure 6). The NO_3 fraction is substantially much higher during the colder months (< 40 F: 27% average) than during the warm months (> 65 F: 8% average). Conversely, SO_4 exhibited lower average percentage fractions for temperatures < 30 F (16%), much higher fractions (28%) for temperatures > 70 F.

Across the temperature spectrum the distribution percentage fractions for NH_4 (9 - 15%) and OC (31 – 5%) are both relatively less variable, more uniform than for either NO_3 or SO_4. This indicates that NH_4 and OC contributions to overall $PM_{2.5}$ mass are less influenced by surface temperature fluctuations than are SO_4 and NO_3.

6.4 Speciated $PM_{2.5}$ distributions vs. increasing daily temperature difference (observed minus climate average).

There is a more noticeable pattern when comparing Milwaukee SER's speciated $PM_{2.5}$ to the differences between MKE's daily average temperature and its daily climatological average (30 years [1971-2000]) (WSCO, 2009) (Figure 8). Namely, all four targeted $PM_{2.5}$ species (NO_3, SO_4, NH_4 and OC) had relatively lower daily average concentrations on days well below climate normal temperatures (< -16 F departure), steadily and sizably increasing to relatively very warm days (> + 20 F departure).

Steadily increasing $PM_{2.5}$ associated with days witnessing climatologically warm temperatures was also noted for the Wisconsin's highest FRM $PM_{2.5}$ days (WDNR, 2009). This earlier $PM_{2.5}$ study indicated that a positive correlation between high $PM_{2.5}$ and climatologically warm days appears to be part of a more complex meteorological scenario which also includes relatively high atmospheric moisture (i.e., relative humidity) and winds with a noticeable southerly wind component.

Figure 9 is similar to Figure 8 except that Milwaukee-SER $PM_{2.5}$ species' percentage fraction profiles of FRM $PM_{2.5}$ are normalized against bins of increasing differences between MKE's daily average temperature and its daily climatological average. The individual percentage fraction profiles for SO_4, NO_3, OC and NH_4 are each largely similar, save for their behavior during the largest negative temperature differences.

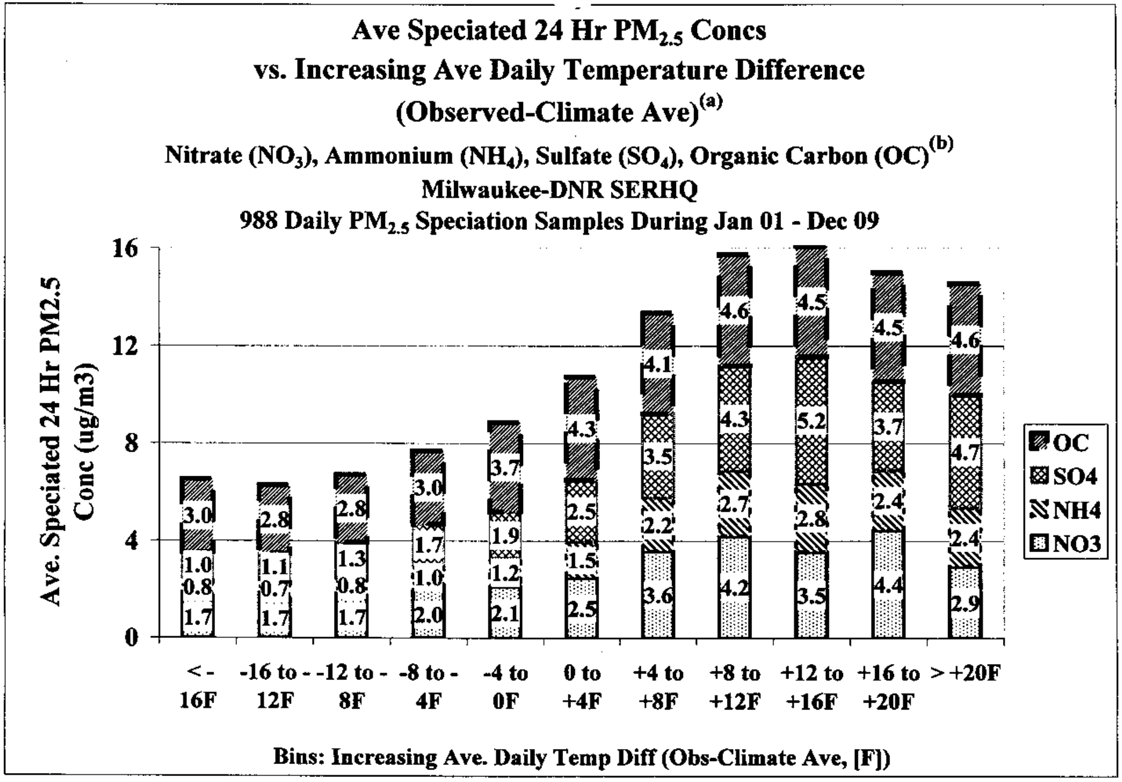
6.5 Speciated $PM_{2.5}$ distributions vs. increasing relative humidity

There is a generally continual increase in the average concentrations of $PM_{2.5}$ species NO_3, SO_4 and NH_4 at Milwaukee-SER as a function of increasing daily average relative humidity (RH) at MKE (Figure 10). Higher $PM_{2.5}$ associated with days that have elevated RH is similarly evident for Wisconsin's 50 highest $PM_{2.5}$ days (WDNR 2009). Organic carbon $PM_{2.5}$ is different from the other species in that there is little variation (min: 3.2 ug/m3, max: 4.1 ug/m3) across the range of RH bins.

Seinfeld and Pandis (1998) noted that the presence of water vapor makes it more efficient to photochemically oxidize gaseous SO_2 into SO_4. Pathak, et.al. (2009) stated that there can be a significant production of secondary aerosols, especially during the summer due, in part, to a "large water vapor content."

Figure 11 is similar to Figure 10 except that Milwaukee-SER $PM_{2.5}$ species' percentage fraction profiles of FRM $PM_{2.5}$ are normalized against bins of increasing MKE daily average relative humidity. The profiles' percentage fractions for NO_3 and NH_4 $PM_{2.5}$ generally get larger with respect to higher relative humidity. This follows the same trend for the speciated $PM_{2.5}$ concentrations (Figure 10).

Figure 8

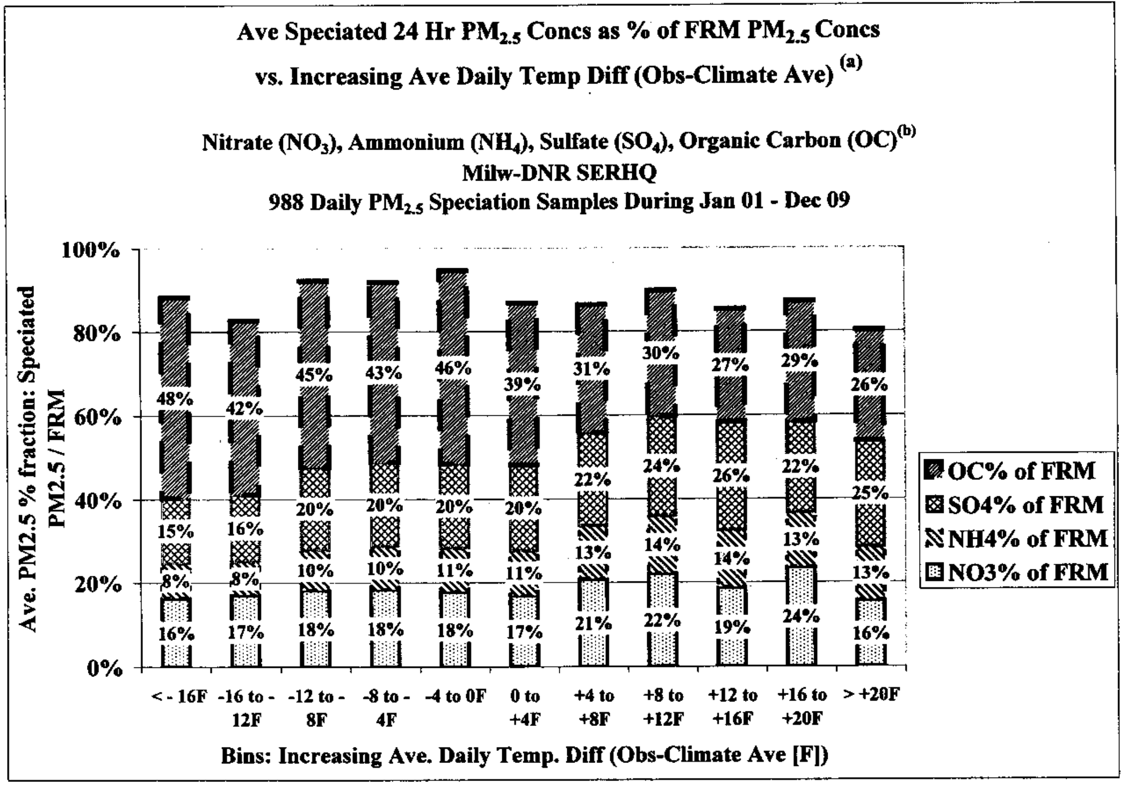


Ave Speciated 24 Hr $PM_{2.5}$ Concs
vs. Increasing Ave Daily Temperature Difference
(Observed-Climate Ave)[(a)]
Nitrate (NO_3), Ammonium (NH_4), Sulfate (SO_4), Organic Carbon (OC)[(b)]
Milwaukee-DNR SERHQ
988 Daily $PM_{2.5}$ Speciation Samples During Jan 01 - Dec 09

(a) Meteorological data from the Nat'l Weather Service (NWS) at Milwaukee Mitchell Airport.

(b) All speciated PM $_{2.5}$ data, including OC, are unadjusted from final validated concs.

Figure 9



Ave Speciated 24 Hr $PM_{2.5}$ Concs as % of FRM $PM_{2.5}$ Concs
vs. Increasing Ave Daily Temp Diff (Obs-Climate Ave) [(a)]

Nitrate (NO_3), Ammonium (NH_4), Sulfate (SO_4), Organic Carbon (OC)[(b)]
Milw-DNR SERHQ
988 Daily $PM_{2.5}$ Speciation Samples During Jan 01 - Dec 09

(a) Meteorological data from the Nat'l Weather Service (NWS) at Milwaukee Mitchell Airport.

(b) All speciated PM $_{2.5}$ data, including OC, are unadjusted from final validated concs.

Organic carbon‘s relative fraction contribution to FRM $PM_{2.5}$ is inverse to that for NO_3 and NH_4. The OC percentage fraction is greatest (58%) for the lowest relative humidity bin (< 40 %) and smallest (25%) for the highest relative humidity (> 90%). Varadarajan (2007) did a study of $PM_{2.5}$ in Ohio, which also revealed that OC had a negative relation to increasing relative humidity.

Sulfate’s percentage fraction of FRM $PM_{2.5}$ (18-26%) is sizable but fairly uniform across the relative humidity spectrum. Robinson, et.al. (2002) evaluated the hygroscopic growth of fresh sulfur-based particles by comparing size distributions measured at different levels of relative humidity during nucleation events in the Pittsburgh (PA) Air Quality Study. They found negligible to modest hygroscopic growth across relative humidity levels ranging from 10 to 55%.

6.6 Analysis of FRM and organic carbon $PM_{2.5}$ and OC’s gaseous precursors

As noted in previous sections, organic carbon is typically the single largest $PM_{2.5}$ constituent (by mass) collected on speciation filters in Wisconsin. Furthermore, the large majority of OC is formed in the atmosphere as secondary organic aerosols (SOA) (Grosjean and Seinfeld, 1989). These SOAs are produced from complicated atmospheric chemistry processes involving a synthesis of sunlight, heat and moisture which transform some of the heavier VOCs (called aromatics) to yield condensable particulates (Grosjean and Seinfeld, 1989).

Section 5.3 provides an overview of the measurements of ambient VOCs (also referred to as total nonmethane organic carbon [TNMOC]), focusing on aromatic species collected at the Milwaukee DNR SERHQ monitoring site.

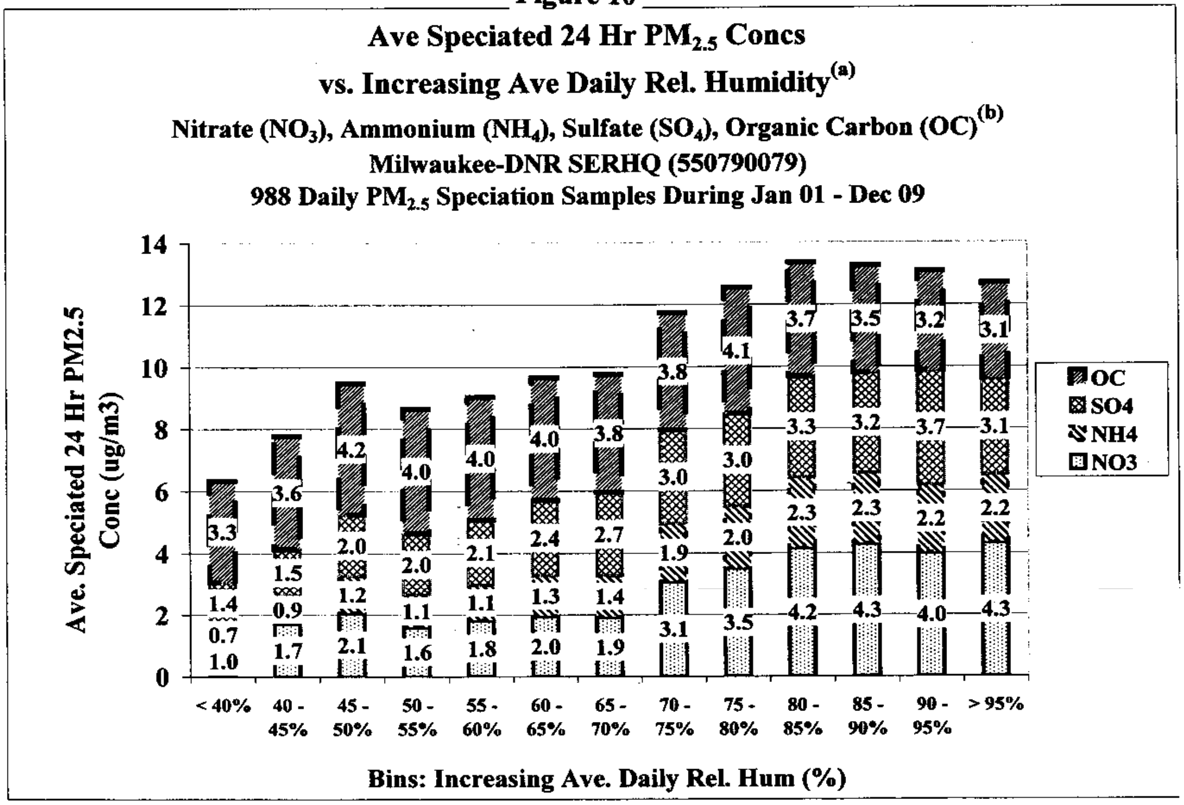
The following discussion and associated graphs describe some long term (2001-2009) relationships between concentrations of ambient VOCs (especially aromatics) and OC at the Milwaukee DNR SERHQ monitoring site.

Figure 12 displays SER’s collective month-of-year median daily concentrations of TNMOCs, aromatics and OC during 2001 - 2009. Consistent with the OC portion of Figure 4 – OC levels peak during the summer months. (July: 5.0 ug/m3). The profile of aromatic VOCs follows an approximately similar pattern. Namely, peak monthly-averages are highest during the summer (but not directly in July). The TNMOCs also generally crest during the summer. However, TNMOCs also exhibits a strong secondary maximum during the winter months.

Figure 13 shows how average OC and FRM $PM_{2.5}$ track against increasing average 24-hour TNMOC concentrations during 2001-2009. From this graph, there is a respectable correlation between increasing TNMOCs and increasing both FRM and OC $PM_{2.5}$ through the TNMOC bin 105-120 ppbC. This correlation is temporarily reversed for TNMOC levels between 120–150 ppbC, only to resume for the next highest TNMOC bin (150-165 ppbC).

Figure 14 is similar to Figure 13, the only difference being that bins of average aromatic concentrations replace TNMOCs as the independent (x-axis) metric. The profiles of average OC and FRM $PM_{2.5}$ tracking with respect to increasing average 24-hour aromatic levels during 2001-2009 is quite similar to tracking of TNMOCs (Figure 13). There appears to be an adequate correlation between increasing aromatics and increasing both FRM and OC $PM_{2.5}$ through the lower half of the aromatics distribution (18-21 ppbC bin). Aromatic concentrations above 21 ppbC yield generally flat profiles for both FRM and OC.

Figure 10



Ave Speciated 24 Hr $PM_{2.5}$ Concs

vs. Increasing Ave Daily Rel. Humidity[(a)]

Nitrate (NO_3), Ammonium (NH_4), Sulfate (SO_4), Organic Carbon (OC)[(b)]

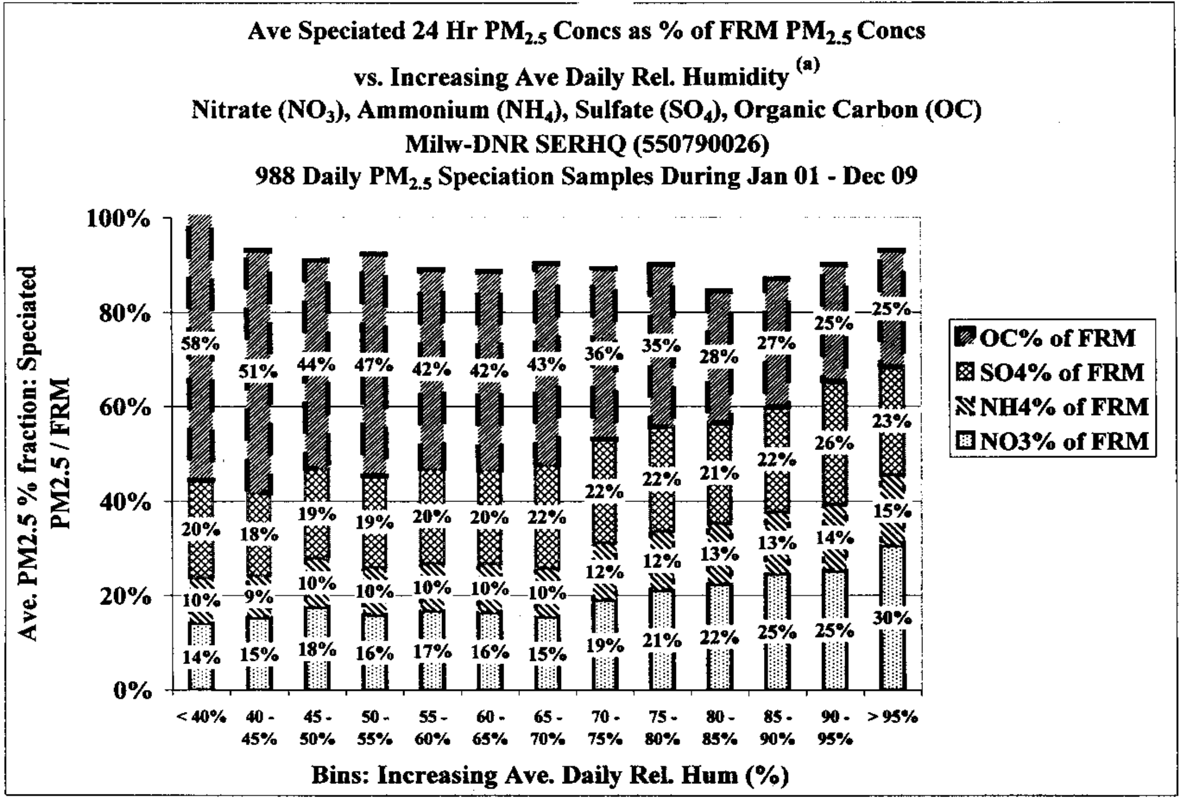
Milwaukee-DNR SERHQ (550790079)

988 Daily $PM_{2.5}$ Speciation Samples During Jan 01 - Dec 09

[(a)] Meteorological data are from the Nat'l Weather Service (NWS) at Milwaukee Mitchell Airport.

[(b)] Speciated PM2.5 data, including OC, are unadjusted from final validated values.

Figure 11



Ave Speciated 24 Hr $PM_{2.5}$ Concs as % of FRM $PM_{2.5}$ Concs

vs. Increasing Ave Daily Rel. Humidity [(a)]

Nitrate (NO_3), Ammonium (NH_4), Sulfate (SO_4), Organic Carbon (OC)

Milw-DNR SERHQ (550790026)

988 Daily $PM_{2.5}$ Speciation Samples During Jan 01 - Dec 09

[(a)] Meteorological data are from the Nat'l Weather Service (NWS) at Milwaukee Mitchell Airport.

[(b)] The speciated PM $_{2.5}$ data, including OC, are unadjusted from final validated values.

Figure 15 tracks SER's OC $PM_{2.5}$ levels as well as its 24-hour-averaged TNMOCs and aromatic concentrations with respect to MKE's increasing daily average ambient temperature during 2001-2009.

In general, all three pollutants exhibit little coherency for temperatures below 40 F. However, starting from the temperature bin of 40-45 degrees Fahrenheit (F), the TNMOCs and aromatic VOCs are generally increasing with rising temperatures. The OC values follow a similar pattern of growing with higher temperatures, but are commencing for the temperature bin 35-40 F.

Explaining factors that contribute to increasing OC with respect to warmer temperatures is difficult because of the highly nonlinear chemistry of secondary organic aerosol (SOA) formation, which dominates OC mass. There is also the smaller fraction of primary OC that is emitted directly. As pointed out by Cabada, et.al (2004), much of the SOA mass can result from long-range transport, not local chemistry. However, ambient temperature has been shown to sizably influence SOA production rates, based upon reaction chamber studies (Warren, et.al., 2009).

6.7 Analysis of nitrate and FRM $PM_{2.5}$ and NOx

Figure 16 displays SER's collective month-of-year average concentrations of 1) median of the daily average 1-hr NOx and 2) same-day daily average NO_3 $PM_{2.5}$ during 2001–2009. The NOx levels display a pattern of being considerably highest during the coldest months (November-February: 24 ppb average), which is twice the levels during the summer months. Since the NOx emissions do not demonstrate a seasonal bias – and boundary layer heights do not appear to be seasonally dependent, -photochemistry must play a dominant role in determining seasonal NOx levels (Hayden, et.al., 2003).

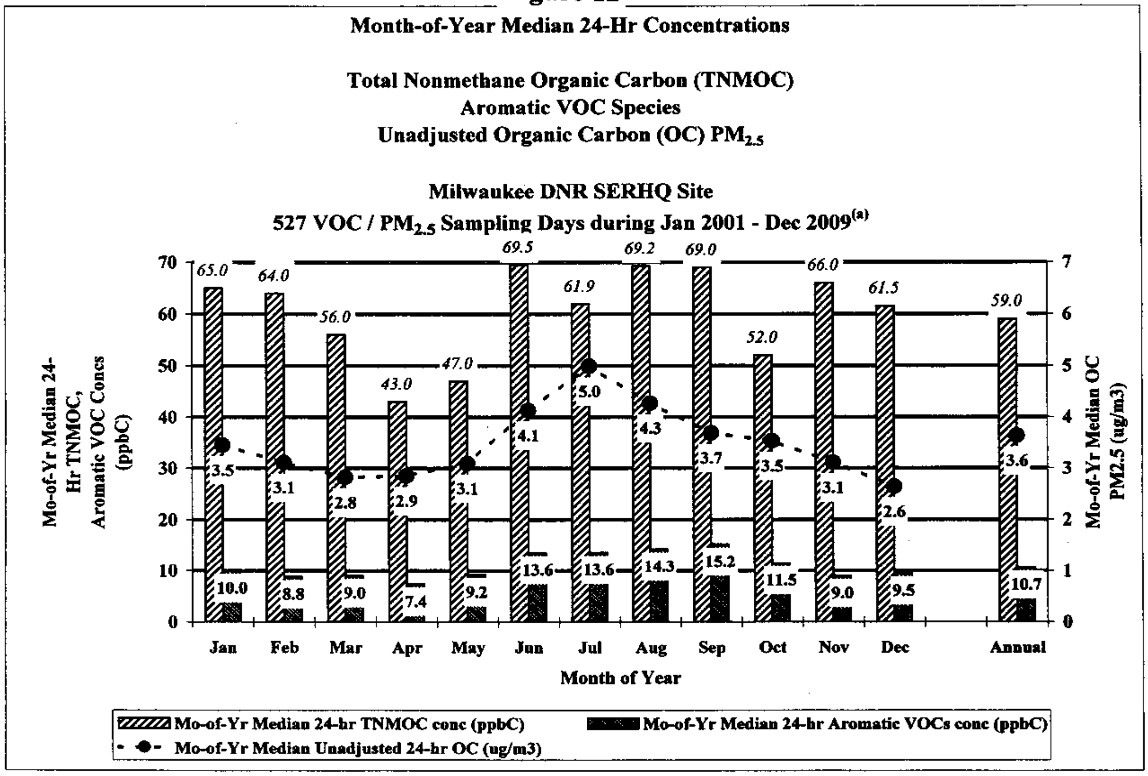
The profile of nitrate concentrations are well correlated with NOx levels. Average NO_3 is substantially biased higher towards the colder months. (5 ug/m3 average during December-February). This is consistent with the NO_3 portion of Figure 4. The seed of most nitrate formation is in gaseous precursor NOx. Gas-phase species nitric acid (HNO_3) is derived from the oxidation of NOx, which is also favored during the colder weather. NO_3 is then produced from equilibrium reactions between HNO_3, and ammonia (NH_3) (Blanchard and Tanenbaum, 2003). The equilibrium favors the condensed phase at lower temperatures and higher humidities.

Additionally, nitrate is semi-volatile and not stable in higher temperatures (Husar, 1999). Consequently, all of the above-described characteristics lead to NO_3 concentrations being generally much higher during colder winter months, significantly lower in summer.

Figure 17 highlights how average NO_3 and its average percentage fraction of overall FRM $PM_{2.5}$ levels track with respect to increasing average daily median 1-hour NOx at Milwaukee-SER during June 2001 – December 2009. This graph reflects the similar NO_3 | NOx characteristics to those displayed in Figure 16. For increasing NOx concentrations (at least up to 35 ppb), there is a strong positive correlation of substantial, steady increases in both average NO_3 levels (min. 0.5 ppb to max. 7.0 ppb) and NO_3's percentage fraction of the overall FRM $PM_{2.5}$ values (min. 8.2% to max. 29.2%). For NOx concentrations above 40 ppb, both the NO_3 concentrations and NO_3/FRM percentage fractions plateau at very high levels.

Figure 18 shows how SER's average daily median 1-hour NOx and average daily NO_3 trend with respect to increasing MKE's average daily temperature during June 2001 – December 2009. As expected from both Figures 6 and 16, these pollutants appear to have generally negative correlations with increasing temperature, at least through the 60-65 F temperature bin. Above 65 F the NO_3 and NOx levels have only minor changes.

Figure 12



[a] 466 days of 24-Hr VOC-avg'd data from lab analysis of canister-based air, 61 days of VOC obs from hrly-avg'd auto GC VOCs. Organic carbon (OC) data from speciation analysis of PM $_{2.5}$ mass.

Figure 13

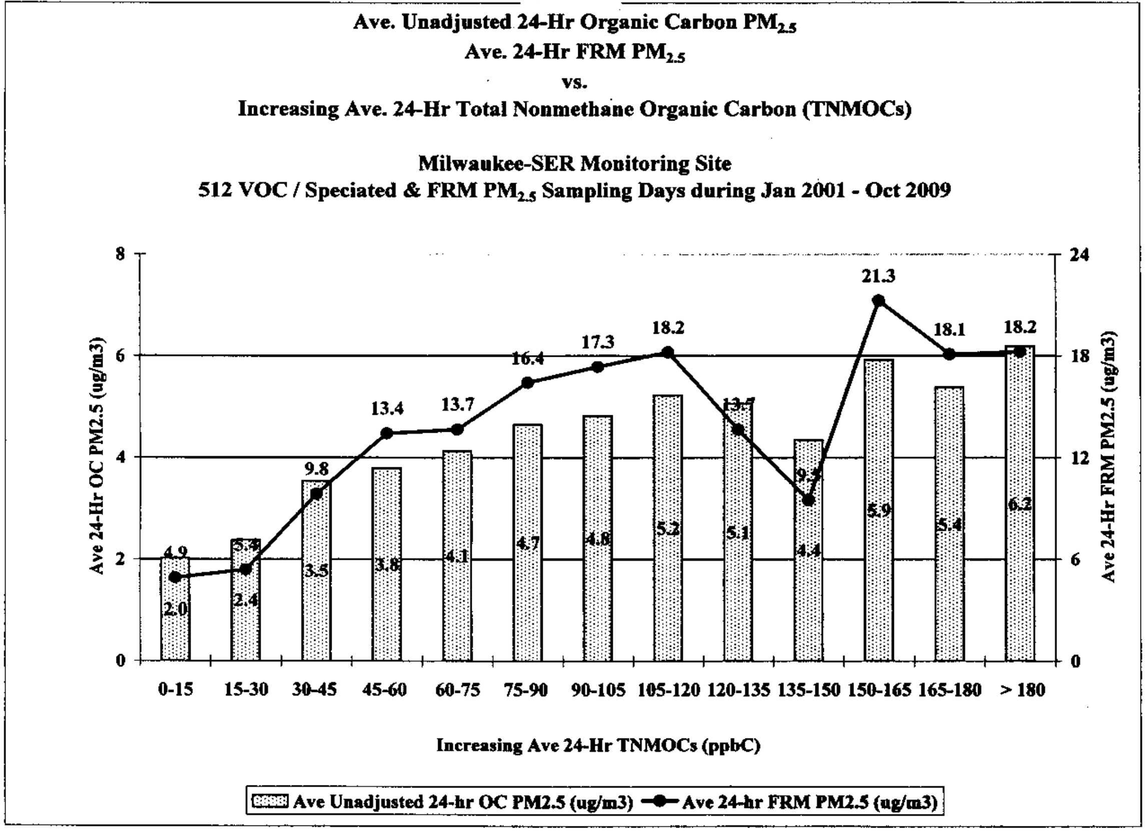
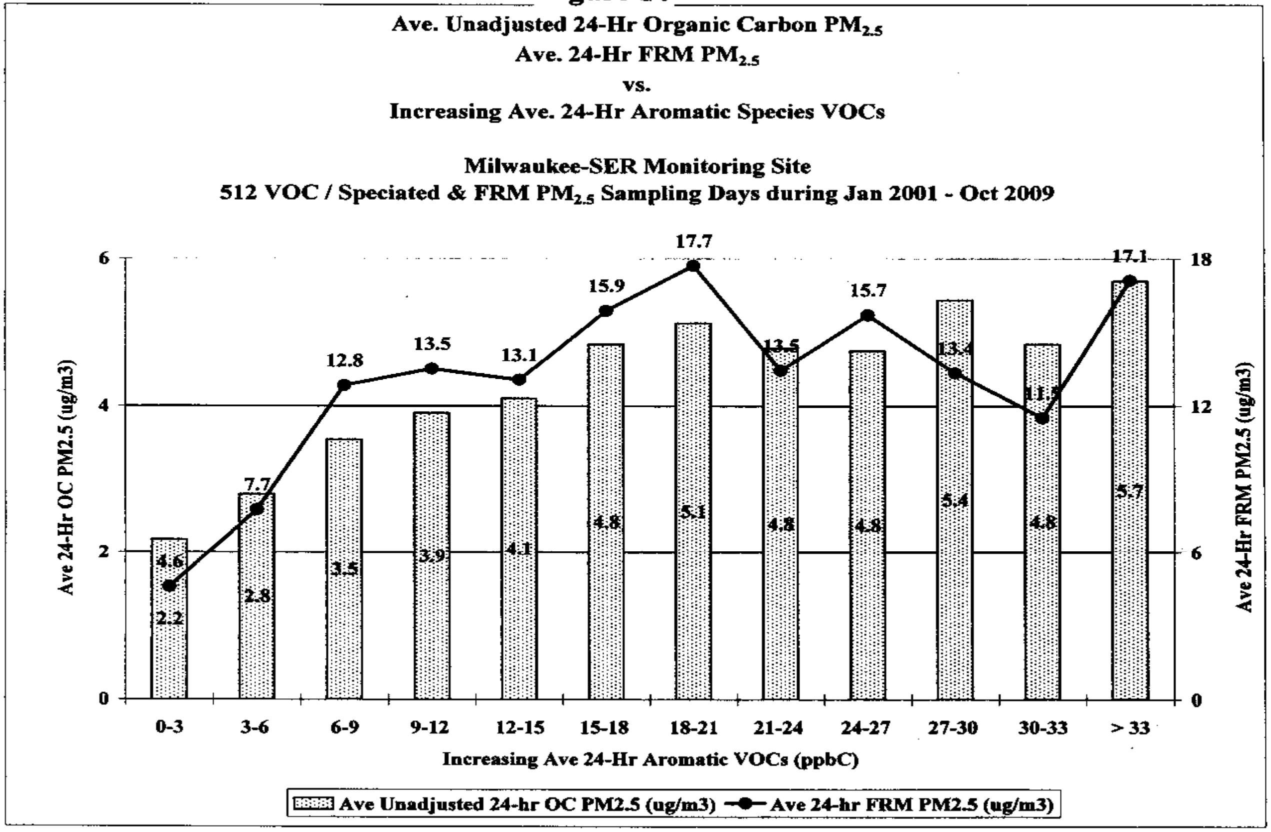


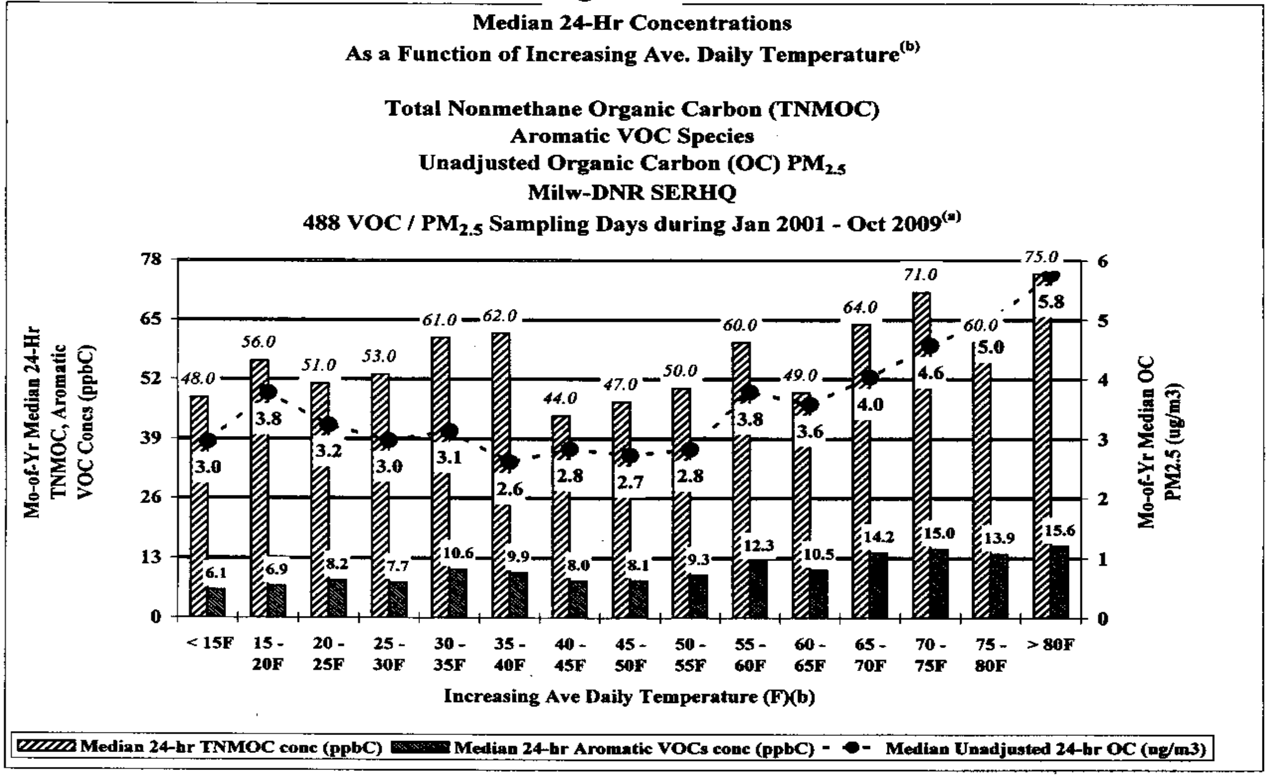
Figure 14



Ave. Unadjusted 24-Hr Organic Carbon $PM_{2.5}$
Ave. 24-Hr FRM $PM_{2.5}$
vs.
Increasing Ave. 24-Hr Aromatic Species VOCs

Milwaukee-SER Monitoring Site
512 VOC / Speciated & FRM $PM_{2.5}$ Sampling Days during Jan 2001 - Oct 2009

Figure 15



Median 24-Hr Concentrations
As a Function of Increasing Ave. Daily Temperature[(b)]

Total Nonmethane Organic Carbon (TNMOC)
Aromatic VOC Species
Unadjusted Organic Carbon (OC) $PM_{2.5}$
Milw-DNR SERHQ
488 VOC / $PM_{2.5}$ Sampling Days during Jan 2001 - Oct 2009[(a)]

(a) 428 VOC samples: lab-analyzed canister air. 60 VOC samples: hrly-avg'd autoGC VOCs. OC data: speciation of PM2.5 mass.
(b) Met. data: Nat'l Weather Service site at Milw Mitchell Airport, 10 mi south of SER site.

Figure 16

Month-of-Year Ave Daily Concentrations

Daily Median 1-Hr Oxides of Nitrogen (NOx)
24-Hr Nitrate (NO_3) $PM_{2.5}$

Milwaukee-SER Monitoring Site
816 NOx / Speciated $PM_{2.5}$ Sampling Days During Jun 2001 - Dec 2009

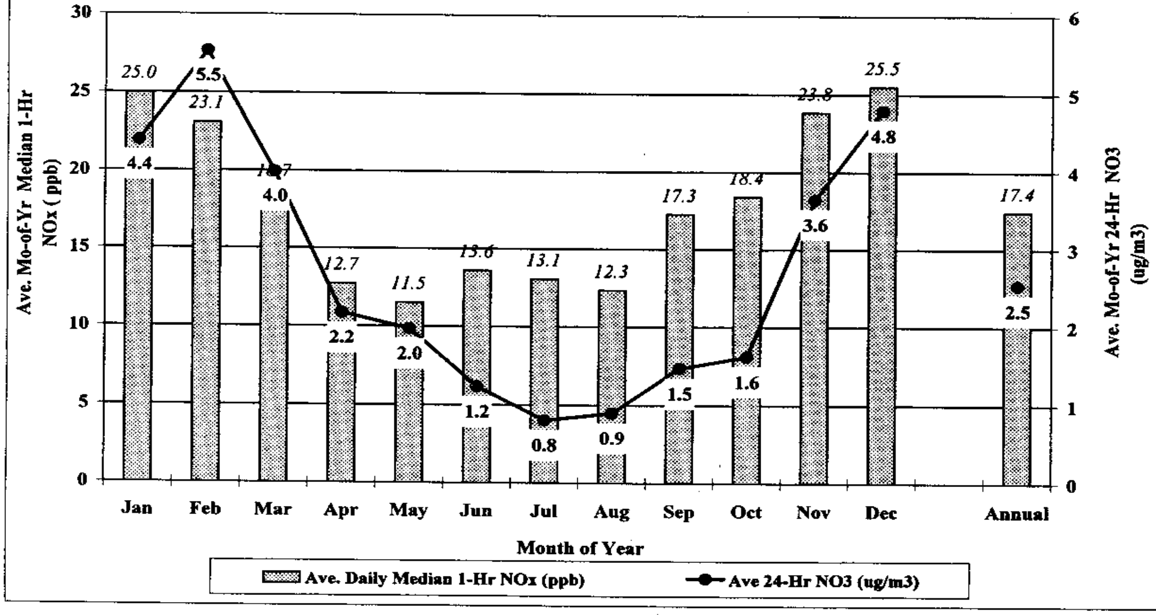


Figure 17

Ave. 24-Hr Nitrate (NO_3) $PM_{2.5}$
Ave. 24-Hr $PM_{2.5}$ Percentage Fraction: NO_3 / Fed Reference Method (FRM)
vs.
Increasing Ave. Daily Median 1-Hr NOx

Milwaukee-SER Monitoring Site
816 NOx / Speciated & FRM $PM_{2.5}$ Sampling Days: Jun 2001-Dec 2009

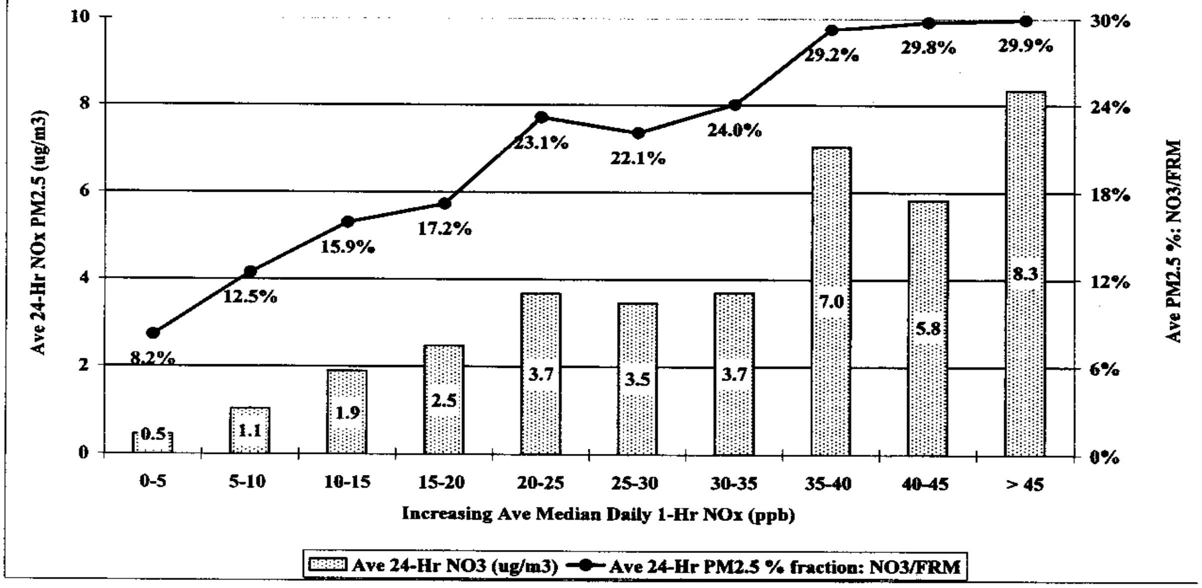
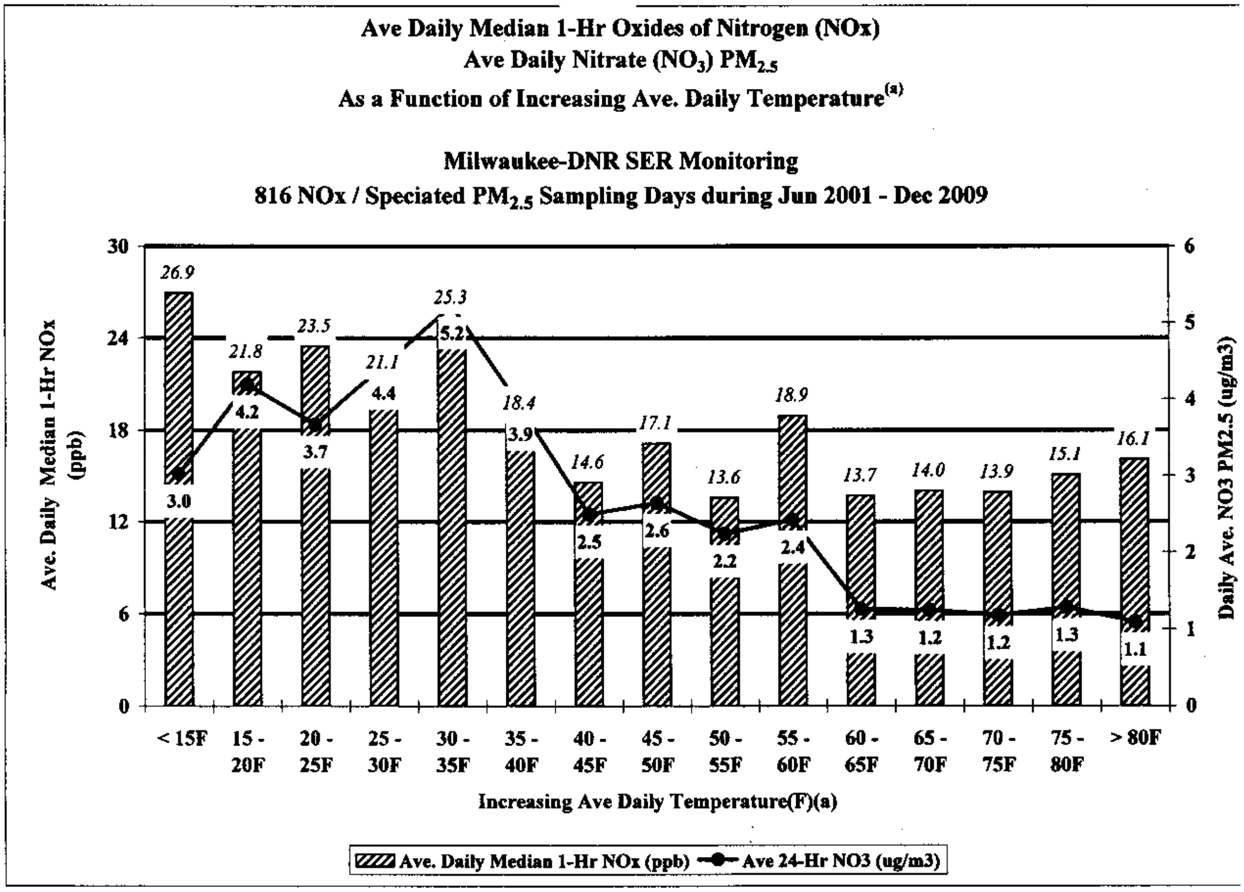


Figure 18



[a] Meteorological data are from the National Weather Service (NWS) station at Milwaukee Mitchell Airport, approx 10 miles south of the Milw-SER monitoring site.

7 Summary

As stated in Section 1, the purpose of this study is to identify long-term characteristics, distributions and profiles in measured $PM_{2.5}$ and some of $PM_{2.5}$ gaseous precursors (TNMOCs, aromatic VOCs, NOx) in southeastern Wisconsin. This assessment, which is required under sections 40 CFR 51.1002(2) and (3) of the federal Clean Air Act, is needed in order to assess if NOx and / or VOC emission inventories need to be constructed as part of the WDNR's request for redesignating to attainment for the $PM_{2.5}$ nonattainment counties in southeastern Wisconsin (Figure 1).

Section 6 details the findings from analyzing these long-term relationships of $PM_{2.5}$ and $PM_{2.5}$ precursors in southeastern Wisconsin. Of the many points identified in this study, the following are probably most pertinent to the purpose of the overall study:

- Figure 2: The collective average month-of-year $PM_{2.5}$ concentration at FRM sites in Milwaukee County for November – March 1999-2011 is 15.0 ug/m3, which is 26% higher than for the remaining seven months (11.8 ug/m3). For these same sites and time period - the collective average percentage rate of high $PM_{2.5}$ days (site-days > 30ug/m3) for November – March (6.68%) is more than twice the rate of high $PM_{2.5}$ site-days during the other seven months (2.97%).

- Figures 4 and 5: Organic carbon (OC) is generally the single largest speciated $PM_{2.5}$ component, with a slight bias towards higher values during the warmer months of June – August and comprises almost half the total $PM_{2.5}$ mass during May - August.

- Figure 12: Milwaukee SER's OC levels peak during the summer months. (July: 5.0 ug/m3). The profile of both TNMOCs and aromatic VOCs also show peak monthly-averages during the summer. However, TNMOCs also exhibits a strong secondary maximum during the winter months.

- Figure 13 and 14: There is a respectable correlation between both increasing TNMOCs (Figure 13) as well as aromatic VOCs (Figure 14) and rising levels of both FRM and OC $PM_{2.5}$.

- Figure 16: SER's NOx levels are considerably highest during the coldest months (November - February: 24 ppb average), which is twice the levels during the summer months.

- Figures 15 and 16: Nitrate concentrations are well correlated with NOx levels. The average NO_3 is also substantially biased higher towards the colder months (5 ug/m3 average during December-February).

- Figure 17: With increasing NOx concentrations, there is a strong positive correlation of substantial, steady increases in both average NO_3 levels (min. 0.5 ppb to max. 7.0 ppb) and NO_3's percentage fraction of the overall FRM $PM_{2.5}$ values (min. 8.2% to max. 29.2%).

8 Proposed Recommendations

Exceedances of the 24-hour $PM_{2.5}$ NAAQS can occur during any time of the year in Wisconsin. However, Figures 2 and 3 demonstrate that $PM_{2.5}$ has a modest tendency to be highest, along with the best potential to exceed the standard, during November-March in Milwaukee and Waukesha counties. From these analyses, it is evident that both organic carbon (OC) and nitrate (NO_3) comprise a substantial fraction of the $PM_{2.5}$ mass measured in southeastern Wisconsin's $PM_{2.5}$ nonattainment area (Figure 1).

These characteristics suggest that the focus of $PM_{2.5}$ SIP work, including emissions inventory development might be most effective if directed towards $PM_{2.5}$-related activity levels and throughput during December-February. This three month period is generally defined as the "meteorological winter" in the upper Midwest of the United States.

Based upon these assessments - at this time it could be practical to consider the following options on developing emission inventories (EI) for the WDNR's request to redesignate to attainment the $PM_{2.5}$ nonattainment counties of Milwaukee, Waukesha and Racine as part of the state implementation plan (SIP) for $PM_{2.5}$:

- Construct additional emission inventories for the $PM_{2.5}$ precursors VOCs and NOx, which are shown in this study to yield substantial contributions to the formation of secondary $PM_{2.5}$ aerosols (organic carbon [OC] and nitrates [NO_3]) in southeastern Wisconsin. This demonstration was completed per the requirements contained in 40 CFR 51.1004(c) ("Pollutants contributing to fine particle concentrations")

- Construct emission inventories for all major $PM_{2.5}$-related pollutants (i.e., direct $PM_{2.5}$, SO_2, NOx and VOCs). These inventories should target activity levels and throughputs representative of that portion of the calendar when $PM_{2.5}$ levels are seasonally highest (i.e., an average winter day).

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