Procedures for Estimating Future PM$_{2.5}$ Values for the CAIR Final Rule byApplication of the (Revised) Speciated Modeled Attainment Test (SMAT)

I. Introduction

EPA has issued draft modeling guidance *(EPA, 2001)* that describes a procedure for combining monitoring data with outputs from simulation models to estimate future concentrations of PM$_{2.5}$ mass. The guidance recommends that model predictions be used in a relative sense to estimate changes expected to occur in each major PM$_{2.5}$ species. The procedure is referred to as the Speciated Modeled Attainment Test (SMAT). A preliminary version of SMAT was applied in the Clean Air Interstate Rule (CAIR) proposal modeling *(EPA, 2004)* to estimate future PM$_{2.5}$ nonattainment in the Eastern United States. A revised version of the SMAT technique has been applied in support of the CAIR final rule. Based on comments received from the CAIR proposal, several improvements have been implemented. The revised SMAT procedures are described below.

A. Default SMAT Procedures

The draft modeling guidance includes a sequence of key steps that are recommended for processing PM$_{2.5}$ ambient and modeling data. The following is a brief summary of those steps:

(1) Derive current quarterly mean concentrations for each of the major components of PM$_{2.5}$. This is done by multiplying the monitored quarterly mean concentration of Federal Reference Method (FRM) *(EPA, 1997)* derived PM$_{2.5}$ by the monitored fractional composition of PM$_{2.5}$ species (at speciation monitor sites) for each quarter. (e.g., 20% sulfate x 15 ug/m^3 PM$_{2.5}$ = 3 ug/m^3 sulfate).

(2) For each quarter, apply an air quality model to estimate current and future concentrations for each of the components of PM$_{2.5}$. Take the ratio of future to current predictions for each component. The result is a component-specific *relative reduction factor* (RRF). (e.g., given model predicted sulfate for base is 10 ug/m^3 and future is 8 ug/m^3 then RRF for sulfate is 0.8).

(3) For each quarter, multiply the current quarterly mean component concentration (step 1) times the component-specific RRF obtained in step 2. This leads to an estimated future quarterly mean concentration for each component. (e.g., 3 ug/m^3 sulfate x 0.8 = future sulfate of 2.4 ug/m^3).

(4) Average the four quarterly mean future concentrations to get an estimated future annual mean concentration for each component. Sum the annual mean concentrations of the PM$_{2.5}$ components to obtain an estimated future annual concentration for PM$_{2.5}$.

EPA is using the FRM data for nonattainment designations. Therefore it is critical that the speciated modeled attainment test described above uses FRM data as the base value for projecting future $PM_{2.5}$ concentrations. As can be seen from the list of steps, the modeled attainment test is critically dependent on the availability of species component mass at FRM sites. The modeling guidance recommends using ambient $PM_{2.5}$ speciation data to estimate the relative mass of $PM_{2.5}$ components at each FRM site. The guidance further recommends using the Interagency Monitoring of Protected Visual Environments (IMPROVE) procedure *(IMPROVE, 2000)* for estimating reconstructed fine mass. In this procedure, the $PM_{2.5}$ mass is assumed to be composed of 6 species: ammonium sulfate, ammonium nitrate, organic carbon mass, elemental carbon, crustal and un-attributed mass which is defined as the difference between measured $PM_{2.5}$ and the sum of the five component species. The relative proportion of each of these 6 species was estimated in the CAIR proposal SMAT analysis.

B. New Species Calculations and Definitions

Recent data analyses as well as a report submited by CAIR commenters *(Glass, 2004)* have noted that the FRM monitors do not measure the same components and do not retain all of the $PM_{2.5}$ that is measured by routine speciation samplers and therefore cannot be directly compared to speciation measurements from EPA's Speciation Network (ESPN). By design, the FRM mass measurement does not retain all ammonium nitrate and other semi-volatile materials (negative sampling artifacts) and includes particle bound water associated with sulfates, nitrates and other hygroscopic species (positive sampling artifacts). This results in concentrations and percent contributions to $PM_{2.5}$ mass which may be different than the <u>ambient</u> levels of some $PM_{2.5}$ chemical constituents. For the purposes of predicting changes in $PM_{2.5}$ chemical components on the $PM_{2.5}$ mass, constructed $PM_{2.5}$ mass should match the composition of mass <u>retained</u> by the FRM. As such, we have made several revisions to the calculation and definition of $PM_{2.5}$ species used in SMAT.

The revised SMAT uses an FRM mass construction methodology which results in reduced nitrates (relative to the amount measured by routine speciation networks), higher mass associated with sulfates (reflecting water included in gravimetric FRM measurements) and a measure of organic carbonaceous mass which is derived from the difference between measured $PM_{2.5}$ and its non-carbon components. This characterization of $PM_{2.5}$ mass also reflects crustal material and other minor constituents. The resulting characterization provides a complete mass balance. It does not have <u>any</u> unknown mass which is sometimes presented as the difference between measured $PM_{2.5}$ mass and the characterized chemical components derived from routine speciation measurements. The net difference between retained mass and measured mass for individual $PM_{2.5}$ chemical components is relatively small when expressed as ug/m3, but can be a large percent for individual constituents.

Below we describe an application of the revised SMAT procedures for a study domain that extends over a large portion of eastern US. The study domain is defined for grids of dimension 36 km X 36 km covering the area enclosed within -100 to -67 longitude and 25 to 49 latitude. Base case and future year model predictions are available for each FRM monitor (and grid cell) that is contained within the domain.

II. $PM_{2.5}$ Mass and Species Data Handling

Speciated $PM_{2.5}$ data from both the IMPROVE and ESPN were used to derive mean concentrations of each of six $PM_{2.5}$ components. No attempt was made to resolve differences in measurement and analysis methodology between the two networks. Since three (or more) years of urban speciation data were not available, calendar year 2002 was used to best correspond[1] to the available 5 years of FRM $PM_{2.5}$ mass data (1999-2003). Quarterly average concentrations between Jan 2002 to December 2002 were retained for sites that had at least 11 monitored values per quarter for each of the major $PM_{2.5}$ species. The quarters were defined as follows: Q1 = January - March 2002; Q2 = April - June 2002; Q3 = July - September 2002; and Q4 = October - December 2002. Major species for ESPN include elemental carbon (EC), organic carbon (OC), ammonium (NH4), sulfate (SO4), nitrate (NO3), and crustal material (which includes the five trace elements aluminum, calcium, iron, silicon, and titanium). The major species for IMPROVE are the same except for ammonium (NH4), which is not routinely measured in the IMPROVE protocol.

All species were used as extracted directly from the Air Quality Subsystem (AQS) with the exception of organic carbon in ESPN. Organic carbon in the ESPN was blank corrected based on measurements from field blanks which indicate a positive bias. The blank corrections were based on a draft report which examined the blank carbon data in the STN network *(Flanagan, 2003)*. The carbon corrections are shown below in Table 1.

Table 1: Organic Carbon Blank Corrections

Sampler Type	Organic Carbon Correction (ugC/m3)
URG MASS	0.29
R and P 2300	0.90
Anderson RAAS	1.19
R&P 2025	0.77
MetOne SASS	1.42

These sampler-specific, network-wide corrections were subtracted from daily measurements of organic carbon and the results multiplied by 1.40 (to convert to organic carbon mass) before aggregating to quarterly and annual levels.

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[1] The CAIR proposal SMAT was based on 2001-2002 data (the last 3 quarters of 2001 and the 1st quarter of 2002). There are 2 complete years of speciation data at a few sites, but we decided to use only the latest complete year of data (2002) for this analysis. There were many more speciation sites available in 2002 and we did not want to use a single year of data at most sites and an average of two years of data at a few sites. That may have led to a regional bias in species composition.

For both ESPN and IMPROVE data (for the year Jan 2002- Dec 2002), the following quality checks were made to screen the raw data:

1. Any observations with one or more missing values of any of the major chemical species were removed.

2. All observations on July 6-9, 2002 for the 10 states most affected by the July 2002 Quebec Fires were removed. The 10 states were: DE, CT, VA, MD, NH, MA, NJ, VT, RI, and PA.

3. Only those sites that had a minimum of 11 observations for ALL the major species were retained in the final database.

These conditions result in the following final quarter-by-quarter number of observations and sites from ESPN and IMPROVE for inclusion in the "SMAT" procedure for CAIR.

Table 2: Number of Eastern sites and observations used in the SMAT analysis for 2002

	January 2002—December 2002			
	ESPN		IMPROVE	
	Total Number of Obs.	Number of Sites	Total Number of Obs.	Number of Sites
Quarter 1	2022	98	1206	49
Quarter 2	2419	131	1131	47
Quarter 3	2844	145	1320	54
Quarter 4	2725	149	1637	58

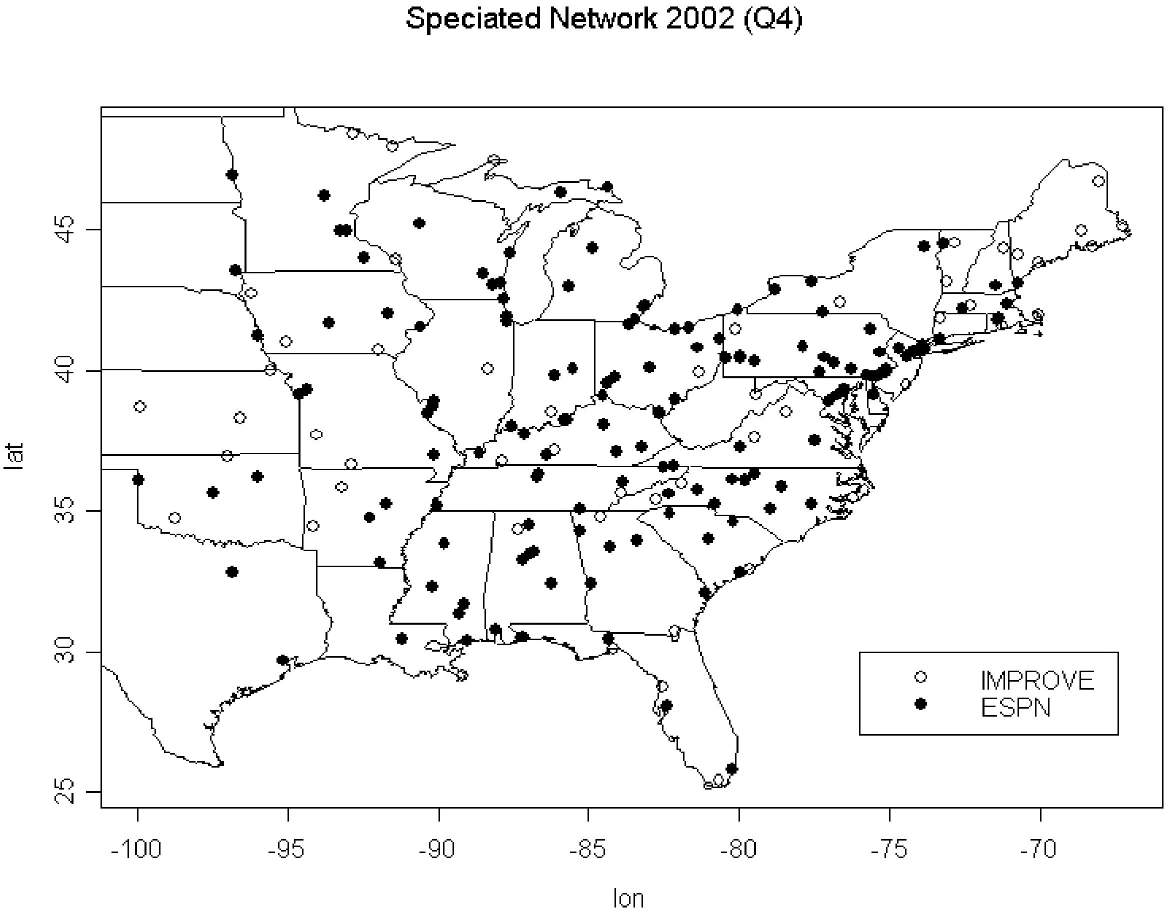

Figure 1- Speciation sites used in the revised SMAT analysis for the 4th quarter of 2002.

To further quality assure the ESPN data, the reconstructed fine mass (RCFM) was compared to measured FRM $PM_{2.5}$ on a quarterly basis[2]. To accomplish this QA check, daily RCFM was calculated for each observation using the following equation:

RCFM = Sulfate + Nitrate + OCM + EC + Crustal + Ammonium

Quarterly average RCFM was calculated using the daily RCFM. These quarterly average RCFM concentrations were then compared to quarterly average FRM $PM_{2.5}$ measurements at co-located sites.

Site-quarter combinations in the ESPN data were removed from the dataset when the quarterly average RCFM was more than 30% higher or 30% lower than the quarterly average

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[2] This QA step was not done for the IMPROVE network because IMPROVE sites are not co-located with FRM sites.

FRM PM$_{2.5}$. This comparison resulted in the removal of 30 site-quarter records from the dataset.

B. Spatial Interpolation of Data

Since roughly 80% of the FRM sites do not have co-located speciation monitors, a spatial interpolation methodology was developed to estimate component species mass at the FRM locations that do not have co-located speciation data. The quarterly average species concentrations at the IMPROVE and STN monitors were used to interpolate concentrations at the latitude and longitude of each of the PM$_{2.5}$ monitoring sites. Kriging was used to perform the interpolation using a software package developed by scientists at the National Center for Atmospheric Research (NCAR) to perform generalized kriging and efficient spatial analysis of large data sets. The Krig function in FIELDS was used to estimate the statistical parameters of the spatial model using the Generalized Cross Validation (GCV) error as the criterion for parameter estimation. Outputs from the Kriging process include the parameter estimates (range, nugget and sill) along with predicted values at each of the PM$_{2.5}$ monitor locations. Figure 2 is an example of the resulting fitted surface using the third quarter data for sulfates and figure 3 shows the intrpolated fields for 1st quarter nitrate concentrations.. Locations of monitoring sites are indicated by circles and concentrations are in ug/m^3.

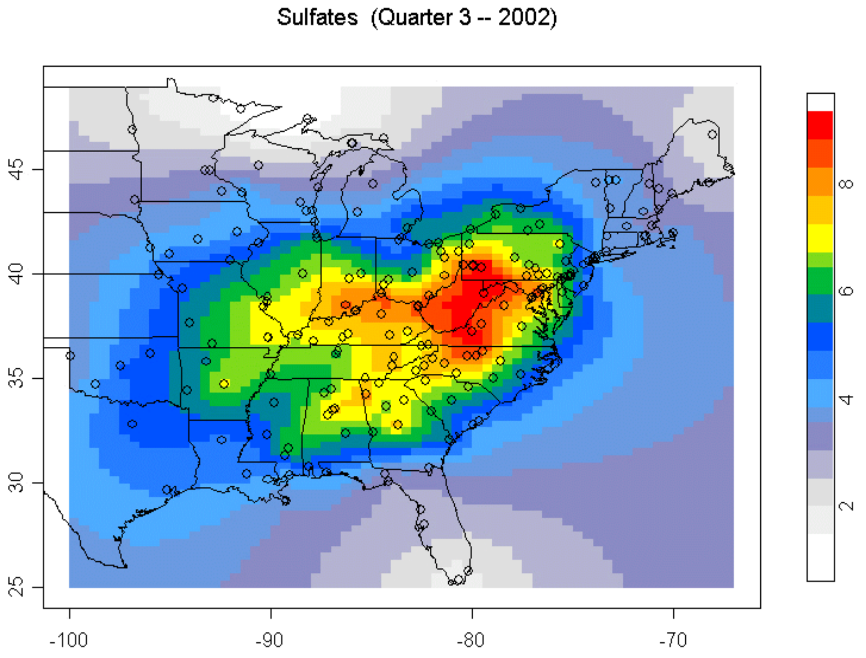

Figure 2- Third quarter 2002 interpolated sulfate concentration

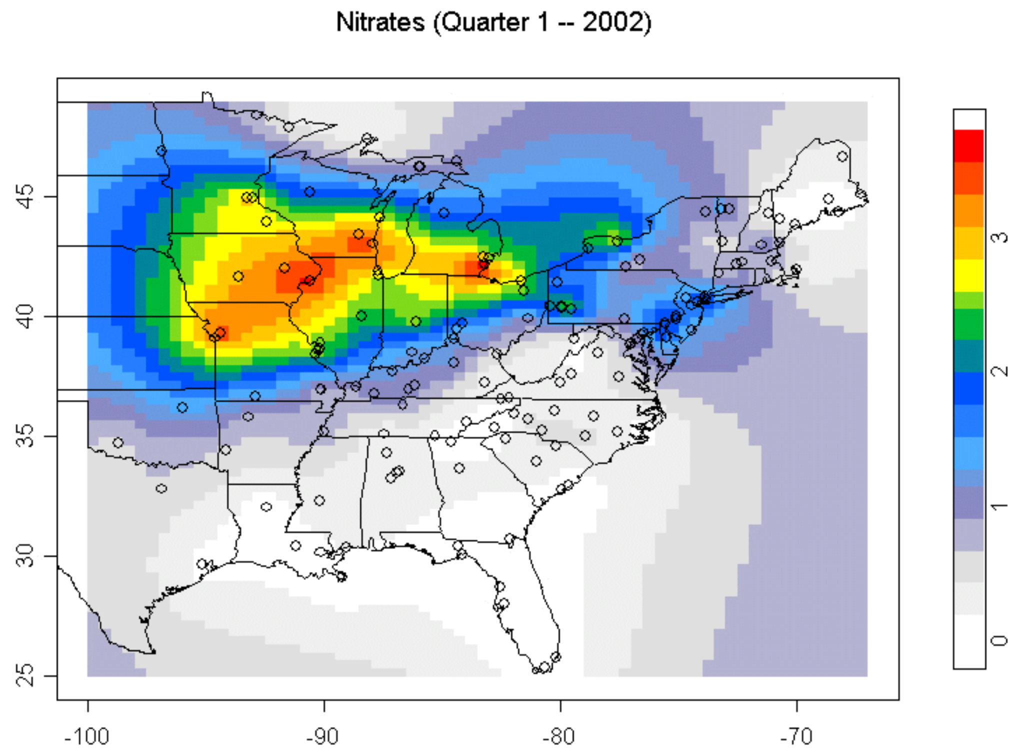
Nitrates (Quarter 1 -- 2002)

Figure 3- First quarter 2002 interpolated "FRM" nitrate concentration

Interpolated spatial fields of quarterly average sulfate ion, "FRM" nitrate, elemental carbon, organic carbon mass (measured organic carbon *1.4), crustal mass, and the degree of neutralization of sulfate (DON) were created using Kriging. Each of these fields were used in the calculation of component mass as described in the procedures below.

III. Components of Measured $PM_{2.5}$ Mass

A. Introduction

As stated in the section I, one of the goals of the revised SMAT methodology is to bettter match the speciation data with the FRM $PM_{2.5}$ retained mass. A series of adjustments and calculations were performed in order to derive the estimated species compositions. Those procedures are described below.

To represent composition of measured $PM_{2.5}$ mass (for NAAQS implementation and more precise representation of regulatory $PM_{2.5}$), the following approach is used for revised

SMAT:

CFM_{FRM} = [Ammoniated Sulfate Mass] + [Retained Nitrate Mass] + [Retained Carbonaceous Mass] + [Crustal] + [Other Components] [1]

In the above characterization, CFM equals constructed fine mass and all of the listed chemical components reflect those retained during sampling and equilibration on the FRM's Teflon filter. Sulfate and nitrate mass include associated ammonium but which may be different than assumed ammonium sulfate and ammonium nitrate compounds. Also, sulfates, nitrates and carbonaceous mass includes particle bound water associated with these hygroscopic aerosols. For these analyses, Crustal is intended to be a more general term that includes fine soil, and oxides that result from other PM emissions.

B. Derivation of $PM_{2.5}$ Species Used in Revised SMAT

1. Calculated adjusted nitrate by applying formula to daily average data

Retained Nitrate Mass The first step in the procedure for identifying mass components was to estimate the retained nitrate mass on the FRM filters. The FRM does not capture all of the semi-volatile components of the ambient air, such as ammonium nitrate. The retained amount of nitrate ion, however, can be accurately estimated by a simple thermodynamic model that involves 24-hr ambient nitrate speciation concentrations (as measured by a standard speciation sampler using a nylon filter preceded by a HNO3 denuder) together with hourly ambient temperature and humidity. Atmospheric nitrates are higher during the cooler months. Retention on the FRM is also higher during the cooler months and essentially all the nitrates are lost during the summer. The retention does not appear to depend on ambient NH3 or HNO3. More NO3 is retained at low temps and high humidity which varies by sampling location and time of year.

Prediction of FRM Nitrates Because nitrate retention varies by site and season, an ammonium nitrate equilibrium model is used to predict the amount of nitrates retained on the FRM teflon filter. As used by Hering *(Hering, 1999; Zhang, 1992)*,

$$\text{delta NO3 (ug/m3)} = 745.7/T_R * 1/24 * \sum_{i=1}^{24} (\mathbf{K}_i^{1/2}) \qquad [2]$$

where T_R is the reference temperature for the sampled air volume in degrees Kelvin and $\mathbf{K_i}$ is the dissociation constant for ammonium nitrate evaluated at the ambient temperature for hour i. This volatilization prediction characterizes depletion of some or all of the nitric acid and ammonia vapors ahead of the filter and specifies a 3-5 degree increase in the filtration temperature above ambient.

This model is used to adjust 24-hr ESPN nitrate ion concentrations to estimate FRM NO3 (NO3FRM) as follows:

$$\mathrm{NO3_{FRM}} = \mathrm{NO3_{ESPN}} - \text{delta NO3 (ug/m3)} \qquad [3]$$

For each hour of the day, the equilibrium dissociation constant for ammonium nitrate, K_i, was calculated from hourly ambient temperature and hourly ambient relative humidity based on Mozurkewich *(Mozurkewich, 1993)* and as applied by Chang et al.

When RH is less than deliquescence point of ammonium nitrate (61%),

$$\text{Ln } K = 118.87 - (24084/T) - 6.025 \ln T, \qquad [4]$$

K in nanobars, T in Kelvins.

When RH is higher than 61%, K is replaced by

$$K' = [P_1 - P_2(1-a) + P_3(1-a)^2]\ (1-a)^{1.75} * K \qquad [5]$$

where Ln P1, Ln P2, Ln P3 are specified as

$\text{Ln}(P_1) = -135.94 + 8763/T + 19.12\ln(T)$

$\text{Ln}(P_2) = -122.65 + 9969/T + 16.22\ln(T)$

$\text{Ln}(P_3) = -182.61 + 13875/T + 24.46\ln(T)$

Equation 4 assumes crystallization of ammonium nitrate when RH is less than 61%. Thus, predicted NO3 loss may be underestimated for situations where solids do not form on the filter. For supersaturated solutions and with lower RH, the estimated dissociation for the solution will be larger than K for the solid. However, there is little (or no) data that can be used to give a reliable result for how much larger.

Based on equations [2]-[5], Figure 4 illustrates the potential nitrate loss as a function of temperature and relative humidity. Temperature is presented as degrees F for more convenient interpretation. It shows that at 50 deg F and RH of 80%, approximately 1.6 ug/m3 nitrate would be lost. At RH less < 61% an additional 0.4ug/m3 could be lost. In both cases, the loss cannot exceed the amount of ambient NO3, as depicted by the ESPN NO3.

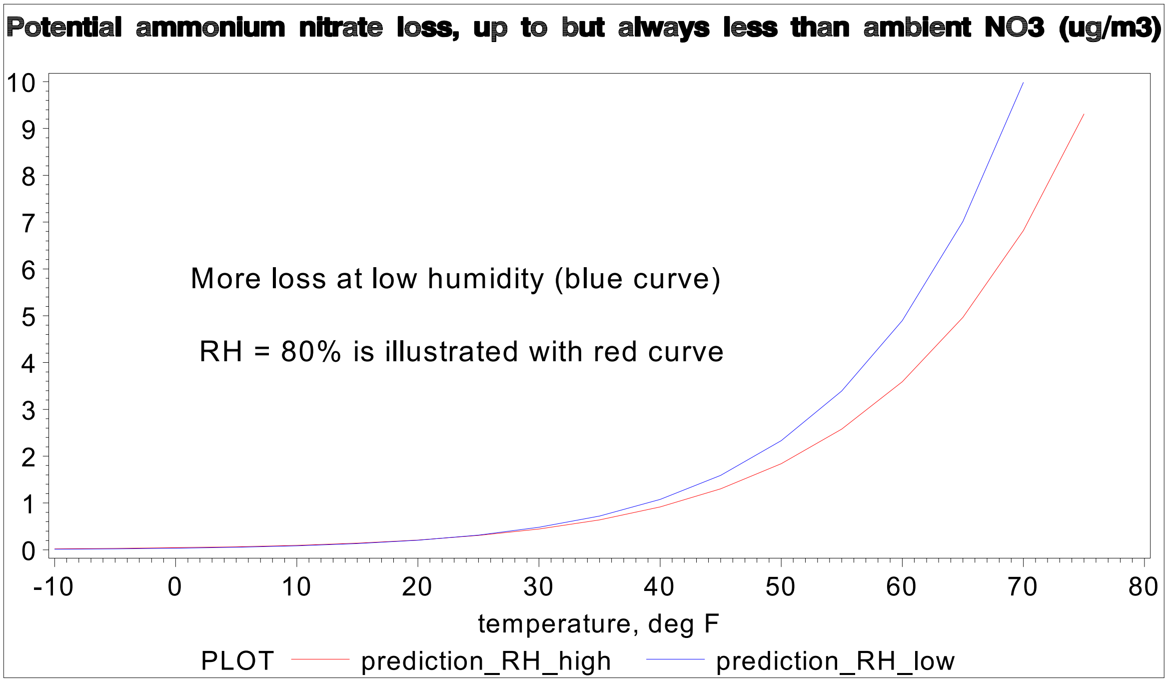

Figure 4- Potential NO3 loss as a function of temperature and relative humidity.

When these predictions are compared with measured FRM nitrates at six eastern US monitoring locations, the annual average prediction errors are <-0.3 - +0.1 ug/m3.

3. Estimated Ammonium associated with sulfates and retained nitrates and sulfates

To determine the mass associated with nitrates, we first assume retained nitrate is probably all ammonium nitrate in the Eastern US. Thus the ammonium associated with nitrates can be derived directly from the measured or predicted $NO3_{FRM}$ as

$$NH4_{NO3} = 0.29 * NO3_{FRM} \qquad [6]$$

Similarly, the dry $PM_{2.5}$ mass associated with nitrates is

$$[\text{Retained dry FRM Nitrates}] = 1.29 * NO3_{FRM} \qquad [7]$$

FRM nitrates retains water. Discussion of hydrated nitrates (and sulfates) are discussed in the next section.

The difference between total FRM NH4 (amount associated with nitrates and sulfates), termed $NH4_{FRM}$, and the ESPN NH4, termed $NH4_{ESPN,}$, is needed to determine the ammoniated form of sulfates as described by equation 4. Recent measurement study by Collett *(Collett, 2004)* shows that NH4 may not be completely retained during collection on nylon filters preceded by a nitric acid denuder. During sampling conditions associated with nitrate volatilization, ammonium nitrate dissociates but the HNO3 downstream of the denuder is recaptured on the basic nylon media and the result is reported as particle nitrate. On the other hand, the NH4+ volatilizes to gaseous NH3 and apparently passes thru the filter. At several FRM study sites, the ESPN NH4 which is adjusted for evaporated NH4NO3 tends to more closely corresponds to the measured NH4 from the FRM teflon filter. However, for other sites, the measured ESPN NH4 appear to agree with FRM NH4.

Because of uncertainty in retained FRM NH4, NH4adj is estimated as $NH_{4\ ESPN}$ minus ½ the amount that would have evaporated with lost NO3 as follows:

$$NH4_{adj} = NH_{4\ ESPN} - \tfrac{1}{2} * 0.29 * (NO3_{\ ESPN} - NO3_{FRM}) \qquad [8]$$

This essentially assumes that 50 % of the ammonium associated with lost nitrate is also lost.

4. Ammoniated Sulfate Mass.

The mass associated with sulfates is first estimated as its dry mass. All estimated sulfates are assumed to be associated with ammonium, but the form of the sulfate compound and the amount of ammonium must be estimated. The form of the ammoniated sulfate compound(s) and the amount of associated ammonium, however, is somewhat uncertain.

Sulfates may not be fully neutralized in all geographic areas or seasons of the year. During winter-time conditions, when nitrates are prevalent in the ambient aerosol, sulfates tend to be fully neutralized and exist as ammonium sulfate. During the summer when sulfates are higher, nitrates are lower and ammonia is less available for reaction with H2SO4 , the resulting aerosol can be acidic and the form of sulfates can include bisulfate or even H2SO4.

The amount of ammonium associated with the sulfate ion can be estimated as

$$NH4_{(SO4)} = NH4_{adj} - 0.29 * NO3_{FRM}, \qquad [9]$$

where 0.29 is the molar ratio of NH4 to NO3 and
$NH4_{FRM}$ and $NO3_{FRM}$ reflect the amounts retained on the FRM filter.

The amount of $NH4_{(SO4)}$ is not allowed to exceed the fully neutralized amount of 0.375 multiplied by the estimated sulfate ion concentration.

Because of uncertainties in NH4 speciation measurements, the spatially interpolated values of NH4 are derived by deriving the degree of sulfate neutralization (DON) from the estimated $NH4_{(SO4)}$ as

$$DON = NH4_{(SO4)} / SO4. \qquad [10]$$

Interpolated values of DON, sulfate and estimated FRM nitrate (adjusted nitrate) are then used to estimate the adjusted ammonia at each FRM site as follows:

$$NH4_{FRM} = DON * SO4 + 0.29*NO3_{FRM}, \qquad [11]$$

where: DON, SO4 and NO3FRM are the interpolated (kriged) quarterly average values at each FRM site. $NH4_{FRM}$ is not a directly measured value, but is derived from the measurements of NH4, SO4, and NO3. The interpolated DON values were used to estimate ammonium due to the uncertainty of the ammonium measurements. The accuracy of the ammonium measurement and the amount of ammonium that is retained on the FRM filter is uncertain. Use of the smoothed, interpolated DON values allows for a relatively smooth field of ammonium concentrations.

5. Particle Bound Water

Because ammoniated sulfate and ammonium nitrate are hygroscopic, the retained sulfate and nitrate mass will include water. Particle bound water (PBW) is estimated using the Aerosol Inorganic Model (AIM) *(Clegg, 1998)*. PBW was derived from quarterly average FRM concentrations of sulfate, ammonium, nitrate as describe above. Estimated hydronium ion, H+, needed to achieve ionic balance was derived from the latter values. The model enables the distribution of water and ions to be calculated between liquid, solid and vapor phases for specific temperature and relative humidity conditions. Typical filter equilibration conditions of 35% RH and 22 deg C (295 deg K) temperature were used.

Application of AIM at the specified FRM filter equilibration conditions show that PBW is much more dependent on sulfate concentration compared to nitrate and that the relationship varies somewhat by season to differentiate the relative amounts of sulfate and nitrate aerosol. There is proportionally less estimated PBW water for wintertime aerosol which has higher NH4 and NO3 and lower SO4.

After running the AIM model, it was determined that the particle bound water concentrations are sensitive to the degree of neutralization of the sulfate particles (determined by the relative concentration of $NH4_{FRM}$). Due to the uncertainty in ammonium concentration estimates, we used a relatively smooth field of interpolated ammonium concentrations as input to AIM. This helped to smooth out some of the "bumpiness" in the water concentration predictions.

For computational convenience, a polynomial regression equation was fit to the calculated water mass from AIM and the three input values that fed into AIM (sulfate, nitrate and ammonium). The polynomial equation is then used in all SMAT analyses to estimate water.

The equation is as follows:

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PBW =(-0.002618) + (0.980314*nh4) + (-0.260011*no3) + (-0.000784*so4)
     + (-0.159452*nh4**2) + (-0.356957*no3*nh4) + (0.153894*no3**2)
     + (0.212891*so4*nh4) + (0.044366*so4*no3) + (-0.048352*so4**2)     [12]
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where nh4 = $NH4_{FRM}$ and no3 = $NO3_{FRM}$

6. Other Non-Carbon $PM_{2.5}$ Components (blank mass)

The other quantifiable components of $PM_{2.5}$ mass include passively collected mass, represented by the field blank concentration of 0.3-0.5ug/m3 *(EPA, 2002)*. This appears to constitute a contamination of the filter resulting from handling or contact with the FRM cassette. This value is deemed to be an important constituent of $PM_{2.5}$ mass (it is assumed to not be dependent on pollutant emissions). A nominal blank mass value of 0.5 ug/m3 will be considered in mass construction computations presented later. This value is assumed to remain constant through time.

7. Calculation of Carbonaceous Mass

Elsewhere, carbonaceous mass is estimated from blank corrected speciation data, where organic carbonaecous mass is first estimated by multiplying the organic carbon concentrations by 1.4 or alternative factors to account for the oxygen, hydrogen and other elements associated with ambient carbon particles. To that amount is added the elemental carbon concentration. An alternative approach to estimate carbon contribution to $PM_{2.5}$ mass is used for revised SMAT because of (1) many uncertainties in estimating carbonaceous mass from carbon measurements *(Turpin, 2001; Chow, 2004)* (2) differences in carbon measurement protocol between urban and rural monitoring locations, (3) a relatively "bumpy" surface of urban carbon concentrations as derived from these urban and rural organic carbon measurements and (4) lack of carbon measurements at all FRM locations. The revised SMAT approach estimates carbon by mass balance comparing precisely measured FRM $PM_{2.5}$ mass *(EPA, 2003)* with the sum of its non-carbon components. The latter are sulfates, ammonium, nitrates, estimated particle bound water, estimated crustal material plus 0.5 ug/m3 as discussed earlier.

This approach estimates retained carbonacous FRM mass and explicitly accounts for the following important and difficult to estimate carbon mass properties: (1) regional and urban-rural differences in the mix of carbonaceous aerosols, i.e. the amount of oxygen, hydrogen, etc; (2) retained water associated with hygroscopic carbon compounds *(Saxena, 1996; Yua, 2004)*; (3) volatile carbonaceous material measured by speciation samplers, but not retained in FRM mass; and (4) uncertainties associated with blank corrections of measured organic and elemental carbon.

Total Carbonaceous Mass by mass balance **(TCM_{mb})** is defined as ,

$$\mathbf{TCM}_{\mathbf{mb}} = PM_{2.5} - \{ [SO4] + [NO3_{FRM}] + [NH4_{FRM}] + [water] + [crustal\ material] + [0.5] \} \qquad [13]$$

In this expression, all of the above quarterly average components represent the mass <u>retained</u> on FRM teflon filters.

The mass associated with organic compounds is defined as

$$\mathbf{OCM}_{\mathbf{mb}} = \mathbf{TCM}_{\mathbf{mb}} - [EC] \qquad [14]$$

where EC is elemental carbon.

This approach completely accounts for FRM mass and OCMmb is often greater than the amount that would be derived directly from speciation measurements. Because of uncertainties in speciation measurements and their estimates from interpolated surfaces, a lower limit (floor) for OCMmb was set so that the OCMmb was not unreasonably low. The floor was set so that OCMmb could not be more than 30% lower than measured OCM. We used the Kriged measured values of OCM to calculate the floor. The lower limit is equal to interpolated (measured) OC * 1.4 * 0.7. If the OCMmb concentration was less than the lower limit, it was set equal to the lower limit.

B. Summary of $PM_{2.5}$ Composition Calculations

Equation 15 shows the final composition of PM species as they relate to the measured FRM values for each quarter of 2002. Quarterly average FRM mass is equal to the sum of the seven species plus blank mass.

$$PM2.5_{FRM} = \{ [OCMmb] + [EC] + [SO4] + [NO3_{FRM}] + [NH4_{FRM}] + [water] + [crustal\ material] + [0.5] \} \qquad [15]$$

The species data is generated in the following order:

1) Adjusted nitrate is calculated using hourly meteorology and 24-hour average nitrate measurements.

2) Quarterly averages are calculated for adjusted nitrate, sulfate, elemental carbon, degree of sulfate neutralization (DON), crustal mass , and measured OCM[3].

3) Quarterly average ammonium is calculated from the adjusted nitrate, sulfate, and DON values.

4) Calculated ammonium, sulfate, and nitrate values are input into the polynomial water

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[3] The measured OCM is only used to calculate the “floor” for OCMmb.

equation to derive particle bound water concentrations.

5) Carbon mass by difference (OMCmb) is calculated from the $PM_{2.5}$ mass, adjusted nitrate, ammonium, sulfate, water, elemental carbon, crustal, and blank mass values.

6) The sum of the 7 species plus blank mass is equal to the FRM mass.

C. Calculation of Quarterly Species Fractions

For each quarter at each FRM site, concentrations for each of the seven species (plus blank mass) are combined with quarterly 2002 $PM_{2.5}$ FRM averages to derive composition fractions in the following manner:

First, the 0.5 ug/m3 of blank mass is subtracted from the FRM $PM_{2.5}$ concentration.

$$PM2.5_{FRM\text{-}Blank} = PM2.5_{FRM} - 0.5\ ug/m3 \qquad [16]$$

The blank mass is subtracted before species fractions are calculated because the blank mass is held constant at 0.5 ug/m3 throughout the analysis. In the example below (table 3a), the measured FRM mass for quarter 3 in 2002 is 22.5 ug/m3. The non-blank FRM mass is 22.0 ug/m3. The mass of the seven species add up to the non-blank mass.

Table 3a

FRM Mass (ug/m3)	Blank Mass (ug/m3)	Non-blank Mass (ug/m3)	Sulfate (ug/m3)	Nitrate (ug/m3)	Organic aerosol (ug/m3)	Elemental Carbon (ug/m3)	Water (ug/m3)	Ammonium (ug/m3)	Crustal (ug/m3)
22.5	0 .5	22.0	8.5	1.1	5.2	0.9	2.3	3.3	0.7

Next, species fractions are calculated for each quarter for each specie. In the example below (table 3b), a fraction of non-blank mass is calculated for each of the seven species. Blank mass remains fixed at 0.5 ug/m3.

Table 3b

FRM Mass (ug/m3)	Blank Mass (ug/m3)	Non-blank Mass (ug/m3)	% Sulfate	% Nitrate	% Organic aerosol	% Elemental Carbon	% Water	% Ammonium	% Crustal
22.5	0 .5	22.0	38.6	5.0	23.6	4.1	10.5	15.0	3.2

The percentages in table 3b above are the relative composition for the 3rd quarter of 2002. For the purposes of this analysis, we are assuming that the relative specie composition for each quarter of 2002 is representive of the 1999-2003 time period.

IV. $PM_{2.5}$ Design Values for Projecting to the Future

A. Defining "Current" Year FRM $PM_{2.5}$ Values

The $PM_{2.5}$ component species fractions are applied to "current" $PM_{2.5}$ design values which are then projected to the future. The CAIR proposal SMAT procedure followed the recommendations in the current draft $PM_{2.5}$ modeling guidance. The guidance recommends projecting the highest of the three design values that straddle the base modeling emissions year. In this case the base emissions year is 2001. The three design value periods that straddle 2001 are 1999-2001, 2000-2002, and 2001-2003. The 2001-2003 data was not available when the CAIR proposal was released, so the highest design value of the 2 available years; 1999-2001 or 2000-2002 were used in the CAIR proposal.

In the revised SMAT procedure we are proposing to revise the methodology to calculate the base year design values for projections. We are proposing to use the <u>average</u> of the 3 design value periods that straddle the emissions year. The average of the 3 design values is not a straight five year average. It is, in effect, a weighted average of the annual averages. The design value periods range from 1999-2003. In the average of 1999-2001, 2000-2002, and 2001-2003, 2001 is "weighted" 3 times, 2000 and 2002 are weighted twice, and 1999 and 2003 are weighted once. This has the desired effect of weighting the projected $PM_{2.5}$ values towards the middle year of the five year period, which is the emissions and meteorology year (2001). The average design value methodology also takes into account the emissions and meteorological variability that occurs over the full 5 year period. The average weighted design value is thought to be more representative of the 2001 emissions and meteorology period than the previous methodology of choosing the highest single design value period. This value provides the "best estimate" current year design value for use in future year model projections. It should be noted that in most cases, the "average" design value will not be the same as the 2001-2003 design value that will be used for the purpose of $PM_{2.5}$ designations. The average design value may be higher or lower than the 2001-2003 value.

There are several steps in the derivation of the average $PM_{2.5}$ design values for projections to the future. Quarterly average values are needed for each FRM site. The following steps were used to derive the quarterly average FRM values.

1) The analysis began with quarterly average FRM data for all quarters from 1999-2003.

2) Completeness was defined as site quarters with11 valid samples per quarter. All site quarters with less than 11 samples were removed.

3) A quarterly average 3 year design value was calculated for each design value period in which a site had all 12 quarters with complete data[4] (1999-2001, 2000-2002, and 2001-2003). This

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[4] Sites were considered to have complete data for the purposes of calculating a 3 year design value if they had 12 complete quarters <u>or</u> were considered to have complete data through data substitution. If a site was complete with data substitution and had 10 or 11 complete quarters, the quarterly design values

results in four quarterly averages for up to three design value periods for each FRM site. Sites had to have complete data for the latest design value period (2001-2003) to be considered in the analysis. Since the $PM_{2.5}$ designation process will use the 2001-2003 data, sites were not used in the analysis if they did not have complete data (as defined in 2 above) for the 2001-2003 period.

4) The (up to) 3 quarterly design value periods were averaged together to get a single quarterly average design value for each site. All complete design value data was used, provided that the 2001-2003 period was complete. A site did not have to have all 3 complete design periods. If 2001-2003 was the only complete period, then that was used as the average design value (even though it isn't truly an average). If 2 complete design value periods were available for a site (1999-2001 and 2001-2003 **or** 2000-2002 and 2001-2003), then those 2 periods were averaged together.

The averaged quarterly average FRM design values were used as the "current" FRM value for each monitoring site. The species fractions from the 2002 speciation data were used to estimate the species concentrations for the current year FRM $PM_{2.5}$ data. The percentage compositions for 2002 are applied to the quarterly average design values as shown in table 4a.. In the example below, the average design value for the 3rd quarter for the site from table 3b is 20.3 ug/m3. This leads to the following concentrations of $PM_{2.5}$ species:

Table 4a. Calculation of the "current" species concentrations

Weighted Avg. FRM Mass (ug/m3)	**Blank Mass (ug/m3)**	**Non-blank Mass (ug/m3)**	**Sulfate (ug/m3)**	**Nitrate (ug/m3)**	**Organic aerosol (ug/m3)**	**Elemental Carbon (ug/m3)**	**Water (ug/m3)**	**Ammonium (ug/m3)**	**Crustal (ug/m3)**
20.3	0 .5	19.8	7.64	0.99	4.67	0.81	2.08	2.97	0.63

This procedure is repeated for each $PM_{2.5}$ site and quarter to complete the calculation of current (or baseline) ambient concentrations used as the basis for future estimates of $PM_{2.5}$ mass and its components.

B. Estimating Future Year $PM_{2.5}$

Future concentrations of $PM_{2.5}$ component species are estimated by assuming that the quarterly average component concentration will change in the same proportion as the model predicted change. Model predicted changes in species concentrations (from a current year to a future year) are used to calculate "relative reduction factors". Relative reduction factors are calculated for each grid cell and species as the ratio of the quarterly average future model predictions to the current base model predictions. The relative reduction factor for each species is then multiplied by the estimated current year ambient species mass for the site to estimate future species concentrations.

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were calculated using only the complete quarters. Incomplete quarters were not used in the calculations.

In the revised SMAT methodology, relative reduction factors are calculated for 5 species; sulfate, nitrate, organic carbon mass, elemental carbon, and crustal mass. The future year concentrations of the 5 components are calculated for each site quarter. The future year ammonium concentrations are calculated from the sulfate, nitrate, and (current year) DON values. Assuming that the DON is unchanged from the current year[5], the ammonium is calculated using the following formula:

$$NH4_{future} = DON * SO4_{future} + 0.29*NO3_{future},$$

The $NH4_{future}$, $SO4_{future,}$ and $NO3_{future}$ concentrations were then run through the polynomial water equation to predict a future year water concentration. The future species concentrations at each FRM site were then summed over the seven species plus blank mass[6] to estimate the future quarterly average $PM_{2.5}$ concentration. The four quarterly values are then averaged to obtain the estimated future annual average $PM_{2.5}$ for each FRM site.

V. Summary

The results of the analysis at each of the FRM monitoring sites (with complete data) were used in the CAIR final rule modeling analysis. The revised SMAT technique has several improvements over the original SMAT application in the CAIR proposal. One goal of the revised SMAT methodology was to estimate the $PM_{2.5}$ mass that is retained on the FRM filters. This provides a more unbiased estimate of future $PM_{2.5}$ concentrations which are based on current year FRM measurements. Averaging of multiple design value periods provides a "best estimate" current year design value. Application of revised SMAT with Kriged spatial fields allows us to take advantage of the measurements at each FRM site. In this way, a more complete attainment/nonattainment picture can be derived by not limiting the predictions of future year design values to only speciation monitoring sites.

Use of SMAT with Spatial Fields for SIPs

The details of this application of revised SMAT are specific to the short term use of the FRM and speciation data (ESPN and IMPROVE) in estimating future year $PM_{2.5}$ concentrations for the CAIR rule. The use of a single year of speciation data interpolated to a modeling grid is

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[5] The DON was assumed to stay constant through time due to the uncertainty in the ammonium measurements. The water calculation is sensitive to the ammonium (and therefore the DON value) concentrations. Keeping the DON constant allows for the future year ammonium and water values to be solely a function of the sulfate and nitrate concentrations. Otherwise, it is possible for sulfate and nitrate to be reduced and water concentrations to increase. This may occur if sulfate becomes more neutralized in the future. But it is somewhat illogical outcome (although scientifically possible) and is highly dependent on an uncertain measurement (ammonium). Therefore we did not allow the DON value to vary with time.

[6] The blank mass value was held constant at 0.5 ug/m3, effectively giving it a relative reduction factor of 1.0.

necessary at this time, due to the relatively sparse ambient data sets. The amount of available ambient data will increase significantly in the future. When ambient data is needed for SIP development, there will be at least 3 years of complete speciation data at hundreds of sites. In many areas, the coverage of speciation data may be adequate so that interpolation of the data through spatial fields is not necessary. It is likely that the routinely measured speciation data will never match up directly with the FRM data, but our understanding of the biases, artifacts, and sampling issues will continue to improve through time. And the monitoring protocols are likely to change in the future. This application should serve as an example that can be replicated in the short term, but the techniques and assumptions will likely evolve over the long term.

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