6.6.3 Chemical Mass Balance

Chemical Mass Balance without Unique Tracer

CMB modeling with the new data has not yet been completed. This subsection is from the April 1989 draft and will be updated when the analysis with the new data is finished.

This section presents interim results of the Chemical Mass Balance model applied to WHITEX data. The results reported represent a Level I assessment and must be considered tentative. A Level I assessment is intended to identify the major contributors to particulate concentrations and to assess the need for additional analysis to increase the accuracy and precision of source apportionment. The initial fine particle source attributions are sufficient to define the additional analysis and testing which need to be performed to complete this component of the WHITEX data analysis.

Chemical Mass Balance Receptor Model

As noted in the introduction to this section, the chemical mass balance consists of a least squares solution to a set of linear equations which expresses each receptor concentration of a chemical species as a linear sum of products of source profile species and source contributions.

The source profile species (i.e., the fractional amount of the species in the emissions from each source type) and the receptor concentrations, with appropriate uncertainty estimates, serve as input data to the CMB model. The output consists of the amount contributed by each source type to each chemical species concentration. The model calculates values for the contributions from each source and the uncertainties of those values. Input data uncertainties are used both to weight the importance of input data values in the solution and to calculate the uncertainties of the source contributions.

The CMB model assumptions discussed in Watson[66] are: 1) compositions of source emissions are constant over the period of ambient and source sampling; 2) chemical species do not react with each other (i.e., they add linearly); 3) all sources with a potential for significantly contributing to the receptor have been identified and have had their emissions characterized; 4) the number of sources or source categories is less than or equal to the number of species; 5) the source profiles are linearly independent of each other; and 6) measurement uncertainties are random, uncorrelated, and normally distributed. The degree to which these assumptions are met in applications depends to a large extent on the characteristics which are determined at source and receptor.

CMB software in current use almost exclusively applies the effective variance solution developed and tested by Watson et al.[67] because: 1) this provides realistic estimates of the uncertainties of the source contributions (owing to its incorporation of both source profile and receptor data uncertainties); and 2) chemical species with higher precisions in both the source and receptor measurements are given greater influence than are species with lower precisions.

Watson[66] observed that individual sources with similar source profiles, such as different soils and road dusts, would yield unreliable values if included in the same chemical mass balance. Henry[68] proposed a quantitative method of identifying this interference between similar source compositions, which is known as "collinearity."

Henry's[68] "singular value decomposition" defines an "estimable space into which resolvable sources should lie." The source types which do not fall into this estimable space are collinear, or too similar to be resolved from a combination of one or more of the source types which do lie within the estimable space. Henry[68] further proposed that linear combinations of source contributions resulting from collinear source compositions would be more representative of the summed contributions of these sources. Several of these measures are used in EPA's Versions 6.0 and 7.0 of CMB software.[69]

The chemical mass balance modeling procedure requires: 1) identification of the contributing sources types; 2) selection of chemical species to be included; 3) estimation of the fraction of each of the chemical species which is contained in each source type (i.e., the source compositions); 4) estimation of the uncertainty in both ambient concentrations and source compositions; and 5) solution of the chemical mass balance equations. These procedures are described in an applications and validation protocol[70] which accompanies EPA's CMB receptor model software, and they are not repeated here in great detail. These procedures were applied to WHITEX data taken with the IMPROVE sampler at Page and Hopi Point using Version 7.0 of the EPA modeling software.

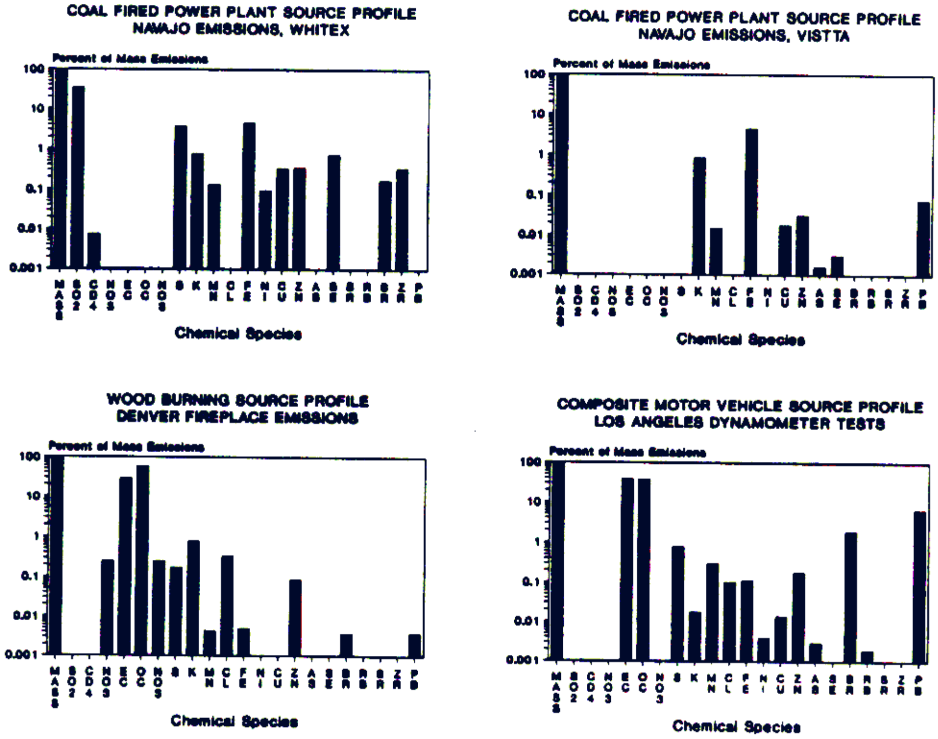
Input Data

WHITEX data consist of six and twelve hour samples. All six hour samples were averaged to obtain twelve-hour averages which correspond to the IMPROVE and SCISAS sampling. Only IMPROVE data in the $PM_{2.5}$ particle size fraction were used in this initial analysis since these are the only data which are common to all sites in the network and which are the major contributors to visibility impairment.

The following sources were identified as potential contributors to fine particle concentrations: 1) primary geological material from roads and the open desert; 2) primary smelter emissions; 3) primary coal-fired power plant emissions; 4) primary motor vehicle exhaust; 5) primary wood burning; 6) secondary ammonium sulfate; and 7) secondary ammonium nitrate. The ammonium sulfate and ammonium nitrate form from precursor emissions of sulfur dioxide and oxides of nitrogen. The major emitters of sulfur dioxide which might affect the WHITEX sampling sites are coal-fired power plants and smelters. The ratio of sulfate to fine particles in these emissions is expected to increase between source and receptor as the precursor gases convert to sulfate particles. With the meteorological information included in the WHITEX data base, it is possible to estimate how sulfate might increase in power plant and smelter source profiles by the time these emissions have reached a receptor. Estimating these changes in source profiles has not been attempted in this preliminary analysis, but it is planned before the completion of this project.

Figure 6.66 compares several of the important source profiles which were compiled for the apportionment of WHITEX $PM_{2.5}$. The first coal-fired power plant source profile was derived from the measurements in Table 6.3. Since mass was not measured in the aircraft tests, the aluminum proportion was set equal to 9% of the mass of primary particulate matter, and all other species concentrations were normalized to aluminum. Aluminum is typically present in flyash in proportions of 7 to 12%. The sulfur dioxide and CD_4 concentrations in the plume are normalized to fine particle mass in this profile. The SO_2 ratio is low compared to other tests. Watson[71] found the ratio of sulfur dioxide to fine particle ratios in Denver coal-fired power plant emissions to be 50 to 100 times higher than those inferred from Table 6.3. The second profile in Figure 6.66 was derived from the hot-stack tests by Calendaria and Palomino[72] which were taken during the VISTTA study. Calendaria and Palomino[72] did not measure sulfur dioxide, nitrate, elemental carbon, or organic carbon. Their hot-stack measurements show substantially lower amounts of selenium than the WHITEX aircraft measurements. The woodburning profile was derived from fireplace tests in Denver by Watson[71] and the mobile source profile was assembled by the South Coast Air Basin. A smelter profile was assembled from aircraft measurements taken by Small et al.[73] in the plumes of southern Arizona smelters. The geological source profile was derived from resuspended dust samples from Las Vegas, NV. These source profiles need improvement in subsequent modeling.

Source profiles were also derived from the satellite sites with the hope that they might differ enough from each other to allow contributions from different source regions to be resolved from each other. An initial examination of these profiles showed that they were collinear. The collinearity may be reduced by meteorological stratification, and this will be examined in additional work.



COAL FIRED POWER PLANT SOURCE PROFILE
NAVAJO EMISSIONS, WHITEX

COAL FIRED POWER PLANT SOURCE PROFILE
NAVAJO EMISSIONS, VISTTA

WOOD BURNING SOURCE PROFILE
DENVER FIREPLACE EMISSIONS

COMPOSITE MOTOR VEHICLE SOURCE PROFILE
LOS ANGELES DYNAMOMETER TESTS

Figure 6.66: Source profiles used in the apportionment of $PM_{2.5}$.

CMB Source Contributions to $PM_{2.5}$

The contributions of seven different source types to $PM_{2.5}$ at Page and Hopi Point are shown in Figure 6.67 through 6.70. Primary wood combustion, presumably from activities in the town of Page, contributed approximately 50% of the $PM_{2.5}$ in almost every sample. Secondary ammonium sulfate is the second largest contributor. On several occasions, notably around 1/16/87, 2/2/87, and 2/5/87, geological material is a significant contributor. The primary coal- fired power plant emissions are definitely detectable, owing to the presence of selenium and strontium in their profiles. These primary power plant contributions are relatively small contributors at Page. Primary emissions from mobile sources and primary smelter emissions were very small contributors, as was secondary ammonium nitrate.

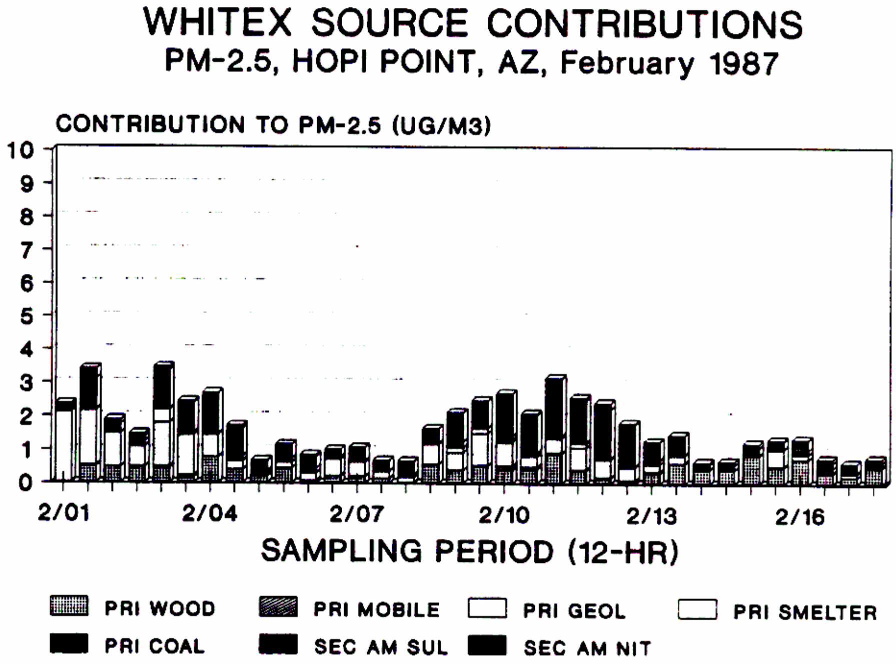


Figure 6.67: WHITEX source contributions — $PM_{2.5}$, Hopi Point, Arizona, January 1987.

The contributions to $PM_{2.5}$ at Hopi Point were about half the values measured at Page. The woodburning contributions were substantially lower when compared to Page. Secondary ammonium sulfate and geological material were the majority contributors during the study period for most samples. Primary coal- fired power plant contributions were detectable at page, although they were generally less than 10% of the $PM_{2.5}$ mass. As at Page, primary mobile emissions and secondary ammonium nitrate were negligible contributors, as were primary smelter emissions.

The elevated $PM_{2.5}$ episode at Page from 1/21/87 through 1/28/87 was not repeated in the Hopi Point data. Both primary wood burning and secondary ammonium sulfate contributions were much larger at Page during this period when compared to the values at Hopi Point. In fact, Hopi Point was relatively clean for the duration of this episode. Similarly, the episode from 2/9/87 to 2/14/87 at Page is not repeated in the corresponding source apportionments at Hopi Point. The secondary ammonium sulfate contribution at Page dominates the $PM_{2.5}$ concentrations at

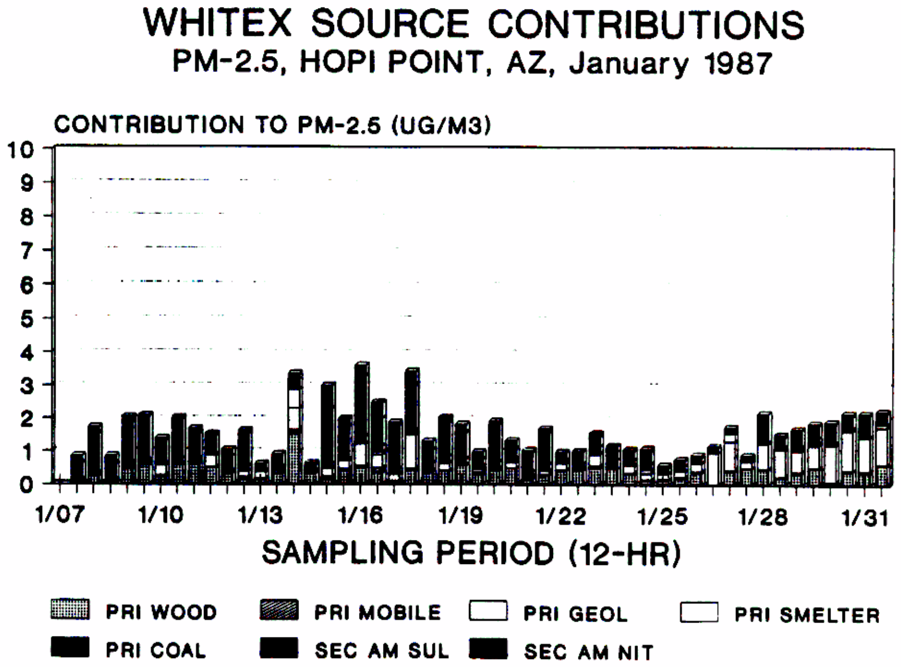


Figure 6.68: WHITEX source contributions — $PM_{2.5}$, Hopi Point. Arizona. February 1987.

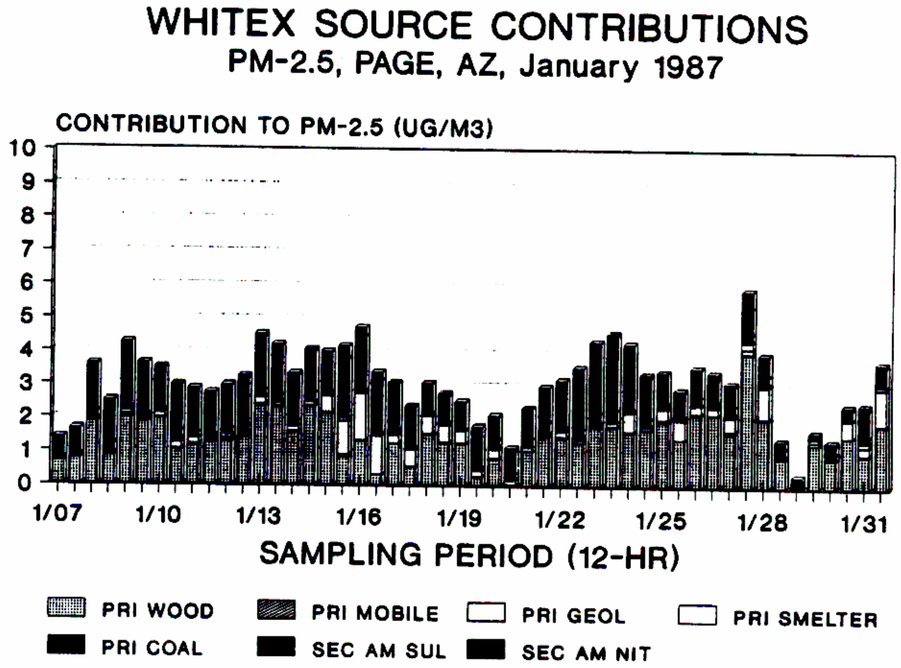


Figure 6.69: WHITEX source contributions — $PM_{2.5}$, Page, Arizona, January 1987.

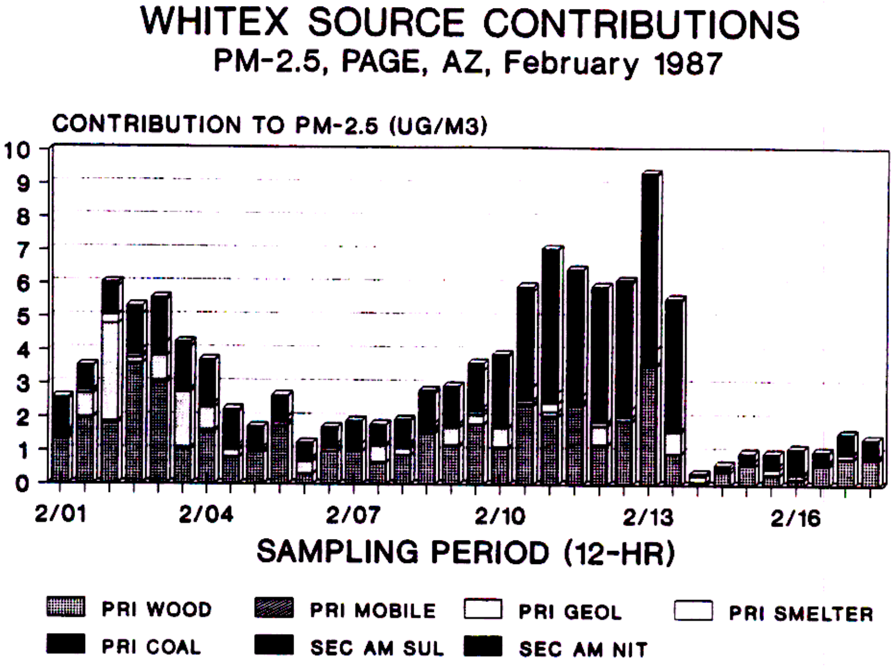


Figure 6.70: WHITEX source contributions — $PM_{2.5}$, Page, Arizona, February 1987.

Page, and the primary contributions of coal flyash are among the highest calculated for these Page samples.

Further CMB Modeling

As noted earlier, these results are preliminary and are subject to several limitations. Many of these limitations will be eliminated by the time this portion of the interpretation is complete and integrated with other source apportionment methods. The following additional efforts need to be made:

- Regional-scale source profiles need to be derived from the satellite sites. While it does not appear practical to apportion the results of individual samples among regions, it may be possible to add a regional-scale profile to the local-scale sources used in the analysis presented here. The satellite profile would be selected when it was upwind of the sampling site. A cursory examination shows substantial sulfur concentrations at satellite sites, and a portion of the secondary sulfate contribution will be apportioned to the regional profile.

- Fractionated coal-fired power plant profiles need to be formed based on typical transport times and transformation rates. During dry periods, transformation rates are slow, but when relative humidity is high, or when fogs are present, sulfate can form quickly. Several of these profiles need to be assembled. They will be selected based on meteorological data.

- The sulfur dioxide and CD_4 ratios to other species in Table 6.3 need to be investigated. The receptor measurements of these species are underestimated by the CMB by factors of 100 to 1000, though the fine particle selenium and strontium concentrations are reproduced within a factor of two. The ratios of these species to fine particle mass in the plume should be much higher.

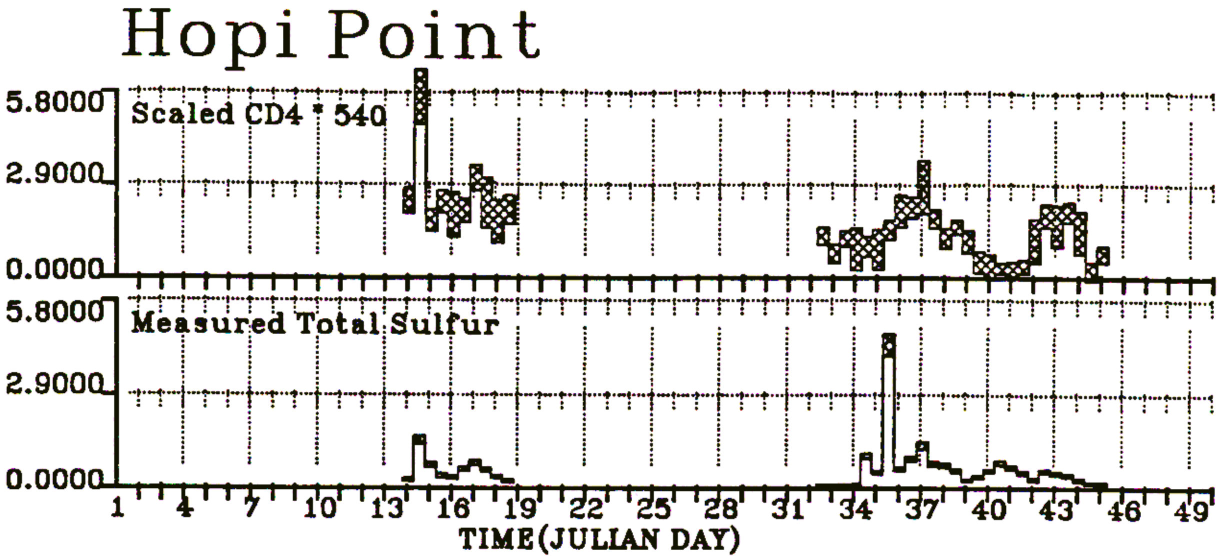


Figure 6.71: Time plot of predicted upper limit of NGS contribution to total sulfur at Hopi Point ($540 \times SCD_4$) and measured total sulfur.

- When additional source profile development has been completed, the CMB analyses should be repeated at these two sites and at the remaining WHITEX core and gradient sampling sites.

Chemical Mass Balance with Unique Tracer

When there is a unique tracer associated with a source and when ratios of tracer to other emissions are known, Equation 6.9 can be used to estimate the upper limit of contributions to ambient aerosol species. For instance, ambient concentrations of total sulfur associated with NGS emissions can be calculated using

$$S_{T,a} = [S_T/CD_4]_p \times CD_{4,a} \tag{6.9}$$

where the subscripts a and p refer to ambient and in-plume concentrations and $S_T = (SO_2/2 + SO_4/3)$ is the total sulfur. For purposes of this study ambient CD$_4$ concentrations were scaled to an equivalent S_T/CD_4 in-plume ratio of 540 $\mu g/m^3 ppt$. Thus

$$S_{T,a} = [540] SCD_{4,a} \tag{6.10}$$

can be used to estimate the upper bounds of NGS contributions at any site for which there are ambient CD_4 data. Figure 6.71 is a time plot of predicted and measured total sulfur as a function of time at Hopi Point. In almost all cases the upper limit of the NGS contribution is considerably greater than that which was measured. The average upper limit of total sulfur calculated using Equation 6.10 is 1.58 ± 0.08 $\mu g/m^3$ while the average measured total sulfur at Hopi Point is 0.61 ± 0.01 $\mu g/m^3$. The upper limit is approximately 3 times higher than the ambient levels.

A similar plot for Page is shown in Figure 6.72 where the average upper limit of the NGS contribution is 3.16 ± 0.15 $\mu g/m^3$ while the average measured total sulfur is 1.75 ± 0.04 $\mu g/m^3$. The mean upper limit at Page is nearly 2 times higher than the mean measured total sulfur.

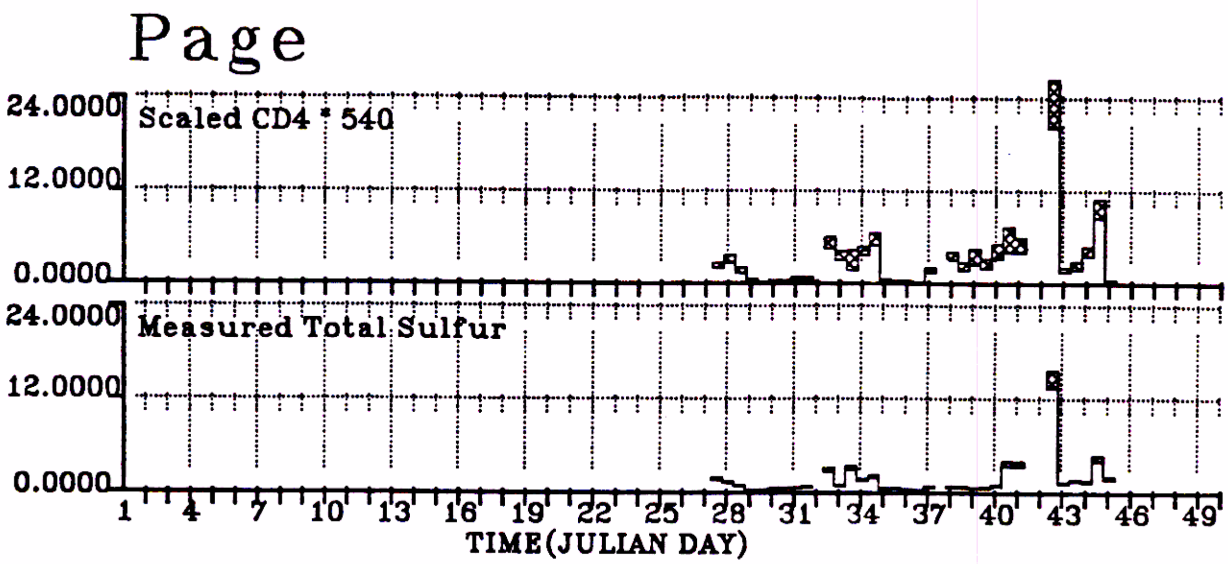


Figure 6.72: Time plot of predicted upper limit of NGS contribution to total sulfur at Page (540 × SCD_4) and measured total sulfur.

6.7 Attribution of Visibility Impairment

The apportionment of light extinction was carried by first estimating the contribution of each chemical species to light extinction using consensus literature values for the extinction efficiencies of each species. These are summarized in Table 6.45. The fs(RH) and fn(RH) terms shown in the Table refer to functions describing the dependence of the sulfate and nitrate, scattering efficiencies on relative humidity. Most efficiencies are based on a literature review by Trijonis and Pitchford.[74] The coarse mass efficiency was adjusted to account for the size range 2.5–15 μm of the WHITEX coarse mass data rather than the 2.5–10 μm data in their study. Similarly, the organic efficiency was scaled by 1.5/1.4 to account for the different scaling ratios used to convert organic carbon to organics. The nitrate efficiency is based on Tang et al.[75] for a mass median diameter of 0.98 μm and a highly polydisperse size distribution. Figure 6.73 shows these functions graphically. The fn(RH) and fs(RH) functions are based on those described by Tang et al.[75]

For purposes of error propagation, all efficiencies in Table 6.45 were assumed to have an uncertainty of 10%. The uncertainty in the RH functions was calculated based on the uncertainties in the RH measurements, which are 2% for RH 0–80 % and 5% for RH 80–100 %. As can be seen in Figure 6.73 when the RH is above 80%, the relatively large uncertainty in the RH causes a large uncertainty in the RH functions. Although uncertainties are calculated for both NGS sulfate and other sulfate, the uncertainties for these components are not independent. For example, if RH was over estimated, the contributions due to NGS sulfate and other sulfate would both be over estimated.

The NGS contribution to light extinction was estimated by determining the NGS sulfate sulfur concentration for each time period based on the TMBR results. The sulfate sulfur due to other sources was then determined by subtracting NGS sulfur from the measured sulfate sulfur concentration. NGS sulfur could also be determined by DMB, and as discussed in Section 6.6.4, the results would be similar.