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9.1 Introduction

The Winter Haze Intensive Tracer Experiment (WHITEX) was designed to evaluate the feasibility of attributing single point source emissions to visibility impairment in selected geographic regions. Specifically, WHITEX was conducted during January and February 1987 in the vicinity of the Navajo Generating Station (NGS), a large (2250 MWe) coal-fired power plant located relatively close to several national parks including the Grand Canyon, WHITEX, primarily an exploratory scientific study, was prompted by the regulatory program and congressional mandate to protect and improve visibility in those national parks and wilderness areas that have been afforded special visibility protection (mandatory PSD Class I areas). Grand Canyon, Bryce Canyon, Capitol Reef, and Canyonlands National Parks, all within the WHITEX study area, are afforded such visibility protection. Because NGS, a power plant without sulfur dioxide (SO_2) emission control equipment, is now estimated to be the largest single SO_2 emission source in the West, its impact on these national parks is of great concern to government, industry, and the public.

The WHITEX study area has long been suspected of experiencing regional stagnation in the winter. Light winds and shallow mixing depths, in conjunction with barriers caused by elevated terrain, suggest the possibility of buildup of NGS emissions over multi-day periods which end when fronts pass through and clean out accumulated pollution. Although ambient aerosol concentrations and light extinction properties of the atmosphere have been measured in the area for several years, and layered haze has been documented photographically, there have not been any measurement studies directed at attributing regional aerosol concentrations and light extinction to NGS and other sources in the area.

Deterministic modeling studies have been carried out in the area in an attempt to understand NGS contributions to regional air quality and visibility problems. A primitive-equation wind field model was implemented for the NGS area. NGS emissions were injected into the model's wind field and ambient concentrations were estimated. However, this study was not specifically directed to source attribution. Another deterministic modeling study was done with a Lagrangian regional dispersion model. Estimates of NGS's contribution to ambient concentrations and to light extinction in the vicinity of NGS (i.e., the WHITEX study area) and the entire Southwest U.S. were made. However, these estimates were deemed uncertain because of (1) uncertain and changing regional emissions (copper smelter emissions have been significantly reduced since the study was carried out in 1985), (2) uncertainties in predicting wintertime stagnation and terrain influenced wind fields, and (3) uncertainties in the SO_2 oxidation rate. Until WHITEX no data were available to estimate homogeneous (gas-phase) and heterogeneous (liquid-phase) SO_2 oxidation rates in winter. From

the insight afforded by WHITEX, this latter modeling study apparently underestimated the liquid-phase SO_2 oxidation rate and, hence, NGS's primary contribution to regional sulfate aerosol and visibility degradation.

The distinguishing feature of WHITEX was the injection of a unique tracer (deuterated methane or CD_4) into the NGS stacks at a rate which could be scaled to the known emissions of SO_2, nitrogen oxides (NO_x), and particulates. Using a variety of statistical and deterministic techniques, measured ambient concentrations of species that interact with light (e.g., sulfate, $SO_4^=$) and NGS-specific tracer were analyzed to calculate NGS's contribution to the measured aerosol at various receptors. For example, the total ambient sulfate concentration is the sum of the contributions from NGS and from background sources (both natural and non–NGS man-made):

$$[SO_4^=]_{total} = [SO_4^=]_{background} + [SO_4^=]_{NGS}, \tag{9.1}$$

where $[SO_4^=]_{NGS}$ is determined from ambient concentrations of CD_4 scaled to NGS sulfur emissions and accounting for oxidation and deposition.

Without the tracer unique to NGS, WHITEX measurements of winds, spatial and temporal trends of ambient concentrations, and light extinction alone could be used to assess qualitatively the contribution of NGS. With this tracer data, a quantitative estimate of NGS's contribution was possible.

9.2 Climatology of the Area

The synoptic meteorology of the WHITEX region was classified into four synoptic categories based on data from the years 1980 to 1984: (1) warm sector ahead of a cold front, (2) cold sector ahead of a warm front, (3) behind a cold front, and (4) under a polar high. Of the four synoptic categories, category 4 is associated with the most stagnant air masses, because of the light winds and limited mixing heights caused by small pressure gradients and subsiding air. This category was found to occur more often than the other three categories: 65 percent of the time during the winter months (defined here as November through March).

The persistence of the stagnant category 4 was analyzed for the WHITEX region. A conservative estimate of persistence was made using the assumption that a category-4 stagnation event ended when any portion of the WHITEX region had non–category–4 meteorology. A nonconservative estimate was made using the assumption that if category–4 conditions existed anywhere in the WHITEX region, the stagnation event was assumed to persist until all parts of the region had non–category–4 meteorology. Using the nonconservative and conservative assumptions, respectively, 42–44 percent and 62–66 percent of the all stagnation events are of 3–5 day duration, 43–45 percent and 29–32 percent are of 6–14 days duration, and 12 percent and 4 percent are of greater than 14 days duration (on the average about once per winter).

The mean length of a stagnation event is approximately 6 days for the conservative method and 8 days for the nonconservative method. Approximately 45 percent of the wintertime days experience stagnation events of three days or longer based on the conservative estimate; 60 percent for the nonconservative estimate.

These statistics suggest that the 9–day stagnation that occurred during the WHITEX study between February 6 and February 14, 1987 and that led to the highest sulfate concentrations in the region, was not anomalous. Persistent stagnation events of this duration or longer are expected 16 percent of the time during the winter months.

9.3 Light Extinction Budget

The contribution of various aerosol species to the total light extinction was ascertained on the basis of simultaneous measurements of (1) ambient concentrations of specific species and (2) light extinction coefficients (b_{ext}) and light scattering coefficients (b_{scat}). Light extinction budgets were developed using light extinction efficiencies determined from multiple linear regression analysis and from the literature. Light extinction budgets were developed for three WHITEX sites: Glen Canyon National Recreation Area (Page), Grand Canyon National Park (Hopi Point), and Canyonlands National Park.

Average total light extinction (including natural blue-sky Rayleigh scattering) during the WHITEX experiment ranged from 0.0161 km^{-1} at Hopi Point, to 0.0246 km^{-1} at Canyonlands, to 0.0291 km^{-1} at Page. These values are 1.69, 2.54, and 2.83 times the natural blue-sky Rayleigh scattering (the light extinction caused solely by the scattering of light by air molecules).

Light scattering by fine particles, i.e., sulfates, organics, fine soil, and nitrate was the major contributor, (approximately 75 percent) to the non–Rayleigh light extinction. Most of the remaining non–Rayleigh extinction was light absorption caused by light absorbing carbon. Extinction caused by coarse particles and by NO_2 were relatively small, each less than 5 percent of total extinction.

The fine-particle light scattering was further subdivided into contributions from fine sulfate, organic carbon, nitrates, and soil components. Sulfate was found to be the largest contributor to fine-particle light scattering. Sulfate was estimated to be 48 to 54 percent of the fine-particle scattering at Page. The first number is based on literature-derived extinction efficiencies and the second is based on the regression analysis; 58 to 60 percent at Canyonlands; and 62 to 72 percent at Hopi Point. Organics were the next largest contributor, estimated to be 33 to 41 percent of fine-particle scattering at Page (In this case, the first number is the regression-derived value, and the second is the literature-derived value.); 20 to 27 percent at Canyonlands; and 15 to 16 percent at Hopi Point. Nitrate was the third largest contributing component with 6 to 14 percent of the fine-particle scattering at Page (The first value is the literature-derived value and the second is the regression-derived value.); 9 to 20 percent at Canyonlands; and 5 to 13 percent at Hopi Point. Fine soil contributed the least, with 0 to 5 percent of the fine-particle scattering at Page (The first value is the regression-derived value, and the second is the literature-derived value.); 0 to 6 percent at Canyonlands; and 0 to 17 percent at Hopi Point.

On the average, during the WHITEX program sulfate aerosol (and associated water) was found to contribute about two-thirds of the non–Rayleigh light extinction at Hopi Point, and one-half at Page. However, during sulfate episodes, the fraction contributed by sulfate increased significantly. For example, during the episode on February 12, sulfate caused 84 percent of the non–Rayleigh extinction in the Glen Canyon National Recreation Area (Page) and 97 percent of non–Rayleigh extinction in Grand Canyon National Park (Hopi Point).

Because the average relative humidity during WHITEX was relatively high, approximately 60 percent, water associated with sulfate and nitrate doubled the light scattering efficiency of these aerosols, from 2.5 m^2/g to 5 m^2/g. Only elemental carbon is more efficient in extinguishing light than sulfate. Its extinction efficiency was estimated to be 9 m^2/g. Scattering efficiencies for organics, fine soil, and coarse mass were estimated to be 4, 1.25, and 0.45 m^2/g, respectively.

9.4 Attribution of Regional Sulfur and Visibility Impairment

The aerosol attribution component of WHITEX was designed to evaluate the feasibility of attributing the emissions of a single source (in this case, NGS) to ambient aerosol concentrations

at a number of receptor sites. The primary receptor sites were Grand Canyon and Canyonlands National Parks and Glen Canyon National Recreation Area (Page).

Several quantitative and qualitative analysis techniques were used to gain insight into the contribution of NGS to ambient aerosol and the performance of the individual receptor modeling techniques. These techniques include:

- Emissions. The relative source strength of NGS compared to other sources in the region and the location of NGS and other regional emissions relative to key receptor sites.
- Trajectory and streakline analysis. The probability was examined that the predicted presence of NGS or other source emissions is coincident with elevated ambient sulfur concentrations or is due to random processes.
- Spatial and temporal patterns in visibility-reducing aerosol concentrations. Spatial patterns in aerosol concentrations as a function of time are examined qualitatively and quantitatively through empirical orthogonal function analysis.
- Synoptic meteorological. Analysis of the synoptic climatology helps to understand the origin of stagnation periods and yields insight into why pollutants were transported along various pathways.
- Deterministic wind field modeling. Model simulations are used to help understand how pollutants can be transported along various pathways and to assist in building conceptual models of physio-chemical processes associated with observed aerosol concentrations and visibility impairment.
- Tracer mass balance regression. As a special case of the general mass balance (GMB) equation, the variation of sulfur and natural or artificial tracers as a function of time were used to attribute emissions.
- Differential mass balance. As a second special case of the GMB formalism, the ambient concentration of a unique tracer, CD_4, was used to estimate dispersion and deterministic model calculations are used to calculate conversion and deposition from estimated plume age.
- Chemical mass balance. As a third special case of the GMB, the chemical mass balance formalism was used to estimate source contributions of primary aerosol species and to set an upper bound on NGS contributions.

9.4.1 Emissions Analysis

Emission inventories and maps indicate that NGS is the largest single point source of SO_2 emissions in the vicinity of Grand Canyon National Park. The sources within approximately 300 km of the Grand Canyon in rank order of estimated 1987 SO_2 emissions are NGS, 163 tons/day; San Juan, 116; Four Corners, 106; Mohave, 52; and Cholla, 45; all coal-fired power plants within the Colorado River basin. Also within the Colorado River drainage are other large coal-fired power plants, including the Huntington Canyon, Hunter, Hayden, Craig, Jim Bridger, and Naughton power plants. However, these sources are much more distant than the others.

The power plant emissions previously mentioned are dwarfed by the emissions from copper smelters during 1987. The largest copper smelters at that time were San Manuel, 480 tons/day; Nacozari, 380; and Cananea, 240, the first being in southern Arizona and the other two being in northern Mexico. The copper smelters are more distant and are not located within the Colorado

River Basin. These sources are south of the Colorado Plateau and the elevated Mogollon Rim, so that elevated terrain would tend to block southerly flows of stable air masses from the copper smelter region.

Although the emission inventory alone does not provide quantitative attribution information, one would expect that NGS could contribute significantly to air quality problems in the winter at the Grand Canyon because (1) the magnitude of NGS emissions, (2) the proximity of these emissions to Grand Canyon, (3) the fact that NGS and the Canyon are in the same air basin, and (4) that downslope drainage flows would funnel NGS emissions directly into the Canyon.

9.4.2 Trajectory And Streakline Analysis

The poor dispersion resulting from light winds and limited mixing heights that is associated with a polar high pressure condition occurred very frequently during the WHITEX experiment. This synoptic meteorological condition occurred on part or all of 41 days out of 49 days of WHITEX. Before and during the worst sulfate episode of the period [Julian Days (Days) 36–44], a polar high pressure condition persisted for nine days. This condition persisted for four days at a time on two other occasions (Days 9–12 and 24–27). Sulfate concentrations in the WHITEX study area were also relatively high during these two periods.

Wind speeds and directions measured at 300, 600, and 1000 meters above ground level (agl) in Page were used to divide the WHITEX study period into 13 time periods of somewhat similar meteorology. Two of these time periods ended with the passage of major fronts that effectively eliminated the regional sulfate that had accumulated in prior days. These major front passages occurred on Days 28 and 44.

Backward air mass trajectories were calculated from the Grand Canyon using National Weather Service upper-air wind data and the ATAD trajectory model. Thus these trajectories were not based on local winds and may not reflect actual transport conditions during the WHITEX experiment. The actual conditions may have been dominated by mesoscale forcing (i.e., drainage, up-slope flows, blocking, and channeling resulting from the complex terrain of the WHITEX region). However, these trajectories were consistent with the meteorological classification of WHITEX time periods that was based on Page winds and synoptic weather maps. These trajectories also suggest the possibility of long-range transport of copper smelter emissions from southern Arizona and northern Mexico into the WHITEX study region on Days 39–40.

Upper-air winds at 300 and 600 *m agl*, measured three times per day at Page during WHITEX, were used as a basis for estimating the position and age of NGS plume parcels throughout the study region and study period. Although these estimates are uncertain because of the assumption of spatially uniform winds, they suggest that NGS plume material was transported frequently toward the major WHITEX receptor sites at Page and Grand Canyon. Because of its proximity to NGS, Page was estimated to be impacted almost every day. Hopi Point was also estimated to be impacted by NGS emissions quite often. Out of 40 days analyzed during WHITEX, the NGS plume was estimated to be impacting Hopi Point on 29 days, or 71 percent of the time. During some of these periods relatively freshly emitted NGS material was estimated to impact Hopi Point, while during other periods, very aged air masses (as old as 5 days) were estimated to be influencing the Grand Canyon. While the average NGS plume age in Page was estimated to be 17 hours, the average NGS plume age at the Grand Canyon was estimated to be nearly two days (46 hours). Because of their proximity to NGS, the Bullfrog and Hite sites were also estimated to be impacted relatively often. The average NGS plume age at these sites was estimated to be 44 hours. Other WHITEX sites more distant from NGS — Green River, Monticello, and Mexican Hat — were

estimated to be impacted much less frequently. The average NGS plume age at these more distant sites was estimated to be 62 to 76 hours.

It might be expected that the prediction of plume position and age based on wind measurements made three times per day at only one site (Page) would be highly uncertain. However, there is remarkable agreement between impacts predicted based on the NGS plume position and observations of elevated CD_4, sulfate, SO_2, and nitrate concentrations. The association between NGS plume "hits" predicted on the basis of trajectory analysis and elevated concentrations was analyzed using a statistical procedure known as multi-response permutation procedures. It was found that the probability that the association between NGS plume "hits" and elevated sulfate could be due to random processes was less than 5 percent. For SO_2 and nitrate the probability of random association was 6 and 10 percent, respectively. Thus, these analyses suggest that the prediction of NGS plume position was not far off target.

9.4.3 Spatial and Temporal Trends in Ambient Concentrations

As previously mentioned, there is a statistically significant correlation between sulfate concentrations and predicted NGS plume "hits." One can also use spatial and temporal patterns of ambient sulfate concentrations to deduce whether this large, local source is a contributor or whether more distant sources contribute.

Over the entire period of the WHITEX study, the average sulfate sulfur concentration was the lowest at Hopi Point (0.17 $\mu g/m^3$) and highest at Page (0.33 $\mu g/m^3$) and at Green River (0.34 $\mu g/m^3$). If the sulfate in the region were due to distant sources, one would expect much more uniform concentrations. Instead, average concentrations vary by over a factor of two. Much larger spatial variations occur during certain episodes. It may not be a coincidence that the highest sulfate concentrations occurred at sites relatively close to uncontrolled sources of SO_2: NGS is near Page and the uncontrolled units at the Huntington Canyon and Carbon power plants are relatively close to Green River. In general, the spatial variation and history of sulfate episodes during WHITEX strongly suggests impacts due to local sources.

A more systematic way of looking at spatial and temporal variation in ambient sulfate concentrations than the case studies and averages previously discussed involves the application of Empirical Orthogonal Function (EOF) analysis. Essentially this technique separates the time/space matrix of ambient concentrations into two sets of matrices, one that is solely a function of space and the other which is solely a function of time. The EOF was applied to sites and time periods for which relatively complete sulfate data were available. Concentrations for a total of 79 12-hour time periods at the following 11 sites were used in the EOF analysis: Canyonlands, Hopi Point, Bullfrog Marina, Page, Green River, Monticello, Mexican Hat, Hite, Bryce Canyon, Navajo National Monument and Wupatki National Monument.

Only two of the unrotated spatial EOF patterns were needed to explain more than 80 percent of the variance in the ambient sulfate data in the WHITEX region. The first, centered on NGS, explains 70 percent of the variance, and the second, with a minimum centered on Bullfrog and Hite and a strong south-to-north gradient, explains 10 percent of the variance. The first pattern (somewhat like a target with NGS as the bulls-eye) is exactly the pattern of sulfate one would expect if NGS were the major contributor during stagnant conditions. Indeed, this EOF is most strongly weighted during the worst sulfate episode (February 11- -14, 1987). This pattern explains 70 percent of the variance in the regional sulfate.

The second EOF has three possible explanations. Its strong south-to-north gradient suggests that when this EOF is positively weighted it could represent sulfate transported from the smelter region to the south. When negatively weighted, the EOF has a maximum at Bullfrog and Hite,

in the middle of the Lake Powell basin. This relative sulfate maximum could result from NGS emissions transported and converted in southwesterly flow or by emissions from the Huntington Canyon, Hunter, and Carbon plants in southerly flow. These three possible contributors to the second EOF pattern are consistent with meteorological analyses. For example, the second EOF is most strongly negatively weighted on February 13, when the emissions from the three northern power plants would most likely be stagnating within the Lake Powell basin. The second EOF is also strongly negatively weighted during the period from January 24 to 28, when NGS emissions are expected to be transported to the northeast. The strongest positive weightings of the EOF occur on January 15 and 16 and February 9 to 11, when transport from the smelter region to the south was identified.

9.4.4 Deterministic Wind Field Modeling

A prognostic meteorological model, based on conservation principles of velocity, heat, mass, and moisture, was exercised over the time period from February 11 to 12. The primary purpose of the wind field modelling was to assist in explaining and development of conceptual models of how material emitted by NGS can be transported towards the Grand Canyon and to assess whether emissions from other coal fired power plants can impact the Grand Canyon region. The model showed that thermally- induced winds associated with the Kaibab Plateau (north rim of Grand Canyon) act to transport NGS emissions toward the southwest and Grand Canyon. Furthermore, the modeling effort showed that locally generated emissions (within 200 km) to the southwest and east of Grand Canyon would not contribute to haze in the canyon but sources to the north of page could. However, a transport time of two days or longer are required under these synoptic regimes.

9.4.5 Tracer Mass Balance Regression (TMBR) Analysis

It is a simple statement of fact that the total ambient concentration of a given species (such as sulfate) is the sum of the concentrations contributed by NGS and by other sources. Since the deuterated methane tracer (CD_4) was unique to NGS, its ambient concentration should correlate with the concentrations of species contributed by NGS. In addition, since the trace metal, arsenic, was below detectable limits in the NGS plume (and presumably from other coal-fired power plants) and arsenic is a known constituent of copper smelter plumes, it was used as a tracer for copper smelters. TMBR analysis was performed to explore the relationship between measured ambient concentrations of sulfur species and CD_4. The portion of the ambient sulfur concentration that correlates with tracer is likely to be due to NGS emissions, while the portion that correlates with arsenic is likely to be due to smelters. That portion that is not correlated with either tracer (the intercept term) is interpreted as background from other sources (e.g., other power plants). Another natural tracer, selenium, is associated primarily with coal combustion; therefore, this tracer was used to attribute sulfate to the general category of coal fired power plants.

TMBR analysis were carried out separately for total sulfur and sulfate sulfur. For some analysis, the relative humidity was factored in to account for sulfur oxidation which is faster in the aqueous phase (which is associated with the high-water content aerosols and fog and cloud droplets that are likely to exist at high relative humidities).

All TMBR regressions were carried out using both ordinary least squares (OLS) regression and orthogonal distance regression (ODR). ODR explicitly takes into account the uncertainties in both the dependent and independent variables. ODR gives more weight to samples with small uncertainties. Intercepts were forced to be positive for all ODR regressions.

Since the sulfur to CD_4 emission rate at NGS were not kept constant, the CD_4 data was scaled to a constant 2.5 mg/MWe-h rate from the known and time-varying tracer emission rate and power generation at NGS. In addition, the CD_4 data was scaled to account for the estimated travel time from NGS to the receptor of interest (e.g., Hopi Point). Thus, if, for a given sample, the plume age is estimated at 48 hours, the tracer emission rate and NGS load for the period 48 hours prior were used for scaling purposes.

TMBR regressions were attempted first using only the scaled SCD_4 concentration as an independent variable. However, these regressions explained very little of the sulfate variation at Hopi Point. Additional TMBR regressions were performed multiplying the SCD_4 concentration by relative humidity to account for faster aqueous-phase oxidation at higher humidities and by adding arsenic as another independent source variable. By so doing, the variance explained increased to 70 percent and above ($R^2 > 0.70$). Thus, it appears that ambient sulfate concentrations are a strong function of humidity as well as the concentrations of the tracers for NGS and smelters.

Best estimates of source attribution of sulfates at Hopi Point for those days that CD_4 data were available are: NGS, 70±4 percent; smelters, 30±3 percent; and all other sources, 0±1 percent. Results are based of ODR regressions. The quoted uncertainties are one standard error on either side of the mean. The error incorporates measurement uncertainty as well as uncertainty in the regression coefficients. Using all TMBR results with $R^2 > 0.7$ and physically reasonable coefficients and intercepts, the average attribution of ambient sulfate at Hopi Point over all days during WHITEX for which CD_4 data are available is as follows: NGS, 62-73 percent; smelters, 23-30 percent; and all other sources, 0-14 percent. When regressions were repeated by substituting selenium (a tracer for all power plants) for CD_4 (a tracer for NGS), comparable results were obtained, suggesting that NGS contributes most of the ambient sulfate contributed by all power plants at Hopi Point. Best estimates of coal fired power plants other than NGS contribution to sulfate at Hopi Point is approximately 5 percent. The period of highest smelter contribution was February 9 and 10, which is consistent with the insight gained from both the meteorological analysis and the EOF analysis.

Additional TMBR regressions were attempted for total sulfur, nitrate, organic carbon, and light-absorbing carbon. Variance of total sulfur explained by CD_4 was only 30 percent, and variance of nitrate explained was only 20 percent. Organic carbon and light-absorbing carbon were totally uncorrelated with tracer, as one might expect since these species are not emitted from NGS.

A similar analysis was carried out for Glen Canyon National Recreation Area (Page, Arizona). At Page the TMBR analysis did not reveal any other sources of sulfate than coal fired power plants, specifically NGS. Furthermore no simple transformation of independent variables involving RH was found that would better account for variance explained than the variable itself. However, the analysis did disclose four data points (JD 42.8–44.3) that fell outside the general relationship between CD_4 and sulfate. On JD 42.8–44.3 the sulfate to CD_4 ratio was high suggesting either contributions from sulfate sources other than NGS, accelerated sulfur dioxide to sulfate oxidation or an aged NGS air mass. Independent analyses of each of these possibilities suggest that the elevated sulfate is most likely associated with accelerated oxidation of NGS emitted sulfur dioxide. If it is assumed that sulfates on JD 42.8–44.3 are primarily associated with NGS it is estimated that for those days for which there is CD_4 data NGS contributed 75 ± 2 percent of the observed sulfate. On the other hand, if it is assumed that a portion of the observed sulfate (determined by subtracting predicted NGS sulfate from observed sulfate) is associated with other sulfate sources NGS is estimated to contribute 62 ± 5 percent of the observed sulfate. Relationships between CD_4 and other aerosols was found to be weak or nonexistent implying NGS did not contribute to their ambient concentrations.

9.4.6 Differential Mass Balance (DMB) Analysis

Differential mass balance (DMB) analysis calculates the fraction of ambient sulfur at a given receptor attributed to NGS by multiplying the measured CD_4 concentration by the ratio of sulfur to tracer emissions at the stack, multiplied by a factor that accounts for the amount of sulfur deposited and converted in the estimated travel time from NGS to the given receptor.

A literature survey was conducted to determine the rates of SO_2 and sulfate deposition. Quite a wide range of values was identified. The deposition velocities for SO_2 measured in prior studies ranged from 0.1 to 2.3 cm/s, with a median of 0.7 cm/s. The deposition velocities measured for sulfate ranged from 0 to 0.9 cm/s, with a median of 0.2 cm/s.

A literature survey was also conducted to determine likely SO_2 oxidation rates. The survey indicated that gas-phase oxidation in winter is likely to be very slow, less than 0.2 percent per hour. However, aqueous-phase oxidation (in aerosol, fog, and cloud droplets) can be very rapid. Major oxidants in the aqueous phase appear to be hydrogen peroxide, ozone, and oxygen (catalyzed by manganese and iron, both plentiful in power plant plumes). The literature survey definitely confirmed the finding previously mentioned that oxidation rates appear to be a function of relative humidity. There is a clear theoretical and empirical basis for such humidity-dependent oxidation. However, the literature review supported a wide range of plausible oxidation rates as it did for deposition rates.

Because the literature survey could not support a single set of deposition and oxidation rates, a sensitivity analysis was performed over the wide range of literature values of deposition and oxidation rates. A total of nearly 4000 different combinations of SO_2 deposition, sulfate deposition, and oxidation rates were tested. The variance of ambient sulfate at Hopi Point explained by each combination was tabulated. The combinations of parameters providing $R^2 > 0.7$ were deemed to be reasonable; there were a total of more than 400 such combinations. The highest R^2 was achieved with SO_2 and sulfate deposition velocities of 0.91 and 0.14 cm/s and an SO_2 oxidation rate of 1.7 percent per hour per fractional humidity (i.e., 1.7 %/hr at 100% RH).

The average NGS contribution to ambient sulfate at Hopi Point during WHITEX was calculated to 68 percent based on the parameters with the highest R^2. For all combinations of parameters yielding $R^2 > 0.7$, NGS average contribution ranged from 43 to 96 percent. Additional sensitivity analyses were carried out with the optimized deposition and oxidation parameters to test the sensitivity to assumptions regarding the plume age. The use of the average of the lower and upper bound of the estimated plume age for Hopi Point yielded the most physically realistic estimates of the average contribution of NGS to SO_2 and sulfate: 83 and 73 percent, respectively.

Additional DMB analyses were conducted for Page. The analyses suggested, within the considerable uncertainty in estimating plume age at Page, that essentially all of the sulfur in Page is attributable to NGS. The most physically realistic estimates of NGS contributions to SO_2 and sulfate in Page were obtained when the average of the lower and upper bound of NGS plume age was used in the DMB calculations.

9.4.7 Attribution of Visibility

The light extinction attributable to scattering by NGS sulfate, scattering by other sulfate, extinction by carbonaceous material (scattering by organics plus absorption by light absorbing carbon), scattering by natural particulates (fine soil + coarse mass), and scattering by nitrate was calculated for both Hopi Point and Page. Reconstructed extinction is defined as the sum of these components. The extinction efficiencies for each chemical species were based on consensus literature values, and the portion of the sulfate due to NGS was determined by the results of TMBR. Some of the extinc-

tion attributed to carbons and nitrates, may be due to NGS emissions also, however apportionment of these species was not possible with TMBR. Uncertainties in the fractions are one standard deviation from the mean based on the measurement uncertainties in the particulate concentrations and relative humidity, the standard errors of the TMBR regression coefficients, and the uncertainties in the extinction efficiencies.

The mean non-rayleigh reconstructed extinction at Hopi Point is 0.0121 ± 0.0009 1/km. The mean fraction of this due to NGS sulfate is 42 ± 13 percent. The mean fraction due to sulfate from other sources is 21 ± 2 percent. The time period with the highest reconstructed extinction (0.073 ± 0.002 1/km) at Hopi Point was JD 42.8 when the fraction due to NGS sulfate was 59 ± 18 percent and the fraction due to other sulfate was 35 ± 27 percent.

At Page, NGS sulfate was calculated in TMBR by two different methods. The first method, assumed that all sulfate not associated with the intercept was NGS sulfate. The second method assumed that all sulfate not associated with the regression coefficient for SCD_4 was due to other sources. The reconstructed extinction using both methods is 0.0253 1/km. The uncertainty for method 1 is 0.0009 1/km and for method 2 is 0.0011 1/km. Using method 1, the mean fractions of the reconstructed extinction at Page are 38± 14 percent NGS sulfate and 8 ± 2 other sulfate. The means for method 2 are 24 ± 8 percent NGS sulfate and 22 ± 2 percent other sulfate.

The time period with the highest extinction at Page was JD 44.3, when the reconstructed extinction by both methods 1 and 2 was 0.082 1/km with the uncertainty for method 1 being 0.007 1/km and for method 2 being 0.009 1/km. Using method 1 the attribution of non-Rayleigh light extinction was 62 ± 9 percent NGS sulfate and 4 ± 4 percent other sulfate. Using method 2 the attribution was 34 ± 5 percent NGS sulfate and 33 ± 11 percent other sulfate.

It should be noted that much of the uncertainty in the sulfate and nitrate portions of the light extinction budgets is due to uncertainty in the relative humidity measurements. Therefore, the uncertainties in the fractions of extinction due to these components are not fully independent. For example if the RH value were underestimated, then the extinction due to NGS sulfate, other sulfate, and nitrate would all be underestimated.

9.4.8 Synthesis

Differential Mass Balance and Tracer Mass Balance Regression are the two receptor oriented modeling approaches that were successfully exercised to yield quantitative attribution of sulfate aerosol concentrations. Chemical Mass Balance was successfully used to attribute primary aerosols to respective sources. Empirical orthogonal function analysis, although quantitative in nature, does not explicitly quantify the contribution of a source to aerosol concentrations to a source in its present formulation. It is primarily used to corroborate and interpret DMB and TMBR results. Likewise, trajectory and streakline analysis are used to evaluate whether or not the DMB and TMBR results are reasonable and to yield insight into the physical and chemical mechanisms that are associated with spatial and temporal patterns of sulfate concentrations.

Figure 9.1 shows a scatter plot of NGS sulfate concentrations at Hopi Point that are predicted by the TMBR and DMB model. Estimated uncertainties are also shown on the graph. The orthogonal departure regression (ODR) calculation yields a slope of 0.99 and an intercept of -0.001 with an R^2=0.90. The agreement between these two independent modeling approaches is better than might be expected. The TMBR approach implicitly assumes that transport times, deposition rates are constant and that SO_2 to SO_4 oxidation is proportional to RH while the DMB calculation explicitly accounts for all these factors. In both modeling approaches dispersion is accounted for by use of ambient CD4 concentrations. Apparently the variation in sulfate concentration resulting

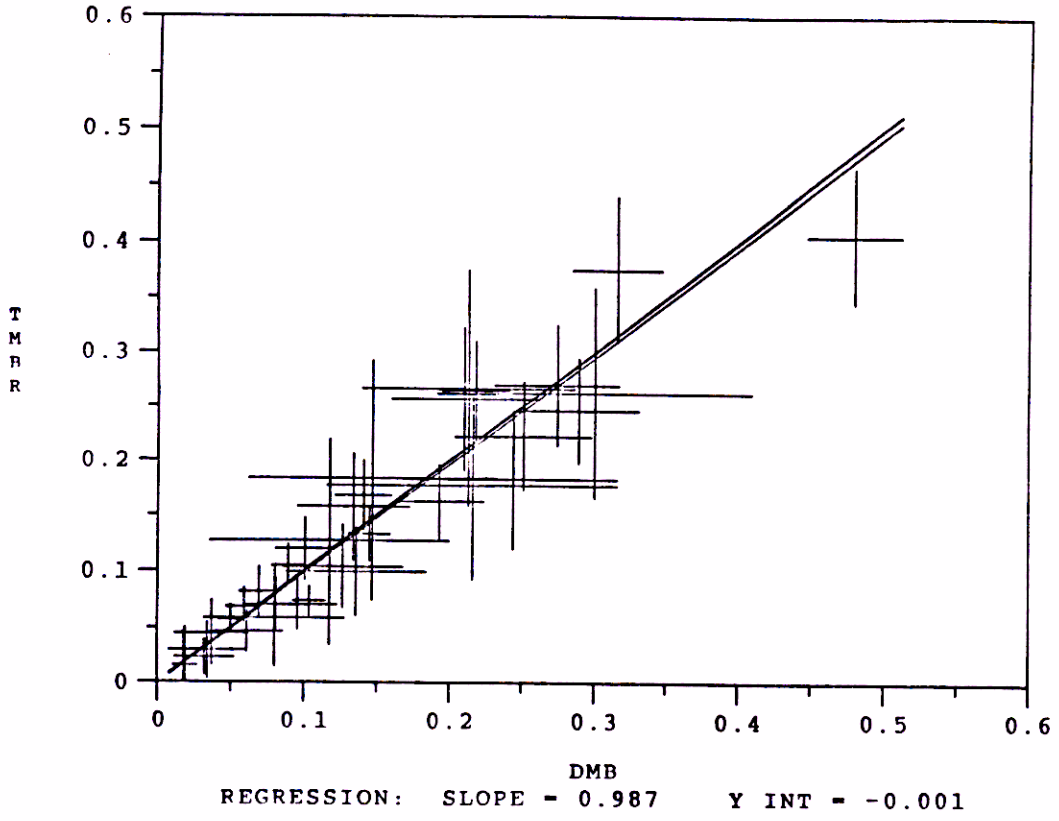

Figure 9.1: Scatter plot of sulfate sulfur ($\mu g/m^3$) due to NGS at Hopi Point as calculated by TMBR and DMB. The lines shown are the 1:1 line and the ODR regression line.

from the RH dependent SO_2 to SO_4 oxidation dominates any uncertainty associated with imprecise knowledge of deposition rates or transport times.

TMBR and DMB attribution results are very similar. For those days that CD_4 data were available the TMBR best estimate of NGS average contribution to sulfate at Hopi Point is 73 $\pm$ 4 percent while the DMB calculation yielded 68 $\pm$ 3.5 percent. The quoted uncertainties are one standard error on either side of the mean. For the TMBR analysis the standard error incorporates uncertainty in the regression coefficient as well as measurement error while the DMB uncertainty is only the result of measurement uncertainty. The best estimate of uncertainty in the DMB calculation associated with imprecise knowledge of variables such as deposition, conversion and travel time is 68 $\pm$ 28 percent. At Page the results from the two techniques are again quite similar. Best estimate of NGS contribution to sulfate are 75 $\pm$ 2 percent while the DMB calculation suggests NGS contribution to sulfate is between 60 and 100 percent depending on whether the average minimum air mass age is assumed to be 6 or 12 hours. It is emphasized that quoted uncertainties are averages of uncertainties associated with each sampling period. Uncertainties for any giving sampling period can be quite high. Furthermore, only uncertainties associated with measurement error and imprecise knowledge of physical variables is addressed. Uncertainty as to the appropriateness of the model used was not addressed.

Both DMB and TMBR suggest that attribution of a secondary aerosol, in this case sulfate, to a specific source (NGS) can be done with a fair amount of certainty. The more qualitative analysis techniques are supportive of this presumption. The exercising of the CMB equations was not

successful in directly attributing sulfate, however, results were consistent with TMBR and DMB. CMB analysis suggests that the only two sources associated with SO_2 emissions were coal fired power plants and copper smelters. Furthermore the time periods where CMB analysis predicted copper smelter and power plant contributions to primary aerosols were the same time periods that TMBR attributed secondary sulfate to these two sources.

A cursory examination of emission strength as a function of distance from Grand Canyon show that NGS is the largest coal fired power plant within hundreds of kilometers of Grand Canyon with copper smelters being a significant SO_2 source that is approximately 300 km to south of Grand Canyon. Based just on emission strengths alone one might expect a large NGS contribution to sulfate at Grand Canyon. The EOF analysis which incorporates spatial and temporal trends show that a sulfate concentration field with highest sulfate concentrations found at NGS and decreasing as one moves radially out from NGS explains 70 percent of the variance in the concentration field. This spatial concentration gradient is predominant under stagnant meteorological conditions. Concentration fields of this nature under stable meteorology are suggestive of NGS emissions as being a significant contributor to ambient sulfate concentrations. Furthermore the strong correlation between predicted "hits" of the NGS plume and all time periods with elevated sulfate suggest a significant contribution to sulfate concentrations by NGS. Finally, deterministic wind field modelling tended to confirm conceptual models suggested by TMBR and DMB models and especially ideas developed from the EOF analysis. Release of particles at NGS plume height into modeled wind fields on February 11 and 12 resulted in transport of those particles into Grand Canyon region.

Finally, based on the results of TMBR, the fraction of the mean non-Rayleigh light extinction at Hopi Point due to sulfate from NGS was 42 $\pm$ 13 percent. For the time period with the highest light extinction the fraction due to NGS was 59 $\pm$ 18 percent.