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HAZE IN THE GRAND CANYON

An Evaluation of the Winter Haze Intensive Tracer Experiment

Committee on Haze in National Parks and Wilderness Areas

Board on Environmental Studies and Toxicology
Board on Atmospheric Sciences and Climate

Commission on Geosciences, Environment, and Resources
National Research Council

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*This study was begun under the Commission on Physical Sciences, Mathematics, and Resources, whose members are listed in Appendix 4, and completed under the successor Commission on Geosciences, Environment, and Resources.

Preface

Many delightful experiences can be enjoyed in our nation's numerous national parks and wilderness areas, but among the finest are the beautiful views of nature found in these locations. Particularly spectacular are the often distant and majestic scenes of mountains, deserts, plains, and ocean. Our concern for maintaining the clarity of views in these areas is reflected in the Clean Air Act, which specifically addresses the protection of visibility in our national parks and wilderness areas. Early in 1990, the National Research Council (NRC) established the Committee on Haze in National Parks and Wilderness Areas to address issues related to visibility degradation in these protected regions. In particular, the committee was asked to consider the relative importance of human-derived and natural emissions that contribute to visibility reduction in these locations and to evaluate possible source-control approaches. As part of its charge, the committee was also asked to evaluate a recent scientific study by the National Park Service (NPS) of visibility degradation and its causes in one of our most beautiful national parks, Grand Canyon. This publication is the committee's evaluation of the NPS report on the Winter Haze Intensive Tracer Experiment (WHITEX) and its conclusion that the Navajo Generating Station (NGS) contributed to wintertime visibility impairment in Grand Canyon National Park during the study.

The committee's task was not an easy one. Source apportionment is a rather inexact but very complex component of the atmospheric sciences. New techniques and approaches are constantly being designed and tested, and personal judgment and experience often play significant roles in evaluation processes. However, I have never worked with a committee more dedicated to the development of a fair, objective, and honest evaluation of what has become a controversial issue. Everyone involved in this NRC project, including the sponsoring organizations, cooperated in every way possible.

The committee met at Grand Canyon National Park from March 28-31, 1990. We were provided with extensive written and oral information by federal personnel and other project sponsors, including the National Park Service, the Bureau of Reclamation, the Department of the Interior's Office of Environmental Quality, the Department of Energy, the Environmental Protection Agency, the Forest Service, and the Arizona Salt River Project (operators of NGS) and their consultants. We were also given an extensive tour of the NGS and of the atmospheric monitoring station at Hopi Point in Grand Canyon National Park. After this meeting, the federal liaison group—representing the sponsoring agencies—and the Arizona Salt River Project continued to provide the committee with information promptly whenever it was requested. This was greatly appreciated. In addition to the committee's formal meetings, committee members and NRC staff spent many hours in conference calls and in individual conversations.

The committee's heartfelt thanks must go to the NRC staff who devoted themselves so thoroughly to this report. Dr. James J. Reisa, the director of the Board on Environmental Studies and Toxicology, and Dr. Robert Smythe, the program director, provided us with guidance, perspective, and oversight. The project director, Kathleen J. Daniel, worked closely with committee members through all phases of the report preparation. Her enthusiasm, knowledge of the field, sense of humor, commitment to a quality report, and true concern about the issues being addressed played a major role in the committee's efforts, and in particular, in our development of a consensus on this controversial issue. We also thank staff member Raymond Wassel, who contributed significantly to the committee's efforts, and Felita Buckner, Boyce Agnew, and Sandi Fitzpatrick, who worked closely and effectively with the committee throughout report preparation and production. Finally, Lee Paulson took our often-tangled prose and provided clear renditions and editorial revisions.

The committee hopes this report will provide useful suggestions and guidance as the nation continues efforts to protect and preserve the natural visibility in our national parks and wilderness areas for ourselves and future generations.

Robert A. Duce
Chairman
October 3, 1990

Contents

Executive Summary

BACKGROUND

The Grand Canyon is one of the most spectacular natural sights on earth. Approximately 4 million visitors travel to Grand Canyon National Park (GCNP) each year to enjoy its majestic geological formations and intensely colored views. However, visibility in GCNP can be impaired by small increases in concentrations of fine suspended particles that scatter and absorb light; the resulting visibility degradation is perceived as haze. Sulfate ($SO_4^=$) particles—largely the result of the atmospheric transformation of sulfur dioxide (SO_2) emissions from anthropogenic sources—are a major factor in visibility impairment at Grand Canyon in summer and winter.

Many wintertime hazes at GCNP are believed to result from the accumulation of emissions from local sources during conditions of air stagnation, which occur more frequently in winter than in summer. In January and February 1987, the National Park Service (NPS)—the managing agency for the GCNP—carried out a large-scale experiment known as the Winter Haze Intensive Tracer Experiment (WHITEX) to investigate the causes of wintertime haze in the region of GCNP and Canyonlands National Park. The overall objective of WHITEX was to assess the feasibility of attributing visibility impairment in specific geographic regions to emissions from a single point source. The experiment called for the injection of a tracer, deuterated methane (CD_4), into one of the stacks of the Navajo Generating Station (NGS), a major coal-fired power plant located 25 km from the GCNP boundary and 110 km northeast of Grand Canyon Village. A network of field stations was established in the vicinity—mostly to the northeast of GCNP and NGS—to measure CD_4 concentrations, atmospheric aerosol and optical properties, and other chemical and physical attributes.

During some haze episodes, significant concentrations of CD_4 were detected at the Hopi Point sampling station on the south rim of the Grand Canyon near Grand Canyon Village to the southwest of NGS. The NPS analyzed data from WHITEX and recently issued a final report concluding that NGS contributed to wintertime visibility impairment in the GCNP during the study period. The report asserted that NGS was responsible for approximately 70% of the mean particulate $SO_4^=$ and approximately 40% of the mean aerosol-related light extinction for selected wintertime periods of haze at the Hopi Point sampling station. In response to the NPS-WHITEX report, the U.S. Environmental Protection Agency (EPA) published a proposal to attribute visibility impairment in the GCNP to NGS and took steps to propose that the level of allowable SO_2 emissions from NGS be reduced by 90%.

THE NATIONAL RESEARCH COUNCIL STUDY

This evaluation of WHITEX was prepared by the Committee on Haze in National Parks and Wilderness Areas, which was convened in February 1990 by the National Research Council's Board on Environmental Studies and Toxicology in collaboration with the Board on Atmospheric Sciences and Climate of the Commission on Geosciences, Environment, and Resources. The committee comprises members appointed for their expertise in meteorology, atmospheric chemistry, atmospheric aerosols, air pollution monitoring and modeling, statistics, environmental engineering, control technology, and environmental law and public policy.

The committee's overall charge is (1) to develop working principles for assessing the relative importance of anthropogenic emission sources that contribute to haze in Class I areas (which include many national parks and wilderness areas) and for assessing alternative source control measures and (2) to recommend strategies for improving scientific understanding and technical information on relative source contributions to haze formation, regional and seasonal factors affecting haze, relevant air quality models, and various emission control measures. The committee's work is sponsored by the U.S. Department of the Interior (National Park Service, Bureau of Reclamation, and Office of Environmental Quality), the U.S. Department of Energy, the U.S. Environmental Protection Agency, and the Arizona Salt River Project (SRP). The committee's final report, which will address this charge, will be issued in 1991.

In addition to the final report, the committee was also asked to provide this special report evaluating WHITEX, the recent site-specific study conducted by NPS. This report evaluates the scientific evidence relevant to EPA's recently proposed finding that NGS contributes to "impairment of visibility" in GCNP. Specifically, the committee was asked to review NPS data and analyses upon which the EPA determination was based and other data and analyses related to source attribution for Grand Canyon haze. It was also asked to evaluate the contribution of the WHITEX study toward the science of source apportionment. The committee reviewed the December 1989 NPS-WHITEX report, other relevant published materials, and some unpublished information. In March 1990, the committee conducted site visits to the GCNP and NGS near Page, Arizona, and heard technical presentations from NPS, SRP, and their scientific consultants. This information was used as part of the basis for the committee's evaluation.

The committee based its evaluation solely on the scientific aspects of WHITEX. It did not consider whether or how EPA should regulate NGS.

QUALITATIVE ASSESSMENT

On the basis of the data presented in the NPS-WHITEX report, the committee concludes that, at some times during the study period, NGS contributed significantly to haze in GCNP. The committee bases this assessment on evaluations of meteorological, photographic, chemical, and other physical evidence. The committee's conclusion is supported by the following qualitative evidence: (1) the haze episodes (periods when visibility was particularly poor) observed during WHITEX occurred under conditions of air stagnation, when sulfur from local sources would be expected to accumulate; (2) $SO_4^=$ aerosol was a significant contributor to haze at Hopi Point during periods when visibility was particularly poor and when CD_4 was detected; (3) NGS is a large source of SO_2 emissions near GCNP and it could potentially account for the total sulfur (SO_2 and $SO_4^=$) observed at Hopi Point during some haze episodes; (4) meteorological analyses and photography indicate air movement from NGS to GCNP during some haze episodes; (5) significant quantities of CD_4 released from NGS were observed at Hopi Point; and (6) the presence of clouds and fog in the vicinity of GCNP and NGS during haze episodes would accelerate the conversion of NGS SO_2 to form $SO_4^=$ aerosol.

The detection of CD_4 at Hopi Point is an unambiguous indicator that air parcels containing NGS emissions did impinge on the GCNP on several occasions. The use of CD_4 in WHITEX was an innovative and important step forward in the field of source attribution, and NPS and the WHITEX team are to be commended for including this tracer in WHITEX.

QUANTITATIVE ASSESSMENT

The NPS-WHITEX report based its quantification of the NGS contribution to $SO_4^=$ aerosol at Hopi Point on two empirical models—Tracer Mass Balance Regression (TMBR) and Differential Mass Balance (DMB)—both of which are based on multiple linear regression techniques. Although multiple linear regression has been used before to apportion primary (directly emitted as particles) source contributions to ambient aerosol mass, there has been little verification of its applicability in the case of a predominantly secondary (particles formed in the atmosphere) species, such as $SO_4^=$. Moreover, the committee identifies problems in the implementation and interpretation of multiple linear regression in the WHITEX analysis: (1) satisfactory tracers were not available for all major sources; (2) the interpretation did not adequately account for the possible covariance between NGS contributions and those from other coal-fired power plants in the region; and (3) both models employ inadequate treatment of sulfur conversion, which is an important controlling factor in the formation of haze at GCNP.

Therefore, the committee concludes that WHITEX did not quantitatively determine the fraction of $SO_4^=$ aerosol and resultant haze in CGNP that is attributable to NGS emissions. The report did not adequately quantify the sensitivity of the analyses to departures from model assumptions, nor did it establish an objective and quantitative rationale for selecting among various statistical models. The conceptual framework for DMB involved physically unrealistic simplifications, the effect of which on quantitative assessments was not addressed. The data base contained weaknesses; especially damaging were the absence of measurements below the rim of the Grand Canyon and the paucity of background measurements. In addition, the background measurements that were made were not adequately incorporated into the data analyses.

ESTIMATES OF THE RANGE OF POSSIBLE IMPACTS FROM NGS

The committee used the WHITEX data obtained during a haze episode in GCNP to estimate the ranges of possible impacts from NGS. These estimates consist of a series of mass-balance calculations made on the basis of simple, but reasonable, assumptions. These calculations were made for illustrative purposes; they cannot, in themselves, be used to quantify the impacts of NGS on visibility in GCNP, in part because measurements needed to confirm some of the assumptions were not made during WHITEX. The committee's analysis indicates that NGS sulfur emissions are sufficiently large to account for even more than the total sulfur concentration measured in GCNP. However, the actual impact of NGS emissions on haze in GCNP depends on the rate of conversion of SO_2 to $SO_4^=$. The extent of conversion is extremely sensitive to meteorological conditions and the availability of oxidants; the extent could range from a very small percentage to nearly 100%. Conversion rates would tend to be high during cloudy and foggy conditions, such as those observed during WHITEX haze episodes. Under these conditions, NGS emissions could produce $SO_4^=$ concentrations similar to those measured in GCNP. However, the WHITEX data also show that there are important sulfur sources in addition to NGS that appear to contribute to regional background $SO_4^=$ aerosol levels. These additional sources evidently account for a significant fraction of the haze observed in GCNP. Thus, if NGS emissions were controlled, then wintertime haze at GCNP would most likely be reduced, but not eliminated.

THE COMMITTEE'S CONCLUSIONS IN PERSPECTIVE

The committee cautions that its conclusions do not resolve whether EPA should require NGS to install the best available retrofit technology (BART). First, the committee's conclusions are not binding on EPA or any other government agency. Second, even if accepted by EPA, the committee's conclusions would not dictate a particular result to EPA's rule making. Section 169A of the Clean Air Act generally requires the installation of BART on any "major stationary source" built after 1962 if that source "emits any air pollutant which may reasonably be anticipated to cause or contribute to any impairment of visibility" in a listed Class I area, such as GCNP. The phrase "may reasonably be anticipated" suggests that Congress did not intend to require EPA to show a precise relationship between a source's emissions and all or a specific fraction of the visibility impairment within a Class I area. Rather, EPA is to assess the risk in light of policy considerations regarding the respective risks of overprotection and underprotection. These considerations transcend scientific issues and are, therefore, outside this committee's purview.

Haze in the Grand Canyon

An Evaluation of the Winter Haze Intensive Tracer Experiment

Haze in the Grand Canyon: An Evaluation of the Winter Haze Intensive Tracer Experiment

BACKGROUND

The Grand Canyon is one of the most spectacular natural sights on earth. The diversity and color of the geological formations are extraordinary, and the geographical scales are immense. In some places the canyon is 1.6 km deep and 30 km wide, and panoramic views typically extend to over 100 km. The aesthetic effect of the canyon depends on many aspects of visibility in addition to distance: the luminous quality of the air; the interplay of color, light, and shadow; the colossal scale; and the clarity of the view. These magnificent and unique qualities attract approximately 4 million visitors to Grand Canyon National Park (GCNP) each year.

The atmosphere in the Grand Canyon is generally very clear, and under ideal "blue-sky" conditions (particle-free, also known as Rayleigh, conditions), visibility approaches the ultimate value of 400 km. However, even small increases in aerosol[1] concentrations can change the appearance of views—dulling the colors, shifting the color spectrum, reducing the contrasts, and decreasing the visual range (see Appendix 1).

When visibility is impaired in the Grand Canyon, suspended fine particles in the air are usually the major cause. Fine particles, which typically are 0.1- to 1.0-μm diam., scatter and absorb light, and the viewer perceives haze. In the Grand Canyon region, sulfates ($SO_4^=$) account for approximately one-third to one-half of the fine-particle-mass concentration in the air. $SO_4^=$ plays a major role in visibility degradation in summer and winter (NPS, 1988; Trijonis et al., 1989); $SO_4^=$ in this area is predominantly the result of atmo-

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[1] An aerosol is strictly defined as suspension of particles in a gas. In this report, "aerosol" is used synonymously with "particle," in conformity with common usage in the atmospheric chemistry literature (e.g., see Buat-Ménard et al., 1989, p. 252).

spheric transformation of sulfur dioxide (SO_2) emissions from anthropogenic sources. Wintertime hazes are believed to result from the accumulation of emissions from local sources during conditions of air stagnation; such conditions occur more frequently in winter than in summer.

The National Park Service (NPS)—the managing agency for the GCNP—believes that the Navajo Generating Station (NGS) is an important source of $SO_4^=$ aerosols that cause wintertime haze in GCNP. NGS is a coal-fired power plant placed in operation in stages between 1974 and 1976. It is owned jointly by the U.S. Department of the Interior's Bureau of Reclamation, the Salt River Project (SRP),[2] and several electric utilities. NGS is located approximately 25 km from the GCNP border at its closest point and about 110 km northeast of the Grand Canyon Village tourist area near Hopi Point (Fig. 1). NGS has a generating capacity of 2,400 MW gross (2,250 MW net), which makes it one of the largest power plants in the United States west of the 100th meridian.

In January and February 1987, a large-scale experiment was carried out by NPS to investigate the causes of wintertime haze in the region between Grand Canyon and Canyonlands National Park. The Winter Haze Intensive Tracer Experiment (WHITEX) was a research project sponsored by a consortium of utilities and governmental agencies called SCENES (Subregional Cooperative Electric Utility, Department of Defense, National Park Service, and Environmental Protection Agency Study). The original objectives of WHITEX were (1) to evaluate an empirical approach for assessing the relative contribution of an isolated source to aerosols at specified locations and (2) to determine the relative contributions of individual aerosol constituents to haze at these locations (SCENES, 1987). The initial plan was for "a scoping study to investigate the feasibility of more extensive source attribution studies in future years" (SCENES, 1987). The original experimental design focused on the area between NGS and Canyonlands National Park, because this region was believed to be most susceptible to effects from NGS emissions due to the presumed prevailing wind flow toward the east. NPS added additional sampling sites in northeastern Arizona and southeastern Utah, including one at Hopi Point on the south canyon rim near Grand Canyon Village to the southwest of NGS.

Except for the Hopi Point site, all of the NPS sampling sites were north and east of GCNP (Figs. 1 and 2). Measurements included atmospheric optical properties, particle concentrations and composition, SO_2 concentrations,

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[2] The SRP, a political subdivision of Arizona (akin to a special district), supplies consumers with water and electrical power. The project is the operating agent of the NGS.

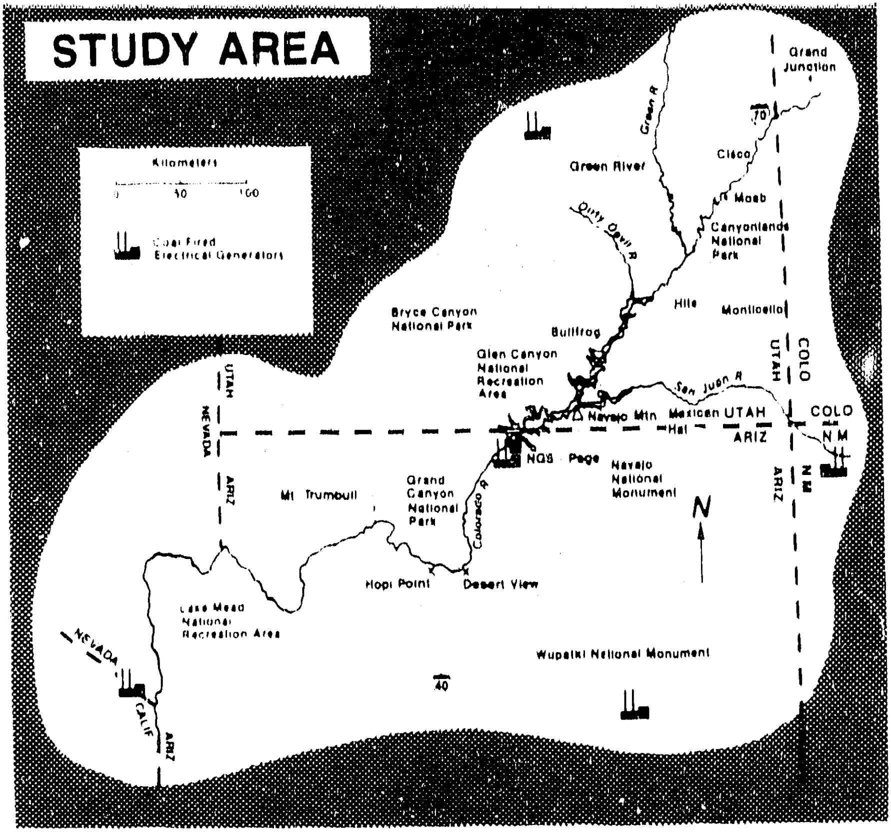

FIGURE 1 SCENES WHITEX study area. Source: Adapted from NPS, 1989.

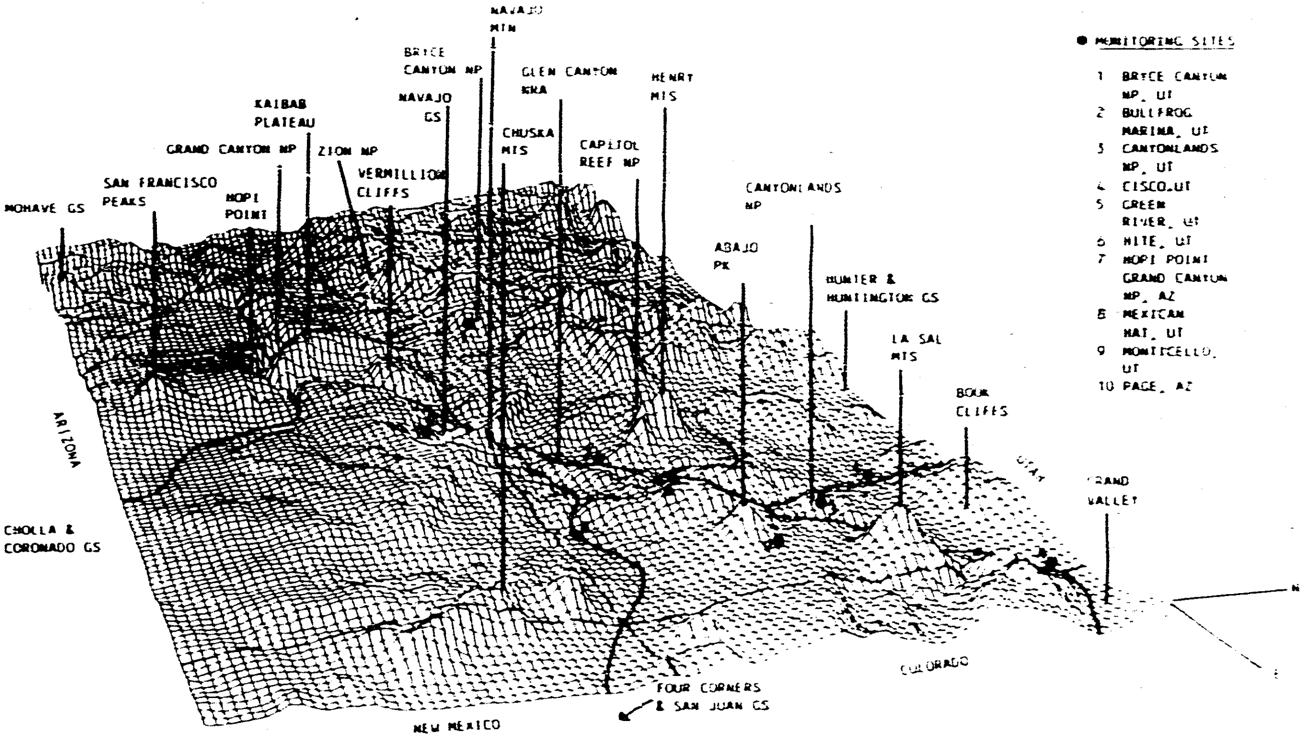

FIGURE 2 Topographical map of WHITEX study area showing location of sampling sites. The boundaries of the figure are as follows: northern boundary, 39° 21′ N. latitude; eastern boundary, 108° 30′ W. longitude; southern boundary, 35° N. latitude; and western boundary 115° W. longitude. Each grid block is 3′ × 3′, or approximately 5,528 meters × 4,435 meters at this location. Source: NPS, 1989.

meteorological variables, and trace elements. Source tracers included particulate selenium (Se), assumed to be a generic tracer for coal-fired power plants; particulate arsenic (As), assumed to be a generic tracer for copper smelters; and deuterated methane (CD_4), which was injected into the NGS stacks to serve as a unique tracer for NGS emissions. NPS analyzed the data from WHITEX to evaluate the effects of NGS emissions on visibility in GCNP. NPS recently issued a final report on the WHITEX study (NPS, 1989), subsequently referred to as the NPS-WHITEX report.

WHITEX focused on NGS because it has large sulfur emissions. NGS is one of the largest single sources of SO_2 in the United States west of the 100th meridian. It emits more SO_2 than is emitted in the Los Angeles basin but less than is emitted in the area of California south of Point Conception.[3] NGS emits approximately the same amount of SO_2 as the combined output of two power plants at Four Corners and San Juan, New Mexico (Appendix 2, p. 80)[4] (EIA, 1987). However, NGS emits less than half the total SO_2 of the group of copper smelters in southeast Arizona and Mexico. During WHITEX, NGS emitted less SO_2 than two or three individual copper smelters whose emissions have since been reduced.[5]

NGS has no technological controls on its SO_2 emissions, although the plant was designed so that flue-gas desulfurization could be incorporated later (SRP, 1971).[6] NGS limits its SO_2 emissions by burning low-sulfur coal, typically 0.45%-0.55% sulfur, which allows NGS to meet Arizona's emission limit of 1.0 lb SO_2/million btu for the plant. Nevertheless, at full operation, NGS emits more than 200 tons SO_2/day through three 236-m tall stacks.[7] These emissions qualify NGS as a major stationary source, defined by Section

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[3] About 120 tons SO_2/day were emitted in 1987 in the Los Angeles Basin and about 300 tons SO_2/day were emitted for all of southern California in 1987 (California Air Resources Board, 1990).

[4] Appendix 2 consists of selected pages from the NPS-WHITEX report.

[5] According to the Arizona Department of Environmental Quality (1989), the three Arizona copper smelters currently emit a total of 170 tons SO_2/day, and the two Mexican smelters a total of 300 tons SO_2/day. During WHITEX, the estimates by ADEQ were 450 tons SO_2/day total from the Arizona smelters and 620 tons SO_2/day total from the Mexican smelters.

[6] NGS is equipped with electrostatic precipitators that limit primary particle emissions to approximately 6.4 tons/day under typical conditions (Appendix 2, p. 82).

[7] During WHITEX, the average emission rate was reported to be 163 tons SO_2/day (Appendix 2, p. 78). This emission rate is reasonably consistent with coal-consumption records for January and February 1987: 648,000 and 488,000 short tons, respectively, with sulfur contents of 0.47% and 0.46% (EIA, 1987).

169A(g)(7) of the Clean Air Act[8] as a source that emits over 250 tons of a regulated pollutant in a year (i.e., 0.68 ton/day).

In an innovative step forward in the field of source attribution, WHITEX injected CD_4 as a tracer into the NGS stacks (Appendix 3). Significant concentrations of CD_4 later were detected at Hopi Point during some haze episodes (periods during which visibility was particularly poor). WHITEX investigators focused their analyses on these episodes. Receptor modeling and statistical techniques were used to estimate quantitatively the fraction of particulate $SO_4^=$ at Hopi Point that could be attributed to NGS. As is often the case when new techniques and approaches are being used, however, unexpected problems arose that made quantitative evaluations of the experimental data difficult. These are discussed in detail in this report.

The NPS-WHITEX report concluded that NGS causes wintertime haze in GCNP (Appendix 2, p. 74). The report claimed that during the days CD_4 measurements were made at Hopi Point, NGS was responsible for about 70% of the mean particulate $SO_4^=$ and about 40% of the mean aerosol-related light extinction. During some wintertime haze episodes,[9] the report claimed that NGS contributed as much as 60% of the aerosol-related light extinction.

On the basis of the WHITEX results, the U.S. Environmental Protection Agency (EPA) initiated regulatory action under Section 169A of the Clean Air Act (U.S. EPA, 1989). This section requires the installation of the best available retrofit technology (BART) on any "major stationary source" placed in operation after August 7, 1962, that "emits any air pollutant which may reasonably be anticipated to cause or contribute to any impairment of visibility" in a Class I area[10] for which EPA has determined that visibility is an important value (Section 169A(b)(2)(A)). EPA has chosen to take a phased approach to the implementation of Section 169A. Consequently the agency's regulations

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[8] References are to the Clean Air Act as amended, 42 USC § 7401-7626.

[9] CD_4 was released for 43 days, from January 7 to February 18, 1987, and was sampled continuously throughout this period. Based on examination of meteorological and other available data, a minority of the CD_4 samples was selected for analysis. At Hopi Point, the selected samples covered 36 half-day periods. The selection process and criteria are not documented in the NPS-WHITEX report, but had the effect of emphasizing periods of higher than average $SO_4^=$ concentrations.

[10] Class I areas are those areas subject to the most restrictive limits on growth in air-pollution concentrations under the Clean Air Act's Prevention of Significant Deterioration program. Section 162(a) of the act classifies 158 national parks, international parks, and wilderness areas as Class I areas whose designation may not be altered. Section 164(a) allows states and Indian tribes to designate additional areas as Class I; to date, this authority has been little used.

currently require BART only when visibility impairment is "reasonably attributable" to an existing major stationary source (U.S. EPA, 1980).

EPA preliminarily attributed haze in the GCNP to NGS (U.S. EPA, 1989). This is the first attempt by EPA to regulate an existing source under Section 169A. The agency is in the process of deciding whether to make its attribution final and, if so, determining what level of control of air pollution from NGS would constitute BART, as defined in Section 169A(g) of the act. The agency placed in the public docket (EPA Docket No. A-89-02-A) a draft notice of proposed rule making pursuant to Section 110(c) of the Clean Air Act. The proposal would require that NGS reduce emissions to 0.1 lb SO_2/million btu, which would reduce the level of allowable emissions by 90%. EPA believes that an approximately 90% reduction in emissions would be required to meet the emission limit reliably.

THE NRC COMMITTEE STUDY

The Committee, Its Charge, and Its Approach

This evaluation of WHITEX was prepared by the Committee on Haze in National Parks and Wilderness Areas, which was convened in February 1990 by the National Research Council's Board on Environmental Studies and Toxicology in collaboration with the Board on Atmospheric Sciences and Climate of the Commission on Geosciences, Environment, and Resources. The committee comprises members appointed for expertise in meteorology, atmospheric chemistry, atmospheric aerosols, air pollution monitoring and modeling, statistics, environmental engineering, control technology, and environmental law and public policy.

The committee's overall charge is:

> to develop working principles for assessing the relative importance of anthropogenic emission sources that contribute to haze in Class I areas and for assessing alternative source control measures; and
>
> to recommend strategies for improving scientific understanding and technical information on relative source contributions to haze formation, regional and seasonal factors affecting haze, relevant air quality models, and various emission control measures.

The committee's work is sponsored by the U.S. Department of the Interior (National Park Service, Bureau of Reclamation, and Office of Environmental

Quality), the U.S. Department of Energy, the U.S. Environmental Protection Agency, and the Arizona Salt River Project. The committee's final report, which will address this charge, will be issued in 1991.

In addition to the final report, the committee was also asked to provide this special report evaluating WHITEX, the recent site-specific study conducted by NPS. This report evaluates the scientific evidence relevant to EPA's recently proposed finding that NGS contributes to impairment of visibility in GCNP. Specifically, the committee was asked to review NPS data and analyses upon which the EPA determination was based and other data and analyses related to source apportionment for Grand Canyon haze. It was also asked to evaluate the contribution of the WHITEX study toward the science of source apportionment. The committee reviewed the December 1989 NPS-WHITEX report, other relevant published materials, and some unpublished information. In March 1990, the committee conducted site visits to the GCNP and NGS near Page, Arizona, and it heard technical presentations from NPS, SRP, and their scientific consultants. This information was used as part of the basis for the committee's evaluation.

The Committee's Specific Interpretation of Its Charge

The committee focused on assessing the methodology and design of WHITEX and the validity of the conclusions. The committee based its evaluation solely on the scientific aspects of WHITEX.

The committee is aware that its assessment is relevant to the regulatory matters currently before EPA. The committee wishes to emphasize that it has not considered regulatory issues relating to NGS and expresses no opinion on them. Such issues involve policy considerations; these matters lie outside the committee's purview.

This review of WHITEX will be considered by the committee in the preparation of its final report. WHITEX is an example of approaches to source attribution in Class I areas. Because WHITEX is one of the most recent studies of this type, it will provide useful insight for the final report.

EVALUATION OF WHITEX

WHITEX Overview

WHITEX was conducted on the Colorado Plateau in Northern Arizona and Southern Utah between January 7 and February 18, 1987 (days 7-49 in 1987).

The objective of the WHITEX research program was to evaluate the suitability of various receptor modelling methods for attributing haze in specific Class I areas (i.e., Grand Canyon and Canyonlands) to emissions from an isolated point source (i.e., NGS). Previous investigations demonstrated that wintertime regional hazes occur during periods of air stagnation and that these hazes are largely attributable to submicrometer particles composed primarily of $SO_4^=$, organic carbon compounds, and black carbon (soot) (Malm and Walther, 1979; Walther and Malm, 1979; Chinkin et. al., 1986). A significant part of WHITEX focused on $SO_4^=$, because it is the dominant light-scattering species during the most severe haze episodes. NGS emissions include primary $SO_4^=$ particles, as well as gaseous SO_2 which is converted to $SO_4^=$ in the atmosphere.

The NPS-WHITEX report contains the following major elements:

- A discussion of the experimental setting, including a review of regional emissions and climatology;
- A description of the optical, particle, SO_2, and tracer measurements, as well as discussions of data quality;
- A description of some preliminary prognostic transport modeling for one 2-day period; and
- Various analyses supporting the attribution of $SO_4^=$ concentrations and haze to NGS.

A distinctive and novel feature of the WHITEX experiment was the use of CD_4. CD_4 is nearly inert; its concentration during WHITEX would not have been significantly affected by chemical reactions, precipitation scavenging, or dry deposition to the surface. The concentration of CD_4 in an air parcel can be reduced only through dilution with air that does not contain CD_4. WHITEX used CD_4 as a tracer to identify air parcels that contained NGS emissions, to estimate the dilution that had occurred during transit, and to estimate the amount of sulfur species that were originally injected into the air parcel by NGS. Knowing the ratio of SO_2 : CD_4 in the stack emissions at NGS and knowing the concentration of CD_4 at GCNP, the concentration of NGS SO_2 that would have been present in the air parcel in the absence of deposition or conversion can be calculated, assuming the CD_4 and sulfur species from NGS travelled by the same trajectory. This calculated upper limit on NGS-derived sulfur is referred to as $S(CD_4)$.

The analyses in the NPS-WHITEX report focused on data acquired at Hopi Point, because higher CD_4 concentrations were found there than at the other sampling stations (except for Page, which is immediately adjacent to NGS). NPS estimates of NGS effects on haze at GCNP depended on the measurements of CD_4 at Hopi Point. However, measurements of CD_4 by themselves could not provide information on the fraction of SO_2 that was converted to $SO_4^=$ in transit, nor could they account for the quantities of these species that were deposited during transit. Thus, $S(CD_4)$ yielded only an upper-limit estimate of possible effects of NGS SO_2 emissions at GCNP. For this reason, statistical and modeling tools were needed to make quantitative estimates of NGS impacts.

The attribution analysis of the NPS-WHITEX report was carried out in two stages: (1) the observed light extinction first was apportioned to fine-particle $SO_4^=$ and other atmospheric species, and (2) the observed $SO_4^=$ concentrations then were attributed to NGS and other sources. The apportionment of extinction among chemical species (extinction budgeting) was largely based on literature and statistical values for the extinction : mass ratios (extinction efficiencies) of the various species. The quantitative attribution of $SO_4^=$ to specific sources rested primarily on semi-empirical statistical models, highly simplified physical models fit to the data through least-squares procedures.

WHITEX Source-Attribution Models

The quantitative attribution of $SO_4^=$ to NGS rested on two empirical models: Tracer Mass Balance Regression (TMBR) and Differential Mass Balance (DMB). TMBR employs multiple linear regression (MLR) of the $SO_4^=$ concentration on selected source-tracer concentrations to estimate the ambient $SO_4^=$: tracer ratios attributable to individual sources. MLR has been used since the mid-1970's to apportion primary (directly emitted as particles) source contributions to ambient aerosol mass, although it has been subjected only to limited testing and verification. The literature does not contain convincing evidence that MLR applications can successfully apportion a predominantly secondary (particles formed in the atmosphere) species, such as $SO_4^=$, among several source types.

In the NPS-WHITEX report, some of the tracer concentrations are multiplied by relative humidity (RH) in an attempt to account for the increased rate at which SO_2 is converted to $SO_4^=$ in liquid-phase reactions in clouds or fogs. RH scaling as used in the NPS-WHITEX report appears to be previously untested.

DMB is an elaboration of TMBR in which the regression variable for the target source is adjusted to reflect the varying ages of emissions at the receptor. The expected proportion of $SO_4^=$: tracer is calculated based on the following factors: 1) assumed and constant values of SO_2 and $SO_4^=$ deposition rates, 2) an SO_2 conversion rate assumed to be in constant proportion to

RH, and 3) plume ages estimated from wind data. Because these factors were not measured during WHITEX, NPS selected them from within a range that they believed to be physically reasonable to maximize the correlation coefficient of the multiple linear regression relating $SO_4^=$ to the NGS tracer term and other source tracer terms. The net effect is one of nonlinear multiple regression.

The use of DMB appears to be unprecedented in the source-apportionment literature. Because it ultimately relies on MLR, its statistical assumptions are similar to those of TMBR. As with TMBR, DMB requires that $SO_4^=$ from untraced sources be only negligibly correlated with the source-tracer terms used in the regressions. The statistical assumptions used in the NPS-WHITEX report are accurately identified in the report (Appendix 2).

Critical Aspects of WHITEX Techniques and Design

The committee assessed the qualitative and quantitative aspects of the NPS-WHITEX conclusions; these two aspects are addressed separately.

Qualitative Assessment

> *The committee concludes that a properly executed experiment using a methodology and design similar to those used in WHITEX could provide qualitative information as to whether NGS emissions contribute to $SO_4^=$ aerosol and resultant haze in GCNP.*

The WHITEX protocol included measurements of ambient optical properties, concentrations of key gaseous and particulate species, tracers for contributing $SO_4^=$ sources (including CD_4), wind-flow patterns and other meteorological data, and time-lapse photography. WHITEX analyses included dynamic meteorological modeling of air movements, tracer mass-balance calculations, and multiple-regression analyses for apportioning $SO_4^=$ among sources. Such information should be adequate to support a qualitative assessment of whether NGS emissions reach GCNP and whether these emissions contribute to haze in GCNP.

The use of CD_4 in NGS emissions could provide definitive evidence of the transport of NGS emissions to the GCNP. Dynamic meteorological modeling could provide supplemental information that could be used to help evaluate the extent to which the emissions are transported into and distributed throughout the Grand Canyon. For any particular site, the contributions of the various aerosol species to optical extinction could be reasonably estimated.

Multiple-regression techniques, such as those used in TMBR and DMB, have a long history of success in many areas of science; they are widely accepted in epidemiology, econometrics, and other disciplines for which cause-effect relationships are complex and for which extraneous factors cannot be controlled. Such techniques clearly could be used in a WHITEX-type experiment if 1) satisfactory tracers were available for all major sources that might affect GCNP, and 2) there were a strong correlation between the NGS tracer and the fraction of haze-forming aerosol (i.e., $SO_4^=$) that was not accounted for by the tracers for all other sources. Under these conditions, the results of multiple-regression analyses would constitute persuasive qualitative evidence that NGS emissions had a detectable effect on haze at GCNP. However, the literature does not demonstrate that previous MLR applications can successfully apportion a predominantly secondary species, such as $SO_4^=$, among several source types. Therefore, it would not seem advisable to rely solely on such models for the success of a major field experiment.

> *The committee concludes that WHITEX qualitatively showed that, at some times during the study period, NGS emissions significantly contributed to* $SO_4^=$ *aerosol and resultant haze at Hopi Point in GCNP.*

This conclusion is based on the data presented in the NPS-WHITEX report. The conclusion is not based on the results of the TMBR and DMB analyses, which contained various shortcomings that are discussed in more detail later in this report. Instead, the committee's qualitative assessment is based on the following observations and measurements made during WHITEX.

Meteorological Evidence. Meteorological analyses support the NPS conclusion that NGS emissions can be transported to GCNP during the wintertime when the air stagnates. The NPS-WHITEX report focused on February 11-14, 1987 (days 42-45 in 1987), for its intensive analyses of the NGS contribution to haze in GCNP. During this time, the region was dominated by a polar high-pressure system that resulted in low-speed surface winds. Under such conditions, surface winds at Page usually alternate between northeasterly during the day and southwesterly during the night (Balling and Sutherland, 1988), and observations at Page during the study period showed this pattern. Furthermore, the upper-air winds measured at Page confirmed the NPS conclusion that winds at the expected plume height flowed from the northeast during much of this period. Deterministic meteorological modeling performed in WHITEX also indicated that winds at the height of NGS stacks could have carried emissions to the GCNP area; however, these simulations did not reproduce the diurnal fluctuations in wind flow observed at the surface at Page.

The meteorological data and the deterministic meteorological modeling do not allow quantification of the contribution that NGS might have made to haze at GCNP. The deterministic meteorological modeling cannot pinpoint the location of the NGS plume nor its entrainment into the canyon. The model uses a grid size of 5 km; hence, it cannot reproduce the complex topography of GCNP (Fig. 2) nor the associated small-scale meteorological effects, such as gravity flows. (For example, the model could not be expected to quantify the mass of sulfur entering the Grand Canyon from the rim versus that transported directly down the Grand Canyon.) Thus, the meteorological studies provide only qualitative evidence of transport.

Photographic Evidence. The wind-field analyses are supported by time-lapse photography and still photographs of cloud, fog, and haze conditions. Photographic evidence was obtained on the rim of the Grand Canyon and elsewhere in the region. The time-lapse images provided particularly striking evidence of the complex meteorological conditions that are due in part to the complicated topography (Fig. 2). Time-lapse video sequences taken on the east end of the south rim during the early part of the period showed well-developed wind flow into the Grand Canyon from the east; in contrast, aloft and at relatively low altitudes, winds flowed strongly from the west.

Still photographs provided additional information on the meteorological context of February 11-14. Photographs from Echo Cliffs looking northeast toward NGS—about 24 km away—showed noticeable haze on February 8 that dissipated on February 9. On the 9th, a brown plume was seen moving in a westerly direction from NGS. On February 10-12, the plume was embedded in fog; when the fog rose, the plume appeared to move to the west. On the afternoon of February 12, skies were clear and visibility was improved, except in the Lake Powell valley, where a haze was obvious. These photographs are evidence that the NGS plume was entrained into a cloudy environment with winds traveling toward the GCNP most of the time during February 11-14. The presence of cloud water within the plume has important implications regarding the conversion rate of SO_2 to $SO_4^{=}$, because the heterogeneous conversion rate in cloud droplets can be much faster than that for homogeneous gas-phase conversion.

Chemical and Physical Evidence. The chemical and physical evidence are summarized by the following statements, most of which are based on data obtained during WHITEX.

1. Averaged over the WHITEX study period, $SO_4^=$ aerosol was a significant contributor to non-Rayleigh light extinction at Hopi Point in GCNP. During certain episodes, $SO_4^=$ was the predominant contributor to non-Rayleigh light extinction. These conclusions regarding the contribution of $SO_4^=$ aerosol to haze at Hopi Point are not sensitive to uncertainties in the WHITEX data (including substantial uncertainties regarding the carbon data). These conclusions are based on visibility and aerosol data taken during WHITEX and on literature values for sulfate light extinction efficiencies and are consistent with prior studies linking $SO_4^=$ to haze in the Southwest (Trijonis et al., 1989).

2. NGS is one of the largest single SO_2 sources in the United States west of the 100th meridian, and during WHITEX, it was also among the largest. Although other large SO_2 sources could affect Hopi Point (e.g., the smelters in southeast Arizona and Mexico, other power plants, and urban areas), NGS is the source closest to Grand Canyon—25 km from the GCNP boundary and 110 km northeast of Grand Canyon Village—while the other major sources are 300-500 km distant. Mass-balance considerations suggest that the rate of SO_2 emissions from NGS during WHITEX was large enough to produce sulfur concentrations at GCNP much greater than those measured at Hopi Point.

3. The $SO_4^=$ measured at Hopi Point during haze episodes probably included contributions from sources within the region. These episodes tended to occur during stagnant wind conditions, which could lead to the accumulation of emissions from sources in the region, as evidenced by the significant spatial inhomogeneities in $SO_4^=$ concentrations. The modeling studies of transport winds during the major stagnation episodes showed that NGS emissions could affect GCNP. However, these findings do not preclude the possibility of significant contributions from other local and regional sources, such as copper smelters, urban areas, and other power plants.

4. During the periods selected for tracer analysis, the tracer data showed that Page and Hopi Point were affected significantly by the NGS plume. During three episodes, average CD_4 tracer concentrations were generally much higher at Page and substantially higher at Hopi Point than at the other six sampling locations. The CD_4 tracer indicated that NGS contributions could account for total sulfur concentrations 2.5 times greater than those actually measured at Hopi Point. However, these tracer studies cannot account for losses in transit, nor can they reduce the large uncertainties regarding the conversion rates of SO_2 to $SO_4^=$.

5. Cloudy conditions were observed during WHITEX haze episodes. These conditions favor the higher conversion rates required to generate significant $SO_4^=$ contributions from NGS at Hopi Point.

Quantitative Assessment

> *The committee concludes that a properly conceived and executed experiment, using a methodology and design similar to those used in WHITEX, might be useful to determine quantitatively the fraction of $SO_4^=$ aerosol and resultant haze in GCNP that is attributable to NGS emissions.*

The committee concludes that an experiment based on the WHITEX methodology could provide a quantitative determination of the fractional contribution of NGS to haze in GCNP in simple—but highly improbable—cases, such as:

- If no CD_4 were measured in GCNP, then the unambiguous conclusion would be that NGS made no contribution to GCNP haze. The absence of measurable CD_4 would be evidence that no material of any kind was transported from NGS to GCNP.
- If CD_4 were measured in GCNP and background measurements showed that $SO_4^=$ from other sources were insignificant at that time, then all $SO_4^=$ detected could be attributed to NGS.

Beyond simple cases such as these, there is little consensus among those in the source apportionment field about which methods might be appropriate for apportioning haze due to secondary $SO_4^=$. Labeling the sulfur or oxygen might provide a definitive test. However, because of the large background ^{34}S and the radioactivity of ^{35}S, use of these isotopes is impractical. Some believe that extensions of receptor-oriented techniques similar to those used in WHITEX, if applied with better tracers and better temporal and spatial resolution, might provide quantitative estimates.

Others believe that alternative analyses would provide more reliable quantitative estimates. For example, a mass balance might be developed to explain measured SO_2 and $SO_4^=$ concentrations across the sampling stations. The mass balance would incorporate emissions from all sources in the region, calculations of convective fluxes based on dynamic meteorological modeling, and wet and dry deposition (using measured values where possible). Others feel that source apportionment can best be achieved using deterministic models that couple transport, deposition, and known SO_2-to-$SO_4^=$ conversion mechanisms. The validity of the models would be tested by comparing simulations with measurements from the sampling stations. This lack of consensus among experts is evidence of the need for further efforts to validate or otherwise evaluate methods used for source apportionment of secondary aerosols.

The committee concludes that WHITEX did not quantitatively determine the fraction of $SO_4^=$ aerosol and resultant haze in GCNP that is attributable to NGS emissions.

The committee found that the data analyses described in the NPS-WHITEX report contain weaknesses that preclude quantitative source apportionment. The report did not attempt to quantify the effects of departures from model assumptions on the analysis, nor did it establish an objective and quantitative rationale for selecting among various statistical models. In addition, the conceptual framework for DMB involves physically unrealistic simplifications, and their impact on quantitative assessments was not addressed. These points are elaborated in the following section.

Limitations of the WHITEX Study

Weaknesses in the Data Base

Uncertainties about Tracer Data. DMB and TMBR require that emissions from specific sources or source types be associated with unique tracers. In WHITEX, these tracers were CD_4 for NGS, As for copper smelters, and Se for coal-fired power plants (although the latter two sources each emit some Se and As, respectively). No tracer in WHITEX was used to evaluate urban emissions; therefore, the fraction of haze attributable to these sources is impossible to calculate. Furthermore, the source profile for power plants was based on limited aircraft measurements of NGS emissions downwind from the stacks. The copper-smelter profile was based on old and uncertain data from the literature. Variabilities and uncertainties in NGS CD_4 emission rates (which ranged from 2 to 5 mg CD_4 per MW during the study (Appendix 2, p. 75)) led to substantial uncertainties in the day-to-day relationship between CD_4 and NGS sulfur emissions. Moreover, at Hopi Point, CD_4 concentrations were determined for only 36 samples, an undesirably small data set for the types and large numbers of statistical analyses performed on the data.

Several questions have been raised about the accuracy of the data regarding CD_4 emissions from NGS and, specifically, the ratio of $CD_4 : SO_2$. The rate of injection of CD_4, normalized to power output, was known to vary during the experiment by a factor of 2.5, and these changes were factored into the WHITEX data analyses. However, the ratio of $CD_4 : SO_2$ was not measured in the stack (samples apparently were collected but not analyzed). The ratio was measured in the plume using samples collected from aircraft. In addition, a small leak was discovered in the CD_4 injection line after the experiment was completed.

The NPS-WHITEX report provides little documentation of procedures and quality assurance for the sampling and analysis of ambient CD_4. Despite the known problems with emissions and the lack of documentation on ambient measurements, the committee concluded that the CD_4 data are among the most useful data obtained in WHITEX, because CD_4 is the most specific tracer available for NGS emissions. In addition, most of the difficulties with the CD_4 data pertain to daily variations in the concentrations, not the overall average concentrations. Nonetheless, deficiencies in the experimental design precluded quantitative results regardless of CD_4 data quality.

Absence of Measurements within the Grand Canyon. One of the greatest weaknesses of the study was that no measurements were made below the rim of the Grand Canyon, within the canyon itself. As suggested by meteorological considerations and supported by still photographs and a time-lapse video of the February 11-14 period, a strong shallow wind flowed over the Colorado plateau and cascaded into the eastern end of the canyon at Desert View. This suggests that sulfur concentrations in the canyon might have been considerably greater than was observed on the rim farther away at Hopi Point.

Inadequacy of Background Measurements. Because the WHITEX study originally focused on Canyonlands National Park, too few sampling stations were located in the area surrounding GCNP. Without data from additional stations, the effect of NGS emissions is difficult to differentiate from those of other sources in the region. These considerations are important for a thorough evaluation of the sources of $SO_4^=$ in GCNP. This issue is addressed in more detail below.

Departures from Statistical Assumptions

The statistical assumptions underlying TMBR are accurately identified in Appendix 6B of the NPS-WHITEX report. Analogous assumptions underlie DMB, because it too is based on regression analysis. The discussion of the TMBR assumptions concludes, "Ideally, if there was a constant background pollutant concentration . . . and if the tracer release was directly proportional to emissions, and emissions were conservative, the reported estimated average NGS contribution should be a reliable estimate of the actual value for the time period in question."

Each of the quoted conditions appears to have been violated by the WHITEX data. The nonproportionality of the CD_4 release rate and the nonconservation of SO_2 emissions are discussed at length in the NPS-

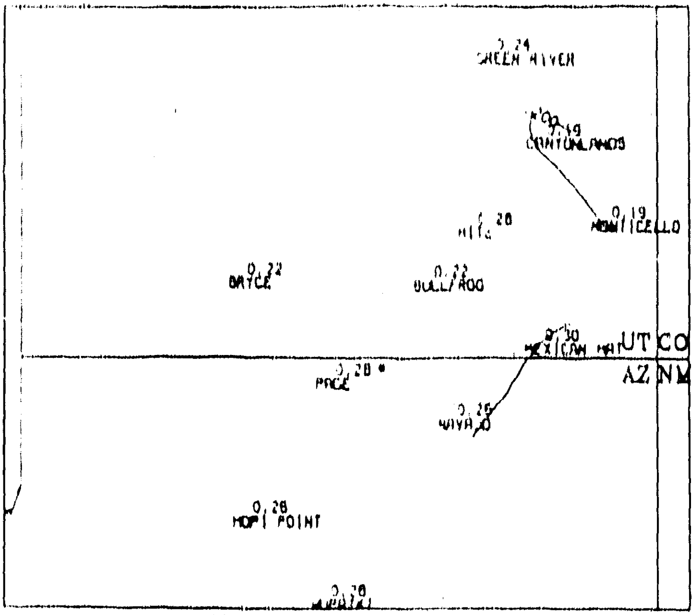
WHITEX report and this report. Less is known about the behavior of the background $SO_4^=$, because insufficient attention was devoted to it in the placement of sampling sites and the selection of CD_4 samples for analysis. However, the concentration of non-NGS $SO_4^=$ in the region clearly varied significantly. For example, concentrations at Monticello increased from 0.27 μg S/m^3 from late February 9 to 0.45 μg S/m^3 early February 10 (Fig. 3); during this period, CD_4 was 9×10^{-5} ppt, corresponding to a maximum possible contribution from NGS of only about 0.05 μg S/m^3 (Appendix 2, pp. 76, 77, 85 (eq. 6-10)). Samples collected at Green River, Canyonlands, and Bullfrog during this period were not analyzed for CD_4.

The NPS-WHITEX report did not attempt to quantify the effects on its analyses of departures from the statistical assumptions that it identified. However, the potential magnitude of such effects is substantial. Unfortunately, the WHITEX design did not provide the data needed for a definitive resolution of this issue.

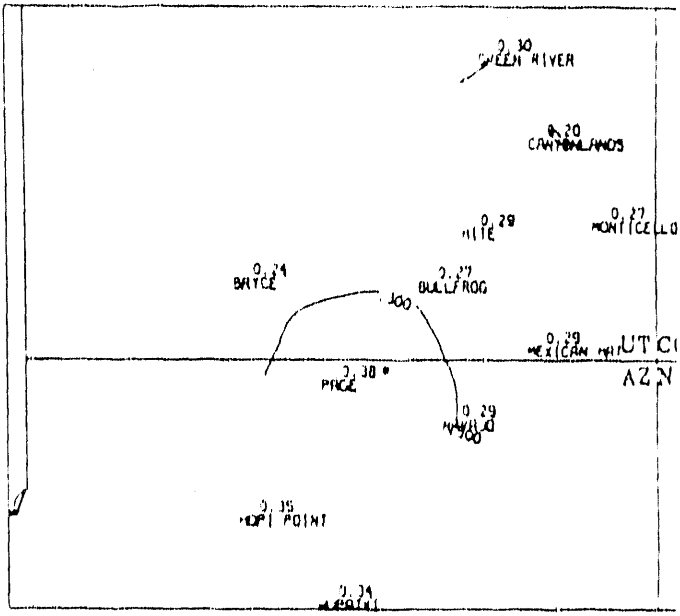
Formulation of Statistical Models

The $SO_4^=$ contribution attributed to NGS depends strongly on the model chosen, the tracers included in the model, and the criteria by which the model is fit to the data. The NPS-WHITEX report attached most significance to the TMBR and DMB models using the variables of CD_4 concentration × RH for NGS and As concentration × RH for copper smelters. Variable selection was critical to the interpretation of the results, because CD_4 is clearly not the only tracer correlating with GCNP $SO_4^=$. Indeed, NPS noted in its reply to SRP's comments that two-thirds of the $SO_4^=$ variance can be accounted for by RH and As alone. To establish a more rational basis for quantitative attribution, more attention must be given to alternative formulations for TMBR and DMB and to criteria for selecting among them. However, even if these criteria were adequately considered, the statistical results would most likely remain nonrobust in the sense that the source attributions generated by the various statistical models would probably still differ substantially from one another. One difficulty is that the number of plausible alternative models is substantial relative to the number of samples for which CD_4 data are available. As the number of models increases, so does the likelihood that one of them will test significant purely by chance.

The NPS-WHITEX report assumed $SO_4^=$ yields from NGS and smelter emissions to have been proportional to the ambient RH, as an index of their exposure to liquid water. This is a simple and indirect assumption, which scales intermittent processes along the entire trajectory at cloud level directly

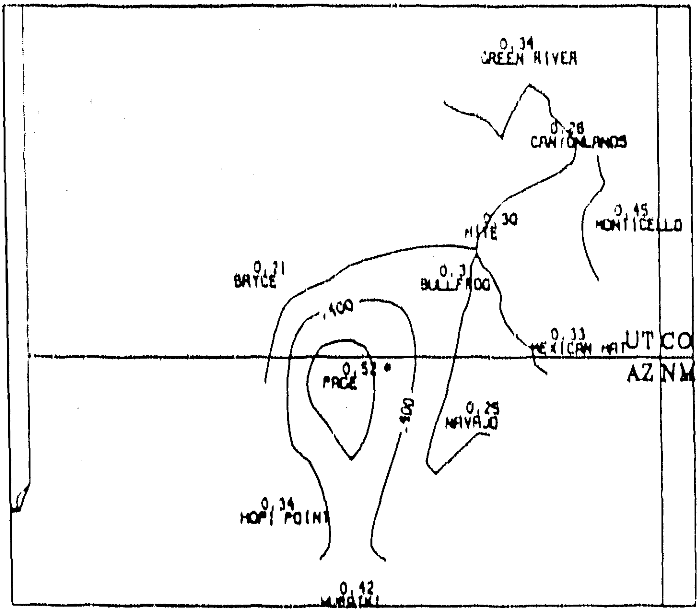


DAY 40 800 AM (FEB 9)

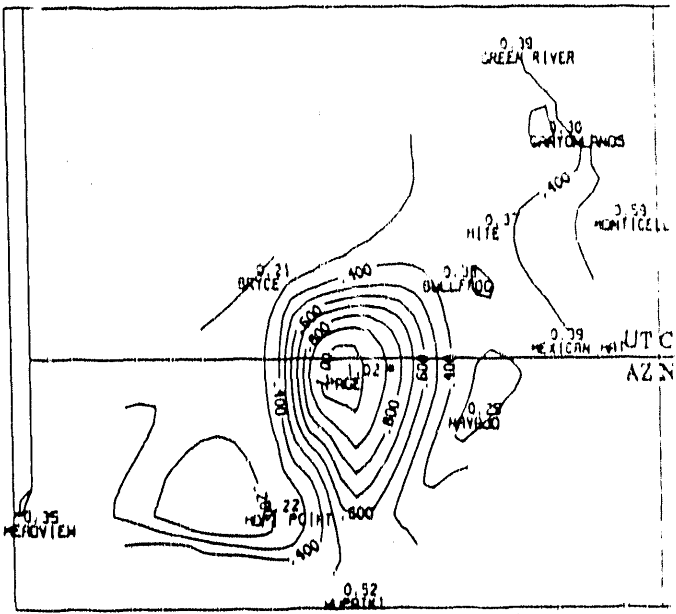


DAY 40 800 PM (FEB 9)

FIGURE 3 Fine particulate sulfur (μg/m3) measured at WHITEX sampling sites, February 9-12, 1987. (Multiply by 3 to get sulfate.) Source: Malm, 1990.

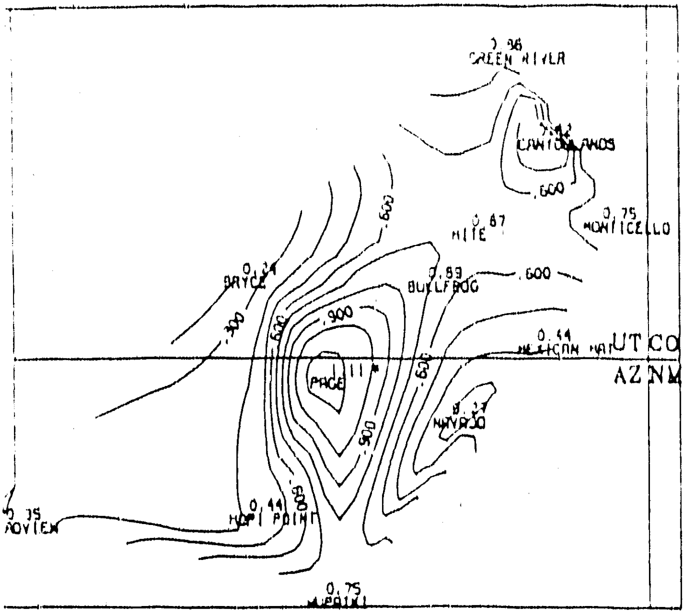


DAY 41 800 AM (FEB 10)

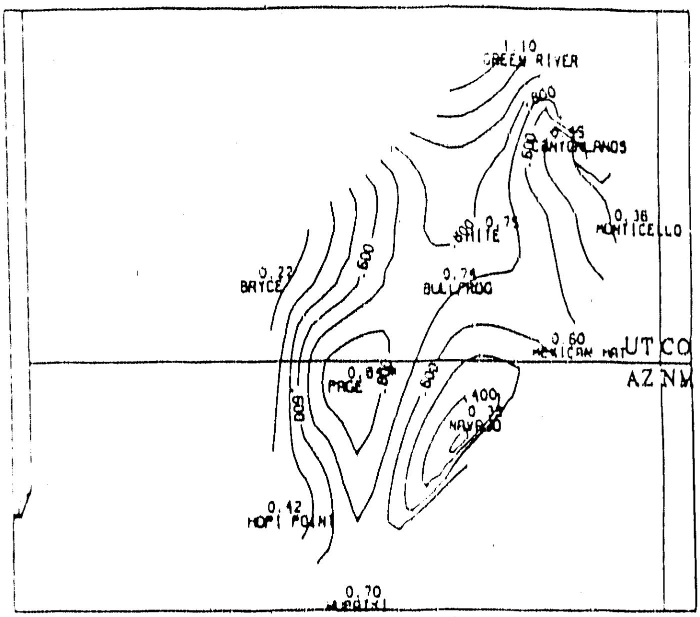


DAY 41 800 PM (FEB 10)

FIGURE 3 (continued).

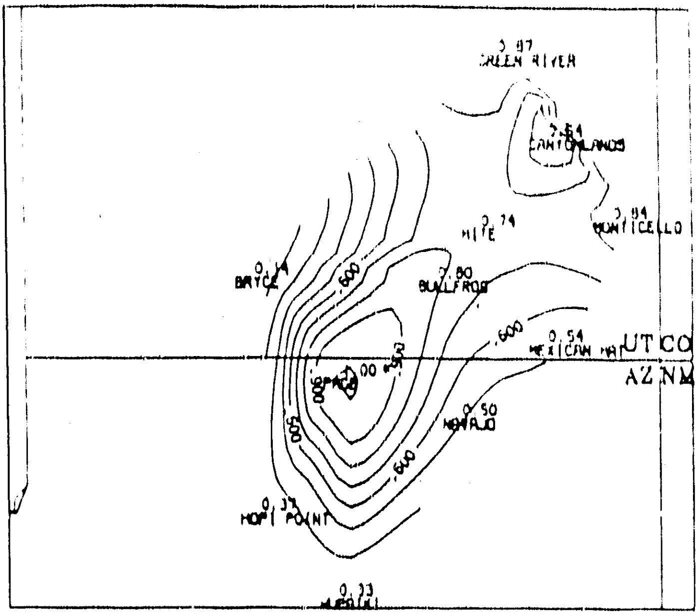


DAY 42 800 AM (FEB 11)

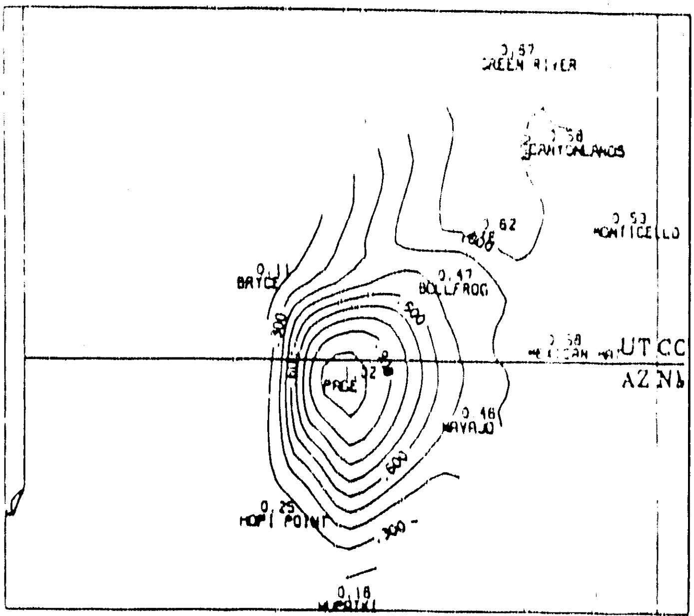


DAY 42 800 PM (FEB 11)

FIGURE 3 (continued).



DAY 43 800 AM (FEB 12)



DAY 43 800 PM (FEB 12)

FIGURE 3 (continued).

to a continuous variable measured locally at ground level. The RH factor is critical to the explanatory power of the statistical models: without it, CD_4 alone can account for only 3% of the observed variance in $SO_4^=$ at Hopi Point and only 6% of the observed variance in total sulfur. Given the overriding importance of the RH scaling factor, the committee believes that the sensitivity of results to alternative assumptions should have been explored in formulating the models used for the TMBR and DMB analyses. The NPS-WHITEX report also assumes that the contributions of background sources, such as other power plants and urban areas, were unaffected by RH. No effort was made to justify this assumption. The committee believes the report should have considered the possibility that yields from other sources were also affected by RH.

Simplifications in the DMB Model

The DMB analyses are dependent on unique "plume ages." The validity of these ages is questionable, given that travel times from NGS to Hopi Point were estimated to be 12-48 h on February 11-12. Slow-moving air parcels typically contain a mixture of materials (possibly more than one plume) emitted from a variety of sources. Furthermore, plume ages were estimated only for NGS emissions and not for other contributing $SO_4^=$ sources. The effects of these simplifications on quantitative apportionment are unknown.

The DMB approach is based on linear models for the oxidation of SO_2 to $SO_4^=$ and for the deposition of SO_2 and $SO_4^=$. In reality, both processes are likely to occur at rates that can vary greatly in time and space. The major transformation process for SO_2 during wintertime conditions is probably oxidation by hydrogen peroxide (H_2O_2)[11] in clouds. Oxidation rates by this process theoretically can exceed several percent per minute. Such high rates are maintained for only short periods due to rapid depletion of either H_2O_2 or SO_2. In the absence of clouds, the photochemical conversion rate of SO_2 is very slow—close to 0%/min—under wintertime conditions at GCNP. The result is that under cloudy conditions, a significant portion of the SO_2 in an air parcel is rapidly transformed to $SO_4^=$ each time the parcel is entrained into a cloud; otherwise, the SO_2 remains essentially unconverted and, hence, cannot contribute significantly to haze conditions in GCNP.

Furthermore, deposition and oxidation are coupled processes. Because of

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[11] A more realistic model should include the heterogeneous oxidation of SO_2 in cloud water by ozone, oxygen (carbon or metal ion catalyzed), and other oxidants.

the nonuniform transformation rate of SO_2 to $SO_4^=$, dry deposition rates also are nonuniform. Rainfall was measured between February 10-12 at the Grand Canyon Airport weather station; consequently, wet deposition occurred. Because rainfall in complex terrain is seldom spatially or temporally uniform, wet-deposition rates were probably not uniform. These nonuniformities in conversion and deposition rates lead to variabilities in the relationship between $SO_4^=$ concentrations measured at the receptor sites and tracer concentrations used in the regression analyses. Because these nonuniformities were not taken into account in the DMB formulation, the DMB results are of questionable applicability.

Potential Covariance of NGS and Other Source Contributions

Even if CD_4, Se, and As were accepted as satisfactory tracers for all major sources that could potentially affect GCNP, a critical gap remains in the chain of evidence—CD_4 was not shown to add anything to the explanatory power of Se and As. In other words, the NGS tracer was not shown to correlate with any of the $SO_4^=$ variability that is not already accounted for by generic source tracers. One reason for this might be that CD_4 and Se are themselves correlated, with a correlation coefficient of 0.6. This suggests that the effects from NGS emissions and those from other Se sources affecting the Grand Canyon were correlated (and perhaps highly correlated considering imprecisions in the data set).

It is true, as stated by NPS, that a high degree of collinearity between CD_4 and Se is consistent with the conclusion that the emissions from other plants did not reach GCNP and that all Se came from NGS. However, the observed degree of collinearity is also consistent with the hypothesis that emissions from other plants did reach GCNP and that their $SO_4^=$ contributions were correlated with those of NGS. The latter hypothesis is not unreasonable, given that most other power-plant emissions occur also to the east and north in the Colorado River drainage basin, and that RH could have had a similar effect on those emissions. Under such conditions, it is difficult to distinguish statistically the relative effect of NGS from those of other coal-fired power plants in the region, given the limited number of data. The committee concludes that GCNP haze due to NGS emissions cannot be quantitatively estimated solely on the basis of TMBR and DMB analyses.

Estimates of the Range of Possible Impacts of NGS Emissions at Hopi Point

The WHITEX data can be used to estimate ranges of possible $SO_4^=$ effects from NGS. These estimates consist of a series of mass-balance calculations made on the basis of simplifying assumptions. These calculations are made for illustrative purposes and cannot, in themselves, prove or disprove that NGS emissions were responsible for GCNP haze, because measurements needed to confirm some of the assumptions were not made during WHITEX. The committee's estimates are summarized below. In discussing these estimates, the committee devised a set of three questions to address specific concerns.

> *Assuming that all NGS emissions are carried into GCNP under typical wind conditions, is the rate of NGS SO_2 emissions sufficiently large to produce total sulfur concentrations in GCNP that are comparable in magnitude to those measured during WHITEX at Hopi Point?*

This is the simplest quantitative question that can be asked about the potential impact of NGS on haze in GCNP. This case ignores all complicating questions and focuses on the worst case—that all NGS sulfur emissions are carried into the Grand Canyon and distributed uniformly throughout it. Using the NGS emission rate during 1987 reported in the NPS-WHITEX report (163 tons SO_2/day) (Appendix 2, p. 80), assuming the width and depth of the Grand Canyon range generally from 8 to 16 km and 0.9 to 1.2 km respectively, and assuming a mean wind speed of 2-4 m/sec (pers. comm., K. Gebhart, NPS, May 25, 1990), the total sulfur concentration within the canyon would be about 10-60 $\mu g/m^3$. This is much greater than the NPS-WHITEX-estimated upper limit of total sulfur attributed to NGS at Hopi Point over the period of the CD_4 analyses. This total sulfur concentration is also significantly greater than the total sulfur measured at this site during this period, when values were typically in the range of 0.2-1 $\mu g/m^3$ (absolute range, 0.07-1.50 $\mu g/m^3$, excluding the single value of 4.4 $\mu g/m^3$) (Appendix 2, pp. 84, 85).

Although crude, this estimate suggests that under appropriate conditions, the rate of SO_2 emissions from NGS is easily large enough to serve as the source of the sulfur measured in GCNP. The implicit assumptions in this upper-limit calculation are: 1) that the meteorological conditions enable the NGS plume to be transported into the Grand Canyon with little dispersion (i.e., that a substantial fraction of the NGS output actually enters the canyon), and 2) that there is relatively little loss of sulfur during transit. It is clear that both assumptions often were not true to some degree during the experiment. Furthermore, this estimate does not address the question of the degree to which SO_2 is converted to $SO_4^=$, a factor that is critically important to haze effects.

> *If the NPS-WHITEX estimates of sulfur transport from NGS to GCNP are correct, how much SO_2 might be expected to be converted to $SO_4^=$ aerosol during transit from NGS to GCNP under winter meteorological conditions such as those observed during WHITEX?*

To address this question, the committee estimated upper and lower limits for the amount of conversion that could take place using data for the haze episode on February 11-12. Data were used from this episode because it is the focus of much of the WHITEX analysis. At Hopi Point on February 11-12, a maximum of about 2 $\mu g/m^3$ $S(CD_4)$ could have come from NGS (Appendix 2, p. 85). This is based on the CD_4 concentrations at Hopi Point and the total sulfur : CD_4 ratio in the NGS plume. The total measured concentration of sulfur at Hopi Point was about 0.5 $\mu g/m^3$ on February 11, and 0.25-0.4 $\mu g/m^3$ on February 12 (Appendix 2, p. 84).

Minimum Conversion of SO_2 to $SO_4^=$. In the absence of clouds, SO_2 conversion is controlled by homogeneous gas-phase photochemistry, and conversion rates are at a minimum. The NPS-WHITEX report provided estimates of the wintertime 12-h average daytime conversion rate (about 0.06%/h) and the 24-h average rate (about 0.03%/h) (SAI, 1985; Appendix 2, p. 81). The NPS-WHITEX-estimated transport times from NGS to Hopi Point during February 11-12 ranged from 12 h to 48 h (Appendix 2, p. 82).[12] The committee assumed that the maximum 2 $\mu g/m^3$ $S(CD_4)$ at Hopi Point began its transit from NGS as SO_2 and that there was no loss from the plume due to wet or dry deposition. For a 12-h transit time and an oxidation rate of 0.06%/h, the maximum amount of secondary $SO_4^=$ aerosol generated during transit would be only 0.043 $\mu g/m^3$ $SO_4^=$. For a 48-h transit and a daily average homogeneous SO_2 oxidation rate of 0.03%/h, the concentration

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[12] Figure 6.10 of the NPS-WHITEX report provides conversion rate estimates for December and March, two periods that bracket the February period of interest. Because the present objective is to estimate a lower limit on the SO_2 conversion, the conversion rate estimates for December are used. These conversion rates are consistent with experimental data on the SO_2 conversion rate that was observed to occur in the NGS plume during another visibility experiment (Richards et al., 1981).

would be only 0.086 $\mu g/m^3$ $SO_4^{=}$. Aerosol concentrations of this magnitude should have little effect on haze at Hopi Point. This conclusion is based on field measurements and on the relationship between $SO_4^{=}$ concentrations and haze (Trijonis et al., 1989).

From data in the NPS-WHITEX report on the primary-particle emission rate from NGS and the primary-particle concentration in the NGS plume, the committee also estimated an upper limit for the transport of primary-particle emissions from NGS to Hopi Point and concluded that NGS primary particles should not play an important role in GCNP haze.

The calculations above assume that the only effective processes are the generation of secondary aerosol through homogeneous gas-phase chemistry and the transport of primary aerosol. In reality, some depositional loss of SO_2 and aerosol during transport to Hopi Point is inevitable. Consequently, the actual contribution of NGS emissions would be lower than that calculated here.

Maximum Conversion of SO_2 to $SO_4^{=}$. The maximum conversion rate would occur through heterogeneous oxidation of SO_2 by H_2O_2 (and O_3) to form $SO_4^{=}$ within cloud droplets. Video tapes show that clouds were present in the vicinity of the Grand Canyon during much of the study period. Measurements of H_2O_2 rarely are made in the atmosphere except in connection with a specific experimental program. None were made at or near the Grand Canyon during WHITEX. The nearest temporal and spatial measurements appear to be those of Van Valin et al. (1987). They found that for cloud-free conditions, H_2O_2 concentrations ranged between 0.1 and 0.5 ppb in February 1987 near Memphis, Tennessee, approximately the latitude of the Grand Canyon. Because H_2O_2 concentrations in the Grand Canyon were not measured, the committee assumed that, for the purpose of estimating the maximum oxidation rate, these data were representative of the NGS plume. If 0.1-0.5 ppb H_2O_2 reacts completely with SO_2 in an oxidant-limited system, about 0.4-2 $\mu g/m^3$ of $SO_4^{=}$ is formed. This concentration range includes the maximum 12-h average total $SO_4^{=}$ concentration measured at Hopi Point, 1.3 $\mu g/m^3$ (derived from Fig. 3) during February 11-12, and is below the limit of the maximum amount of NGS-sulfur that potentially could be present—6 $\mu g/m^3$ $SO_4^{=}$ (2 $\mu g/m^3$ $S(CD_4)$).

This estimate suggests that the heterogeneous conversion of NGS-emitted SO_2 could account for virtually all of the $SO_4^{=}$ measured at Hopi Point on February 11-12. If all of the $SO_4^{=}$ measured at Hopi Point over February 11-12 were due to NGS emissions, then NGS definitely would have contributed to haze at Hopi Point. However, the validity of the assumptions regarding heterogeneous conversion are unknown.

Was there evidence that regional background $SO_4^=$ could have accounted for a significant fraction of the 1.3 $\mu g/m^3$ $SO_4^=$ at Hopi Point on February 11?

This question can be addressed by examining the WHITEX data obtained at all sampling stations. Late on February 9, $SO_4^=$ levels were relatively uniform throughout the area northeast of NGS, in the range of 0.6-1 $\mu g/m^3$ (Fig. 3). The same was true early on February 10, at all sites northeast of NGS except Monticello, where the concentration was about 1.4 $\mu g/m^3$. (Data from Page were excluded from this background determination, because this site clearly was too close to NGS.) Thus, values in the range of 0.6-1 μg $SO_4^=/m^3$ could be concluded to constitute the regional background for February 9, and early February 10.

Subsequent NGS emissions can be added to the background as the air mass passes over NGS and proceeds to GCNP. At Hopi Point on February 11, $SO_4^=$ concentrations were near 1.3 $\mu g/m^3$. On February 12, the total $SO_4^=$ measured at Hopi Point was about the same as the initial regional $SO_4^=$ background estimate. If the committee's estimate of background $SO_4^=$ is correct, then the $SO_4^=$ increment above regional background that might be attributed to recent NGS emissions would be in the range of 0.3-0.7 $\mu g/m^3$ out of the total 1.3 $\mu g/m^3$ measured at Hopi Point on February 11.

The committee's assumption of the existence of background $SO_4^=$ concentrations says nothing about the possible sources of that background $SO_4^=$. It does not preclude the possibility that a significant portion of background $SO_4^=$ was derived from NGS emissions in the days preceding February 11. CD_4 concentrations at Mexican Hat and Monticello on February 9-10 were 8-9 × 10^{-5} ppt (Appendix 2, p. 76-77). Samples collected at Green River, Canyonlands, and Bullfrog during this period were not analyzed for CD_4. The measured concentrations imply an upper-bound NGS contribution of 0.15 $\mu g/m^3$ $SO_4^=$ to the regional background, suggesting that on this occasion, most of the regional background $SO_4^=$ was actually not derived from NGS.

This illustration obviously is inexact; its primary purpose is to show the importance of accurate data on background concentrations for each air-parcel trajectory. Unfortunately, background $SO_4^=$ was not adequately addressed in the NPS-WHITEX report. A further analysis of the WHITEX data is warranted to assess the effect of regional background $SO_4^=$ on the amount of $SO_4^=$ measured at Hopi Point. Even if this analysis were pursued, background estimates at GCNP would remain uncertain, because the number of sampling stations was inadequate to evaluate this aspect. The existence of significant background $SO_4^=$ concentrations implies that, if NGS emissions were controlled, wintertime haze at GCNP likely would be reduced but not eliminated.

THE COMMITTEE'S CONCLUSIONS IN PERSPECTIVE

The committee cautions that its conclusions do not resolve whether EPA should require NGS to install the best available retrofit technology. First, the committee's conclusions are not binding on EPA or any other government agency. Second, even if accepted by EPA, the committee's conclusions would not dictate a particular result to EPA's rule making. Section 169A of the Clean Air Act generally requires the installation of BART on any "major stationary source" built after 1962 if that source "emits any air pollutant which may reasonably be anticipated to cause or contribute to any impairment of visibility" in a listed Class I area, such as GCNP. The phrase "may reasonably be anticipated" suggests that Congress did not intend to require EPA to show a precise relationship between a source's emissions and all or a specific fraction of the visibility impairment within a Class I area. Rather, EPA is to assess the risk in light of policy considerations regarding the respective risks of overprotection and underprotection (U.S. Congress, 1977). These considerations transcend scientific issues and are, therefore, outside this committee's purview.

CONCLUSIONS

The committee concludes that an experiment such as the WHITEX study provides a valuable data base that sheds light on the nature and magnitude of the haze problems at GCNP. The use of CD_4 as a tracer was innovative and added considerable power to the program. NPS and the members of the WHITEX team are to be commended for including the use of this unique and powerful tracer in WHITEX and for attempting to use CD_4 in qualitative and quantitative assessments of the impact of NGS emissions on haze at GCNP. The NPS mounted a very complex atmospheric measurement and analysis program at many field sites in a region that is logistically difficult to service, and NPS went well beyond the original planned feasibility study. On the basis of the data presented in the NPS-WHITEX report, the committee concludes that, at some times during the study period, NGS contributed significantly to haze at Hopi Point in GCNP. The committee bases this qualitative assessment on evaluations of meteorological, photographic, chemical, and other physical evidence.

The committee also concludes that aspects of the WHITEX data analysis preclude a quantitative determination of the exact fraction of the Grand Canyon haze problem that is attributable to NGS. These aspects are primarily related to problems with implementation and interpretation of multiple linear regression models. The NPS-WHITEX report makes few attempts to quantify

References

ADEQ (Arizona Department of Environmental Quality). 1989. EPA Air Docket, A-89-02, II-D-06. Environmental Protection Agency, Washington, D.C.

Balling, R.C., Jr., and J.L. Sutherland. 1988. Diurnal and seasonal wind direction pattern within the mountain-valley terrain near Glen Canyon Dam, Arizona. J. Appl. Meteor. 27:594-598.

Buat-Ménard, P., H. Cachier, and R. Chesselet. 1989. Sources of particulate carbon in the marine atmosphere. P. 252 in Chemical Oceanography, J.P. Riley, R. Chester, and R. Duce, eds. Vol. 10. New York: Academic Press.

California Air Resources Board. 1990. Emission Inventory for 1987. Technical Support Division, Emission Inventory Branch. Sacramento, CA: California Air Resources Board.

Chinkin, L.R., and D.A. Latimer, and H. Hogo. 1986. Layered haze observed at Bryce Canyon National Park: A statistical evaluation of the phenomenon. Pp. 709-735 in Transactions of the APCA International Specialty Conference: Visibility Protection, Research and Policy Aspects, P.S. Bhardwaja, ed. Pittsburgh, PA: Air Pollution Control Association.

EIA (Energy Information Administration). 1987. Electric Power Quarterly. DOE/EIA-0397(87)1Q. Energy Information Administration. Washington, D.C.: U.S. Department of Energy.

Malm, W.C. 1990. Presentation to the National Research Council Committee on Haze in National Parks and Wilderness Areas. March 28, 1990. Grand Canyon National Park, AZ.

Malm, W.C., and E.G. Walther. 1979. Reexamination of turbidity measurements near Page, Arizona, and Navajo Generating Station. J. Appl. Meteor. 18(7):953-955.

NPS (National Park Service). 1989. National Park Service Report on the Winter Haze Intensive Tracer Experiment (WHITEX). Final Report, December 4. Air Quality Division, National Park Service, Ft. Collins, CO.

Richards, L.W., J. A. Anderson, D. L. Blumenthal, A. A. Brandt, J. A. McDonald, N. Walters, E. S. Macias, and P. S. Bhardwaja. 1981. The chemistry, aerosol physics, and optical properties of a western coal-fired power plant plume. Atmos. Environ. 15:2111-2134.

(SRP) Salt River Project. 1971. The Navajo Power Project and Environmental Protection Plans. Brochure #CR16-470-25C. Salt River Project: Phoenix, AZ.

SCENES (Sub-Regional Cooperative Electric Utility, Department of Defense, National Park Service, and Environmental Protection Agency Study on Visibility). 1987. Winter Haze Intensive Tracer Experiment (WHITEX). SCENES Newsletter 1(2):1-4.

(SAI) System Applications, Inc. 1985. Modeling Regional Haze in the Southwest: A Preliminary Assessment of Source Contributions. SYSAPP-85/038. San Rafael, CA.: Systems Applications Publication Center.

Trijonis, J., R. Charlson, R. Husar, W. Malm, M. Pitchford, and W. White. 1989. Visibility: Existing and Historical Conditions—Causes and Effects. State-of-Science and State of Technology Report No. 24, Draft for Public Review. National Acid Precipitation Assessment Program (NAPAP). Washington, D.C.: National Acid Precipitation Assessment Program.

U.S. Congress (House). 95th Cong., 1st Sess. 1977. The Clean Air Act Amendments of 1977, a report by the Committee on Interstate and Foreign Commerce. H. Report No. 95-294:43-51.

U.S. EPA (Environmental Protection Agency). 1980. Visibility Protection for Federal Class I Areas: Final Rule. Fed. Reg. *45*(233):80084-80095.

U.S. EPA (Environmental Protection Agency). 1989. Assessment of Visibility Impairment: Proposed Rule. Fed. Reg. *54*(170):36948-36953.

Van Valin, C.C., J.D. Ray, J.F. Boatman, and R.L. Gunter. 1987. Hydrogen peroxide in air during winter over the south-central United States. Geophys. Res. Lett. 14:1146-1149.

Walther, E.G., and W.C. Malm. 1979. The excellent but deteriorating air quality in the Lake Powell region. APCA Journal 29(4):378-380.

Appendices

Appendix 1:
Nature of the Visibility Problem

A person's judgment of aesthetic damage is related to the ability to see form, texture, and color of scenes at various distances. Visibility can be quantified directly in terms of human judgments or in terms of indices, such as light extinction, that can be related to judgments.

Visibility can be described quantitatively in terms of the following indices:

- Contrast—the relative brightness of various features in a scene;
- Discoloration—shifts in the wavelength distribution of light as it moves through the atmosphere;
- Visual range—the farthest distance at which an observer is able to distinguish a large black object against the horizon sky; and
- Extinction coefficient—the fraction of light that is attenuated per unit of distance as a light beam traverses the atmosphere.

A decrease in visual range from 130 to 110 km produces a noticeable change in the contrast (relative brightness of various features within a scene) and coloration (distribution in wavelengths of received light) of a view only 30 km away. Contrast and coloration yield the best correlation with subjective human evaluations of visual air quality.

Of the four visibility indices, the extinction coefficient is the one that is most directly related to the composition of the atmosphere. The total amount of light extinction is the sum of scattering and absorption of light by particles and gases. The extinction coefficient, B_{ext}, in conventional units of Mm^{-1} $[(10^6 m)^{-1}]$, thus comprises four additive components, $B_{ext} = B_{sg} + B_{ag} + B_{sp} + B_{ap}$:

B_{sg} = light scattering by gas molecules. Gas scattering is almost entirely attributable to oxygen and nitrogen molecules in the air, and it is often referred to as Rayleigh or natural "blue-sky" scatter. It is essentially unaffected by pollutant gases, such as SO_2, because of their low relative concentrations.

B_{ag} = light absorption by gas molecules. Nitrogen dioxide (NO_2) is the only significant atmospheric trace gas that absorbs visible light.

B_{sp} = light scattering by particles. B_{sp} usually is dominated by fine particles, because the scattering efficiency/unit particle mass exhibits a pronounced peak in the range of 0.1-1.0 µm. Many pollutant aerosol species occur in this size range.

B_{ap} = light absorption by particles. B_{ap} arises almost entirely from black carbon particles.

In the absence of particles, visibility is limited by the Rayleigh scattering of air molecules. Under such conditions, the nominal visual range, which is one component of visibility, is on the order of 330-400 km. Fluctuations of mass concentration up to a few tenths of a $\mu g/m^3$ should cause little perceptible change in the optical properties of the atmosphere, except perhaps under conditions of high RH. At an aerosol mass of a few tenths of a $\mu g/m^3$, aerosol extinction starts to become significant compared with Rayleigh scattering. Increases in aerosol concentrations above this level could cause significant decreases in visual range and shifts in color and contrast. RH affects visibility significantly—especially for aerosols that are hygroscopic, such as those containing $SO_4^{=}$. The size of hygroscopic aerosols can change dramatically with changes in RH. However, the factors controlling growth are quite complex and very sensitive to the composition of the aerosol. During WHITEX, the mean fine particle concentration at Hopi Point was reported as about 1.6 $\mu g/m^3$; of this, $SO_4^{=}$ contributed about 0.5 $\mu g/m^3$.

Past estimates (Trijonis et al., 1989) suggest the following annual average apportionment of B_{ext} in the region of GCNP:

B_{sg} = 10 Mm^{-1}.
B_{sp} (natural) = 7 Mm^{-1}.
B_{sp} (regional anthropogenic average) = 8 Mm^{-1}.

These values suggest a natural background extinction (B_{sg} + B_{sp} (natural)) of about 17 Mm^{-1} out of the current regional average of about 25 Mm^{-1}. Accordingly, pollution aerosols from all sources have on the average resulted in about a 50% increase in light extinction above natural conditions. During haze episodes, pollution aerosols can produce extinction values 2 or more times higher than natural levels (Trijonis et al., 1989), so that pollution effects dominate natural contributions. Under such circumstances, visibility will be severely degraded.

Appendix 2: Selected Pages from the NPS-WHITEX Report

Page[1]

CHAPTER 1

CHAPTER 9

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[1] NPS-WHITEX page numbers are shown in parentheses.

OTHER PERTINENT NPS-WHITEX REPORT PAGES

APPENDIX 6B

Chapter 1

INTRODUCTION

THE DESIGN AND IMPLEMENTATION OF THE WINTER HAZE INTENSIVE TRACER EXPERIMENT - WHITEX

1.1 Overview

Protection of vistas for certain national parks and wilderness areas as provided by the Clean Air Act Amendments of 1977[1] has stimulated an interest in visibility research. Methods are being developed and used to characterize atmospheric transparency, to identify the relative importance of the various particulate and gaseous atmospheric materials and to determine the role of man-made emissions. Much of the research has been conducted in the desert Southwest, in particular in northern Arizona and southern Utah. The juxtaposition of energy resources (especially coal) and national parks (including Grand Canyon, Bryce Canyon and Canyonlands) in an area where small changes in aerosol concentration can significantly affect visibility justifies concern by government and private organizations for visibility impacts resulting from industrial emissions. Figure 1.1 is an emission density map showing locations of major SO_x sources and national parks on the Colorado Plateau.

Accordingly, a cooperative effort, the Subregional Cooperative Electric Utility (comprised of the Electric Power Research Institute, Southern California Edison and the Salt River Project), National Park Service (NPS), Environmental Protection Agency (EPA) and Department of Defense (DOD)) Study, SCENES, is centered in this area. It operates on a five-year plan (1984–1989) involving continual visibility and aerosol measurements at a dozen locations, plus more in-depth intensive and special studies conducted over shorter, seasonally representative periods. One of these, the Winter Haze Intensive Tracer Experiment (WHITEX) was conducted in January and February 1987 in the Colorado River area of the Colorado Plateau.

1.2 Background

The Colorado Plateau, with its many associated class I national park areas, was chosen as the location to implement a scoping study designed to evaluate the ability of a variety of receptor modeling approaches to attribute visibility impairment in a number of class I areas to emissions from a single point source, the Navajo Generating Station. The area, shown in Figure 1.3, is by most standards remote, undeveloped and sparsely populated. The nearest large urban areas are over 300 km away. Only a few smaller urban areas or towns are within the area; these include Moab, Utah, Page, Arizona and at the most western end of the study area, Las Vegas, Nevada.

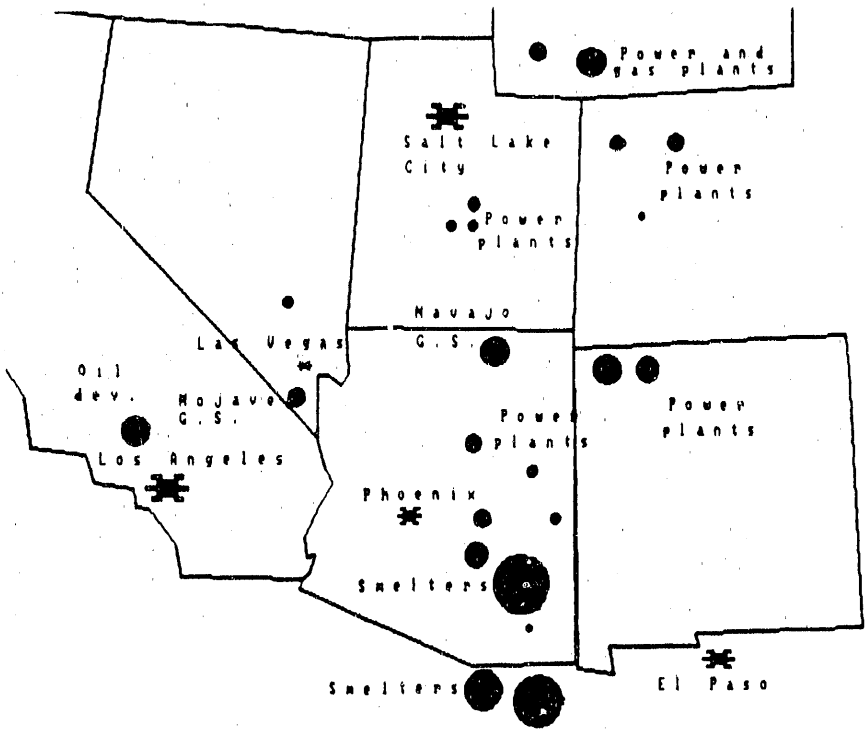


Figure 1.1: Approximate SO_x emissions from major point sources and urban areas in the southwest United States for 1987.

There are a few small industrial enterprises in the vicinity such as sawmills, mining and milling operations and a number of large coal fired electric generating facilities, one of which is the Navajo Generating Station (NGS) located near Page, Arizona. The Navajo Generation Station is a large (2300 MWe) coal-fired power plant without sulfur dioxide control equipment; thus, it is a significant single contributor of sulfur species — sulfur dioxide (SO_2) and sulfate particles ($SO_4^=$) — to the atmosphere of the region. With the control and shutdown of several smelters in the western U.S., NGS has become the largest single SO_2 emission source in the West.[2]

The terrain surrounding the lower Colorado River rises to about 800 meters above the water's surface. Wintertime meteorology in the area is characterized by several periods of stagnation, of about one week each. Air pollutants can be trapped by a persistent thermal inversion below the height of the surrounding terrain during the stagnation periods, resulting in a distinct visible surface haze layer. These stagnant periods are interrupted by synoptic-scale fronts with associated strong winds sweeping rapidly through the area.[3] The winter haze over the Colorado Plateau area has been routinely documented with photographs since 1978 by the EPA, NPS and BLM (Bureau of Land Management). The haze is usually seen as a bright white layer with a distinct upper edge and it occasionally includes one or more perceptible layers.[3, 4]

A number of earlier investigations have been prompted by the need to determine the origins of the haze. NPS sponsored several modeling efforts to evaluate the possibility that the Navajo Generating Station is partially responsible for the haze.[5, 6] A wind field model was adapted for the area's terrain and winter meteorology to investigate transport and diffusion. In a separate study, ambient nitrogen chemistry was theoretically simulated to estimate the role of particulate nitrates.[7] Though both efforts added to the knowledge of the source of the haze, the uncertainties in modeling this situation led to approaching the question with observational studies.

A SCENES special study was previously conducted in 1986 at Glen Canyon to provide information to aid in planning subsequent observations.[8] The primary objectives of this exploratory study were to determine the horizontal and vertical extent of the haze and to identify major constituents of the haze. Aircraft-based measurements confirmed the haze to be more extensive horizontally than just the Glen Canyon area (e.g., extending at least to Bryce and Grand Canyon to the west). This greater horizontal extent enlarges the number of possible emission sources to be considered. This complicates the source attribution because the contribution of any one source may vary considerably with time and location within the haze. In mapping the vertical extent of the haze with an instrumented aircraft, the air above the inversion layer was found to be essentially particle-free, while below the layer, scattering coefficients varied from two to five times clean air values. Sampling at the south end of the lake only, the particles were found to be composed largely of sulfates and organics. Nitrates were found to be primarily gaseous, with about a tenth of the total being particulate nitrate.

1.3 Study Plan

Shortly after the completion of the winter 1986 study, the SCENES participants began planning a more comprehensive effort for the winter of 1987 to address persistent questions about the nature and sources of winter haze conditions. The overall study objective was to assess the feasibility of attributing emissions from a single point source to visibility impairment in prespecified geographic regions. Specifically, various receptor and deterministic models were to be evaluated and intercompared as to their ability to link Navajo Generating Station emissions to visibility impairment at Grand Canyon and Canyonlands National Park and Glen Canyon National Recreation Area. Meeting this objective is a three tier process. First the relative contribution at the receptor site of primary and secondary aerosols associated with the NGS must to be achieved. Secondly, the contribution of these aerosol species to atmospheric optical variables needs to be established, and finally the contribution of optical variables associated with power plant emissions to an incremental decrease in visibility below that which would have existed otherwise needs to be examined.

The major focus of the WHITEX study is centered around the evaluation of receptor oriented approaches for linking NGS emissions to aerosol concentrations in Grand Canyon and Canyonlands National Parks and Glen Canyon National Recreation Area. In a receptor type model the atmosphere is treated as a black box through which source emissions are transferred to the receptor site. Source receptor relationships are empirically developed using statistical inference techniques. Historically, the chemical mass balance (CMB) formalism has been most often used to link source emissions to aerosol concentrations at a receptor site. The CMB approach essentially uses ratios of trace material associated with different sources in combination with trace material measured at the receptor site to apportion primary (nonconverting) aerosol species. However, CMB has serious short comings in that it is not designed to apportion secondary aerosols, such as ammonium sulfate, to its SO_2 source. Other common types of receptor models include principal component analysis (PCA) and multiple linear regression (MLR). Explanations of these models are given by Watson,[9] Chow,[10] and Hopke.[11] Furthermore, Dzubay et al.,[12] Lewis and Stevens,[13] and Stevens and Lewis[14] have integrated a number of these approaches into a hybrid receptor model that can be used to apportion secondary aerosols. All these models can be shown to be special cases of a deterministic statement, referred to in this report as the general mass balance model (GMB), of how gases and aerosols are transported and transformed as they pass through the atmosphere. The GMB model is discussed in detail in Appendix 6A.

In this report a regressional model, derivable from the GMB equations and referred to as the tracer mass balance regression (TMBR) model, will be used to apportion secondary aerosol species. A full derivation of TMBR can be found in Appendix 6B. TMBR is formulated to apportion secondary aerosols if certain assumptions are met. First, a unique trace material must be associated with a source or group of sources and secondly the atmospheric transfer processes must be approximated be a linear model. If a unique tracer is not available CMB can be used to apportion non-unique tracer species to source types and the analysis can still be carried out. TMBR essentially relies on relative changes in secondary aerosol and tracer concentrations over time to yield the desired apportionment.

Finally, a differential mass balance model (DMB) having elements of both deterministic and receptor modeling approaches will be used to apportion secondary aerosols. The term differential is derived from the use of unique trace material spatial concentration gradients to calculate atmospheric dispersion. Atmospheric deposition, chemical conversion and transport time are calculated from first principles. A full derivation of the DMB model can be found in Appendix 6C.

Table 1.1 outlines the different approaches as well as summarizes the major advantages and disadvantages of each technique. For the sake of completeness, advantages and disadvantages of deterministic modeling are also included in Table 1.1.

Several less quantitative approaches are also used to gain insight into basic physio-chemical processes at work over the time period for which apportionment estimations are carried out. These include evaluation of the relative emission strengths, plume trajectory and streakline analysis, spatial and temporal trends, analysis of synoptic meteorological conditions, and deterministic wind field modeling on the mesoscale level (<200 km).

The focus of attributing NGS emissions to optical variables will be directed toward the relationship between various attributed aerosol species and optical extinction. Since a change in atmospheric transmittance (extinction) under a variety of conditions has been shown to be a good approximation to the change in the atmospheric modulation transfer function.[15] The optical ex-

Table 1.1: Brief description of the advantages and disadvantages of various receptor techniques examined in the Winter 1986 WHITEX study.

RECEPTOR MODELING METHOD	DESCRIPTION	ADVANTAGES	DISADVANTAGES
Tracer Mass Balance Regression (TMBR)	Passive tracer release from point source over extended period of time. Measurement of tracer and aerosol species at receptor site over time allows for building a regression model relating aerosol species to point source emissions.	Allows for establishing fractional contribution of point source emissions to various aerosol species relative to other sources and background.	Unique tracer for each source of interest may not be available. Collinearity between tracer material may lead over or underestimation of source contribution
Chemical Mass Balance (CMB)	Measurement or knowledge of source natural tracer profile along with measurement of some natural tracers at receptor sites.	Yields fractional contribution of each source to various aerosol species at receptor site	Model requires conservation of mass over transport distance of interest. Requires all source profiles to be known. Natural tracer profiles from different sources may be similar
Differential Mass Balance (DMB)	Passive tracer release from point source with measurements of aerosol and tracer concentrations at receptor site.	Yields insight into chemical conversion rates and deposition velocities. Yields fractional contribution of point source emissions to aerosol species at receptor site	Results are confounded by uncertain knowledge of background aerosol concentrations and relative importance of deposition and conversion rates
Deterministic Model Calculations	Deterministic model calculations of temporal and spatial aerosol concentration gradients are compared directly to field measurements of those same aerosol species.	Historically, experience offers a basic understanding of the chemical and physical processes involved in the production and dispersion of various aerosol species	Requires validated models of wind fields and chemistry modules. No widely accepted models at this time

tinction associated with particles can be calculated using Mie theory if the particle characteristics are well documented. The size distribution, shape, density and refractive index of the particles are needed for such a calculation. This information is generally either unavailable or available with insufficient detail, so that Mie theory must rely upon a number of assumptions. Mass size distribution data can be obtained using size segregating samplers, however, the capability of such samplers to correctly represent the particulate nitrate or the labile fraction of organic carbon is questionable. For instance, the mass of the most common labile component, water, is not accounted for.

A second approach for attributing aerosol species to extinction is a statistical methodology that relies on multilinear regression (MLR) analysis where it is assumed that the relationships between atmospheric extinction, b_{ext}, and aerosol species mass concentrations, m_i, are represented by $b_{ext} = \sum_i \sigma_i m_i$. The measured m_i's are assumed to be independent variables, b_{ext} is the dependent variable and regression coefficients, σ_i's, are interpreted as *extinction or scattering efficiencies* depending on whether b_{ext} or b_s is used in the analysis.

For the relationship between b_{ext} and the m_i's to be linear requires many restrictive assumptions. Assumptions associated with inherent unknown and physical processes are discussed in some detail by White.[19] To minimize uncertainty in estimated extinction efficiency, MLR is compared to efficiencies derived from other studies.

Two ways of apportionment of extinction will be examined in this report, first by fine mass:

$$b_{ext} = a_1 m_f + a_2 C_e + a_3[NO_2] + b_{RAY} \tag{1.1}$$

where m_f is fine mass associated with scattering, C_e is elemental carbon which is primarily a particle absorption term, $[NO_2]$ is nitrogen dioxide concentration, and b_{RAY} is scattering due to atmospheric gases. The second procedure is apportionment by aerosol/chemical species:

$$b_{ext} = a_0 + a_1 S + a_2 N + a_3 C_o + a_4 C_e + a_5[NO_2] + a_6 Soil + a_7 R \tag{1.2}$$

where S, N, C_o, C_e are particulate ammonium sulfate, ammonium nitrate, organic and elemental carbon respectively, soil is the fine mass oxides associated with Ca, Si, Fe, K and Ti, and R refers to mass between 2.5 μ and 10 μ.

Once source emissions have been attributed to extinction it is possible to estimate whether those emissions will effectively reduce the ability to see a landscape feature. Two optical variables which effectively characterize the visual effect of atmospheric haze on vistas are the change in contrast of adjacent scenic features or those features against the horizon sky as a function of aerosol concentration and/or composition and the contrast of the haze itself as seen against the sky or terrain background. Calculation of the change in contrast of adjacent scenic features as a function of aerosol concentration in the most general case requires a knowledge of the atmospheric modulation transfer function, $M_{tf,a}$ which, in turn, requires information on inherent scene brightness, path radiance and atmospheric transmittance between scene and observer. However, as stated above, atmospheric modulation transfer can be approximated by atmospheric transmittance under a wide variety of conditions.[21] Under these circumstances,

$$\frac{dC_r}{C_r} = -R\,db_{ext} \tag{1.3}$$

where dC_r/C_r is the percentage change in apparent contrast of a vista at a distance R and db_{ext} is the incremental change in extinction coefficient derived from the extinction attribution portion of the program. Thus, Equation 1.3 can be used to assess the amount of vista contrast reduction associated with NGS emissions. The calculation is straightforward and can be carried out by the interested reader. However, these calculations will not made as part of this report.

1.4 Interrelationships Between Aerosol, Optical and Visibility Apportionment

The interrelationship between measurements and apportionment methodologies as designed for the WHITEX program are schematically represented in Figure 1.2. For purposes of understanding the relative accuracy of the various receptor modeling approaches, the study was designed to calculate aerosol and optical apportionment in at least two separate ways. In this way, a relative accuracy of each technique can be estimated. For instance, measurement of b_{ext} and aerosol composition are combined in an MLR model to apportion extinction to aerosol species. An independent analysis using a literature review of theoretically derived extinction efficiencies allows for an independent estimation of extinction apportionment. The two estimations can then be intercompared, and differences, if any, reconciled. Similarly, tracer (CD_4) released over time can be used in a TMBR analysis to apportion sulfur and nitrate aerosols to NGS emissions, while DMB analysis will yield an independent estimation of NGS emission contribution to secondary aerosols at the receptor site. The NGS sulfate and nitrate contribution to total particulate matter at the receptor sites is then combined with the extinction apportionment analysis to yield the extinction that can be attributed to NGS. The two techniques can then be intercompared and differences, if any, reconciled. Finally, the extinction apportionment data can be combined with information from radiative transfer calculations and radiance measurement program to apportion visibility impairment.

1.5 Measurement Program

The measurement program consisted of four different types of ground station configurations and one airborne platform. The configurations are classified as major receptor, satellite, gradient, and background sites. Table 1.3 summarizes the variable measured, the methodology used to collect the data and the frequency at which the measurement was made while Table 1.2 summarizes the function of each monitoring site. Figure 1.3 shows the location of each monitoring site.

Major receptor (Type A) sites had all those measurements required for aerosol, extinction, and visibility impairment attribution while satellite sites consisted only of trace element, wind speed, and wind direction measurements. Satellite sites were used to characterize air masses flowing into and out of the study region and were used to explore temporal and spatial trends. At gradient and background sites b_{scat}, fine mass, ions, carbon, trace elements, and tracer concentrations and meteorological variables were measured. Gradient sites were also used to examine spatial and temporal trends while the background site helped characterize air masses on a regional scale.

A full description of how each parameter was measured is discussed in chapter three. Therefor only a brief description of the measurements will be presented here. Atmospheric extinction was measured with a newly developed long path transmissometer.[20] Atmospheric scattering was measured with MRI 1550 integrating nephelometers which were zeroed with clean air every few hours and span calibrated twice during the course of the study.[22] Haze, contrast, and $M_{ij,a}$ can be calculated from reconstructed radiance fields derived from slides taken during the course of the study.[23] The color slides were taken using automatic photographic monitoring instrumentation comprised of 35 mm cameras using 135 mm lenses and loaded with Kodachrome 25 color slide film.

Particulate measurements were made by the IMPROVE sampler[24] at nine sites and by the stacked filter unit[25] (SFU) at three additional sites. At three of the twelve sites, the size-classifying isokinetic sequential aerosol sampler[26] (SCISAS) collected fine and total (smaller than 15 μm) samples on four filters. The SCISAS sampler was used primarily to establish the relative accuracy and precision of the various sampling systems.

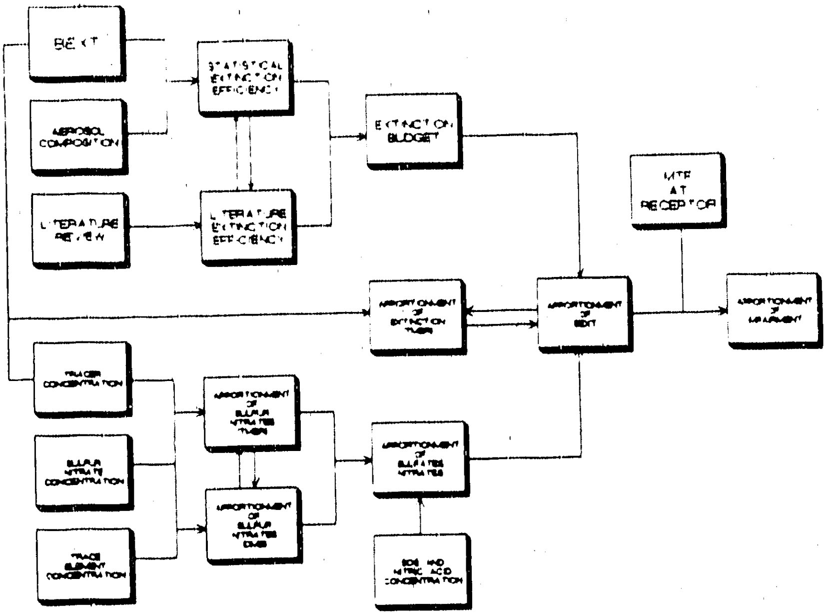


Figure 1.2: Flow diagram showing the relationship between measurement and apportionment of visibility impairment.

A "DRUM" sampler was operated to yield size resolved atmospheric element concentrations.[9] The version used for this study consisted of six rotating drums of the Mercer impactor type and to low pressure rotating drums. The nominal size ranges (aerodynamic diameter in μm) for five stages are 0.6-1.2, 1.2-2.4, 2.4-4.85, 4.85-9.6, 9.6-16.0 μm.

The optical absorption of particles on the fine teflon filter were measured by a laser integrating plate method (IPM). Light of a 633 nm wavelength from the $He(Ne)$ laser was diffused and collimated to provide a uniform beam of around 0.7 cm^2 at the sample. The light transmitted through the sample was collected with an ORIEL photodiode detection system.[10]

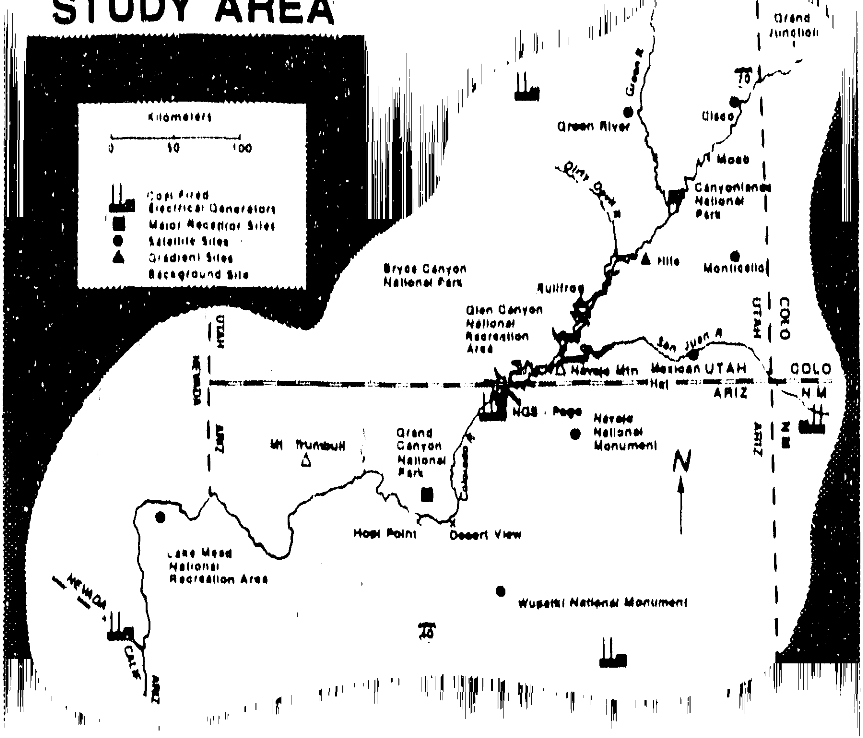
The tracer injected into NGS stacks was deuterated, or "heavy", methane, CD_4.[11] Though chemically similar to normal methane, heavy methane has a higher molecular weight which allows it to be distinguished by mass spectrometry at very low concentrations (1 part in 10^7). CD_4 was released continuously in proportion to NGS emissions in the time period of study. At receptor sites, 60 liters of air were pumped into large mylar/polyethylene bags and then concentrated under pressure into steel pressurized containers. The containers were shipped to Los Alamos National Laboratory for mass spectrometer analysis.

Meteorological variables were gathored using standard sensors, while upper air winds, temperature and dew point temperature were gathered using airsondes. The aircraft was equipped with an SO_2 monitor, an integrating nephelometer, a particulate monitor used for NGS plume characterization and bottles used for collecting large volumes of air required for the CD_4 analysis.

Table 1.2: List of the function associated with each of the monitoring sites.

SITE	SITE TYPE		FUNCTION
Glen Canyon National Recreation Area Grand Canyon National Park Canyonlands National Park	Receptor site	→	Calculation of the relative contribution of each aerosol species associated with NGS emissions
Lake Mead National Recreation Area Wupatki National Monument Navajo National Monument Monticello, Utah Cisco, Utah Hanksville, Utah	Satellite	→	Characterize the inflow/outflow of tracers of opportunity and spatial and temporal trends
Hite, Utah Bullfrog, Utah	Gradient	→	Characterize spatial and temporal trends
Bryce Canyon National Park	Background	→	Used to estimate background associated with long range transport from distant sources

STUDY AREA


Kilometers
0
50
100
Coal Fired Electrical Generators
Major Receptor Sites
Satellite Sites
Gradient Sites
Background Site
Grand Junction
Green R
Green River
Cisco
70
Moab
Canyonlands National Park
Dirty Devil R
Hite
Monticello
Bryce Canyon National Park
Bullfrog
Glen Canyon National Recreation Area
San Juan R
Navajo Mtn
Mexican Hat
UTAH
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N M
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NGS · Page
Navajo National Monument
Mt Trumbull
Grand Canyon National Park
Colorado R
Hopi Point
Desert View
Lake Mead National Recreation Area
Wupatki National Monument
40
N
NEVADA
CALIF
ARIZ

Table 1.3: List of the optical variables, aerosol species, meteorological variables, and measurement methodologies used at each of the monitoring sites.

	Location*	Method	Substrate	Frequency
Optical				
b_{scat}	A,C	Nephelometer	NA	Continuous
b_{ext}	A	Transmissometer	NA	Continuous
M_{ERA}	A,D E, Cedar Mt., Echo Cliffs, Arches	Photographic	NA	Hourly
Haze Contrast	D, Cedar Mt., Echo Cliffs	Photographic	NA	Hourly
Particulate				
Fine Particles				
Mass	A,B,C,D	**IMPROVE/**SCISAS	Teflon	12 hr
Ions	A,D	IMPROVE/SCISAS	Teflon	6 & 12 hr
Nitrate (denuder)	A,D	IMPROVE/SCISAS	Nylasorb	12 hr
Elemental & Organic Carbon	A,D	IMPROVE/SCISAS	Quartz	12 hr
Trace Elements	A,B,C,D,E	IMPROVE/SCISAS/ **SFU	Teflon	6 & 12 & 24 hr
Size Segregating				
Trace Elements	A	**DRUM	Teflon	6 hr
Giant Particles (>10.0 μ)	Canyonlands	--	--	--
Large Particles (2.5-10.0 μ)	Grand Canyon, Bryce, Glen Canyon, Lake Mead	SCISAS	Teflon	12 hr
Gases				
SO_2				
Gas chromatograph	Canyonlands	Gas Chromatograph	NA	2 & 4 hr
K_2CO_3 Impregnated Filter	A	K_2CO_3 Impregnated Filter	Same	12 hr
CD_4 Tracer	A	Grab Sample & Gas Chromatograph	NA	6 hr
Meteorological				
WS,WD	A,B,C,D	--		10 min
Temperature, RH	A,B,C,D	--	--	10 min
Upper Air	Canyonlands, Glen Canyon	Airsonde	-	Twice/Day

* A = Major receptor
B = Satellite
C = Gradient
D = Background
E = Airborne Platform

** IMPROVE, SCISAS, SFU and DRUM refer to types of samplers which are discussed in some detail in the text

1.0 Report Outline

Chapter 2 examines the climatology of the study area during the time period the WHITEX study was carried out. Chapter 3 presents the measurement program. A description of each sampling procedure and method of establishing accuracy and precision is presented. When a variable was obtained by more than one method an intercomparison of those variables is examined. Finally CD_4 injection and measurement is described. Chapter 4 is an overview of the data used when making attribution calculations. First the temporal history of each variable is presented along with pertinent descriptive statistics. Finally relationships among variables is explored with simple scatter plots of one variable plotted as a function of another. Chapter 5 examines the optical characteristics of pertinent aerosol species. Average extinction budgets are calculated for the full WHITEX time period as well as on a daily basis. Chapter 6 is the heart of the WHITEX report. The ability of various receptor modeling techniques to attribute secondary aerosols to their respective sources is explored. Chemical mass balance, tracer mass balance and differential mass balance are quantitative models investigated while several non quantitative approaches are used to either confirm or negate quantitative calculations. The non quantitative procedures were also used to gain insight into physicochemical processes at work during the study period. Appendices present a complete description of each of the receptor modeling techniques. Chapter 7 presents a deterministic calculation of wind fields and transport pathways of conservative tracers during one particular low visibility episode. The possibility of transport into and out of the study area is also explored. Chapter 8 explores the climatology of extreme (high) sulfate episodes and compares the WHITEX climatology to historic records of other sulfate episodes. Finally, Chapter 9 presents an overview of conclusions that can be drawn from the WHITEX study.

References

[1] 42 U.S.C. 7475(d)(2), Pub. L. 95-95 Stat. 745.

[2] Chinkin, L.R., D.A. Latimer, L. Mahoney, "Western States Acid Deposition Project Phase I Volume 2 — A review of emission inventories needed to regulate acid deposition in the western United States," *SYSAPP-87/072*, Systems Applications, Inc., San Rafael, CA.

[3] Chinkin, L.R., D.A. Latimer, H. Hogo, "Layered haze observed at Bryce Canyon National Park. A statistical evaluation of the phenomenon." In: *Proceedings of the Air Pollution Control Association International Specialty Conference "Visibility Protection: Research and Policy Aspects"* September 8-10, 1986, Jackson Hole, Wyoming. P.S. Bhardwaja, Editor. 1987.

[4] Malm, W.C., R. Eldred, T. Cahill, "Visibility and particulate measurements in the western United States." In: *Proceedings of the 78th Annual Meeting and Exhibition of the Air Pollution Control Association*, June 1985, Detroit, Michigan. Paper #85-11.3.

[5] R.A. Pielke, "The use of mesoscale models to assess wind distribution and boundary layer structure in complex terrain," *Boundary Layer Meteorology*, 31:217-231.

[6] Yu, C.H., R.A. Pielke, "Mesoscale air quality under stagnant synoptic cold season conditions in the Lake Powell area," *Atmos. Environ.*, 20:1751, 1986.

[7] Latimer, D.A., M.W. Gery, H. Hogo, "A theoretical evaluation of the role of nighttime nitrate formation in the formation of layered haze," Systems Applications, Inc. Report *SYSAPP-86/107*, November 1986.

[8] Fitz, D.R., P. Bhardwaja, J. Sutherland, G.M. Markowski, "Characterization and extent of winter hazes in the vicinity of Lake Powell," Presented at the 1987 Annual Meeting of the American Association for Aerosol Research, September 1987, Seattle, Washington.

[9] Watson, G.W., "Overview of receptor model fundamentals," *JAPCA*, 34:619, 1984.

[10] Chow, J.C., *Development of a composite modeling approach to assess air pollution source-receptor relationships*, Doctor of Science Dissertation, Harvard University, Cambridge, MA.

[11] Hopke, P.K. "Receptor Modeling in Environmental Chemistry," *Chemical Analysis*, 76, John Wiley & Sons, New York, NY.

[12] Dzubay, T., R.K. Stevens, G.E. Gordon, I. Olmez, A.E. Sheffield, W.J. Courtney, "A composite receptor method applied to Philadelphia aerosol," *Environ. Sci. & Technol.*, 22(1), 1988.

[13] Lewis, C.W., R.K. Stevens, "Hybrid receptor model for secondary sulfate from an SO_2 point source," *Atmos. Environ.* 19(6):917-924, 1985.

[14] Stevens, R.K., C.W. Lewis, "Hybrid receptor modeling." In: *Extended Abstracts for the Fifth Joint Conference on Applications of Air Pollution Meteorology with APCA*, November 18-21, 1986, Chapel Hill, N.C. Published by the American Meteorological Society, Boston, Mass.

[15] Malm, W.C., R.C. Henry, "Regulatory perspective of visibility research needs." In: *Proceedings of the 80th Annual Meeting of the Air Pollution Control Association*, June 21-26, 1987, New York, NY, 1988.

[16]Henry, R.C., C.W. Lewis, P.K. Hopke, H.J. Williamson, "*Review of receptor model fundamentals*," *Atmos. Environ.*, 18:1507, 1984.

[17]Malm, W.C., M. Pitchford, H.K. Iyer, "Design and implementation of the Winter Haze Intensive Tracer Experiment — WHITEX," presented at the APCA International Specialty Conference "Receptor Models in Air Resource Management," February 1988, San Francisco, California.

[18]Malm, W.C., R.C. Henry, "Regulatory *perspectives of visibility research needs*," In, *Proceedings of the 80th Annual Meeting and Exhibition of the Air Pollution Control Association*, June 21-26, 1987, New York, NY.

[19]White, W.H., "On the theoretical and empirical basis for apportioning extinction by aerosols: A critical review," Atmos. *Environ*, 20:1659, 1986.

[20]Malm, W.C., G. Persha, R. Tree, R. Stocker, I. Tombach, H. Iyer, "Comparison of atmospheric extinction measurements made by a transmissometer, integrating nephelometer and teleradiometer with natural and artificial black target," In, *Proceedings of the Air Pollution Control Association International Specialty Conference 'Visibility Protection: Research and Policy Aspects'*, September 8-10, 1986, Jackson Hole, Wyoming. P.S. Bhardwaja, Editor. 1987.

[21]Malm, W.C., "An examination of the ability of various physical indicators to predict judgment of visual air quality," In, *Proceedings of the 78th Annual Meeting of the Air Pollution Control Association*, June 16-21, 1985, Detroit, MI. Paper #85-10.1. 1986.

[22]Charlson, R.J., H. Horvath, R.F. Pueschel, "The *direct* measurement of atmospheric light scattering coefficient for studies of visibility and pollution," *Atmos. Environ.*, 1:469, 1967.

[23]Johnson, C.E., J.V. Molenar, J.R. Hein, W.C. Malm, "The use of a scanning densitometer to measure visibility-related parameters from photographic slides," In, *Proceedings of the 77th Annual Meeting and Exhibition of the Air Pollution Control Association*, June 1984, San Francisco, CA. Paper #84-61P.1. 1985.

[24]Eldred, R.A., T.A. Cahill, M. Pitchford, W.C. Malm, "IMPROVE — A new remote area particulate monitoring system for visibility studies," In, *Proceedings of the 81st Annual Meeting of the Air Pollution Control Association*, June 19-24, 1989, Dallas, TX. Paper #88-54.3. 1989.

[25]Cahill, T.A., R.A. Eldred, P.J. Feeney, "The stacked filter unit revisited," In, *Proceedings of the AWMA/EPA International Specialty Conference 'Visibility and Fine Particles'*, October 15-19, 1989, Estes Park, CO. 1990. To appear.

[26]Rogers, C.F., J.G. Watson, C.V. Mathai, "Design and testing of a new *size classifying* isokinetic sequential aerosol sampler," *JAPCA*, December 1989. To appear.

[27]Sutherland, J.L., P.S. Bhardwaja, "Composition of the aerosol in northern Arizona and southern Utah," In, *Proceedings of the Air Pollution Control Association International Specialty Conference 'Visibility Protection: Research and Policy Aspects'*, September 8-10, 1986, Jackson Hole, Wyoming. P.S. Bhardwaja, Editor. 1987.

[28]IMPROVE Sampler Manual, Version 2. Robert A. Eldred, Crocker Nuclear Laboratory, University of California, Davis, CA 95616. January 1988.

[49] Cahill, T.A., P.J. Feeney, R.A. Eldred, W.C. Malm, "Size/time/composition data at Grand Canyon National Park and the role of ultrafine sulfur particles," In, *Proceedings of the Air Pollution Control Association International Specialty Conference 'Visibility Protection: Research and Policy Aspects'*, September 8-10, 1986, Jackson Hole, Wyoming. P.S. Bhardwaja, Editor 1987.

[50] Eldred, R.A., P.J. Feeney, T.A. Cahill, W.C. Malm, "Sampling techniques for fine particle/visibility studies in the National Park Service network," In, *Proceedings of the Air Pollution Control Association International Specialty Conference 'Visibility Protection: Research and Policy Aspects'*, September 8-10, 1986, Jackson Hole, Wyoming. P.S. Bhardwaja, Editor 1987.

[51] Alei, M., J.H. Cappis, M.M. Fowler, D.J. Frank, M. Goldblatt, P.R. Guthals, A.S. Mason, T.R. Mills, E.J. Mroz, T.L. Norris, R.E. Perrin, J. Poths, D.J. Rokop, W.R. Shields, "Determination of deuterated methanes for use as atmospheric tracers," *Atmos. Environ.*, 21:909, 1987.

Chapter 9

Conclusions

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 extinction 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 50 ± 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

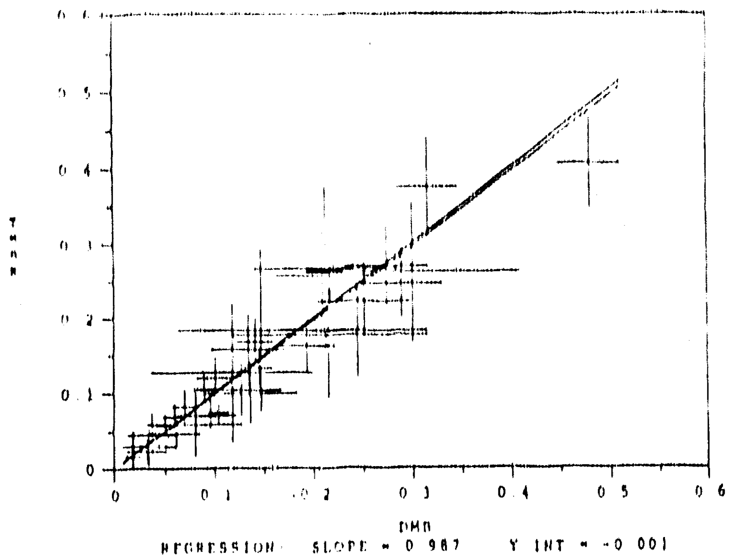

Figure 9.1. Scatter plot of sulfate sulfur $(\mu g/m^3)$ due to NGS at Hopi Point as calculated by TMBR and DMB. The lines shown are the 1:1 line and the ODR regression line.

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 ± 4 percent while the DMB calculation yielded 68 ± 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 ± 28 percent. At Page the results from the two techniques are again quite similar. Best estimate of NGS contribution to sulfate are 75 ± 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 ± 13 percent. For the time period with the highest light extinction the fraction due to NGS was 59 ± 18 percent.

- fine particles. Fine particles (smaller than 2.5 μm) were collected on Teflon, nylon, and quartz filters by IMPROVE,[4] SFU[5] and SCISAS samplers. These filters were analyzed by a variety of methods: gravimetric analysis, particle induced x-ray emission (PIXE), x-ray fluorescence (XRF), proton elastic scattering, ion chromatography, and thermal carbon methods. Concentrations were determined for mass, major and trace elements, hydrogen, sulfate, nitrate, nitrate plus nitric acid vapors, and organic and elemental carbon. Comparisons were made between IMPROVE and SCISAS samples at Page. The model analyses were based primarily on the measurements of the IMPROVE sampler.
- coarse particles. Coarse particles (2.5 μm to 15 μm) were collected on Nuclepore filters by SFU samplers at four sites and analyzed by gravimetric analysis. Total particles (smaller than 15 μm) were collected on Teflon filters by SCISAS samplers at four other sites and analyzed by gravimetric analysis; the coarse mass was estimated by subtraction.
- particles in multiple size ranges. Particles in nine size ranges were collected by the DRUM (Davis Rotating Unit for Monitoring) sampler and analyzed by PIXE.[6]
- SO_2. SO_2 was measured by the IMPROVE sampler using the impregnated filter method; in this method, SO_2 was converted to sulfate on K_2CO_3 impregnated filters and analyzed for sulfate by ion chromatography. Results were compared with measurements on impregnated-filter and annular denuder samplers operated at Page by Brigham Young University (BYU).[7]
- CD_4. CD_4 was released from the Navajo Generating Station. Air samples were collected in 60 liter bottles at the sampling sites and analyzed for CD_4 by gas chromatography/mass spectrometry.[8]

3.2 CD_4 Tracer Injection

During the WHITEX period, 4.9 kg of CD_4 was released through the stacks of the Navajo Generating station. A manifold and valve system permitted the release through any of the three stacks. Preliminary experiments determined that the CD_4 was well mixed and conserved in the stack. The release rate was based on the power output of the station. From January 7 to 30, the ratio of tracer released to the power output was held between 2.0 to 2.5 mg CD_4/MW. Beginning on January 30, the rate was increased to approximately 3.5 mg CD_4/MW. However, between February 6 and 10, the ratio rose because of an unanticipated outage (to nearly 5 mg CD_4/MW), and on February 13, the ratio decreased to 2.5 mg CD_4/MW, because of an unanticipated early restart. The details of the injection are discussed in Appendix 3B. The analysis of the samples is discussed in section 3.5 and in Appendices 3A and 3B.

3.3 Sample Collection

A complete suite of measurements were made at the three receptor sites: Canyonlands National Park, Hopi Point (Grand Canyon National Park), and Page (Glen Canyon National Recreation Area). Each site had (1) a multimodule version of the IMPROVE sampler that collected fine particles on 6 filters and SO_2 on another filter, with durations ranging from 6 to 24 hours; (2) a DRUM sampler that collected particles in nine size ranges, (3) a system to collect 6-hour air samples for CD_4 analysis, and (4) a transmissometer to measure b_{ext}, an integrating nephelometer to measure b_{scat}, and a metorological package. SCISAS samplers operated at Hopi Point and Page as part of the SCENES network, with the sampler at Page following the time schedule of the

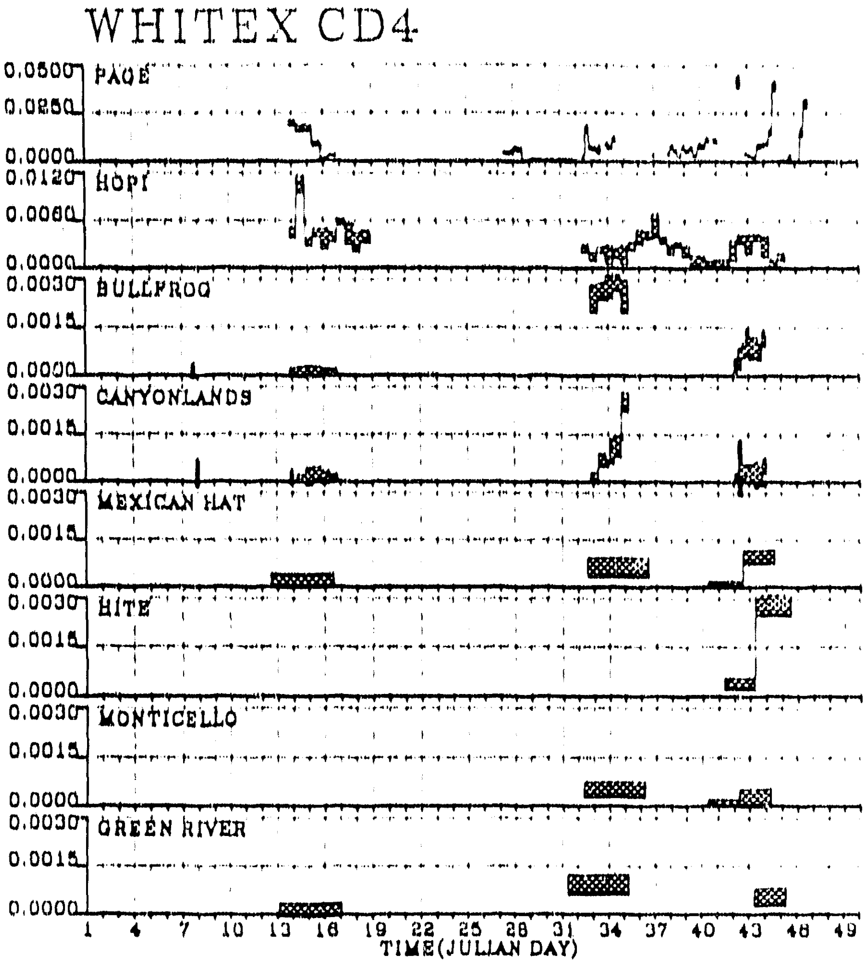

Figure A.15 CD_4 concentrations (ppt) at eight WHITEX receptor sites

Table 4.5: Statistical summary of elemental sulfur concentrations ($\mu g\ m^{-3}$) during the WHITEX study period.

ELEMENTAL SULFUR ($\mu g\ m^{-3}$)

SITE	NO of OBS	STD DEV	MAX	90th PRCNTL	75th PRCNTL	MEAN	MED	MIN
GREEN RIVER	81	0.1913	1.0960	0.5786	0.4217	0.3451	0.3141	0.0398
PAGE	133	0.2723	4.2724	0.7403	0.3861	0.3320	0.2852	0.0157
CISCO	44	0.1243	0.5759	0.4868	0.3813	0.3031	0.2847	0.0297
MEXICAN HAT	71	0.1121	0.6048	0.4602	0.373[illegible]	0.2920	0.3016	0.0169
HITE	80	0.1840	1.0732	0.4655	0.3676	0.2826	0.2599	0.0216
BULLFROG	166	0.2034	4.7449	0.4308	0.3382	0.2656	0.2230	0.0105
CANYONLANDS	163	0.1215	1.8883	0.4225	0.3149	0.2424	0.2278	0.0142
MONTICELLO	72	0.1559	0.8355	0.3870	0.3274	0.2421	0.2020	0.0336
WUPATKI	43	0.1331	0.7264	0.3779	0.2792	0.2238	0.2343	0.0000
NAVAJO	42	0.0981	0.47[illegible]	0.3025	0.2360	0.1662	0.1416	0.0197
HOPI POINT	167	0.1341	1.955[illegible]	0.3498	0.2374	0.1652	0.1212	0.0032
MEADVIEW	16	0.0860	0.3067	0.2815	0.2466	0.1589	0.1461	0.0405
BRYCE CANYON	39	0.0699	0.2805	0.2276	0.1592	0.1125	0.1061	0.0053

Table 4.6: Statistical summary of CD_4 (ppt) at eight receptor sites using fully scaled CD_4 at Page and Hopi.

CD_4 (ppt)

SITE	NO of OBS	STD DEV	MAX	90th PRCNTL	75th PRCNTL	MEAN	MED	MIN
PAGE	32	00803	04328	01066	00781	00587	00421	00000
HOPI POINT	36	00192	01051	00470	00388	00293	00285	00034
HITE	2	00171	00279	00279	00279	00158	00158	00037
BULLFROG	20	00102	00288	00275	00207	00101	00077	00009
GREEN RIVER	3	00040	00093	00093	00093	00053	00053	00013
CANYONLANDS	20	00057	00253	00111	00050	00045	00023	00009
MEXICAN HAT	4	00040	00095	00095	00087	00046	00041	00008
MONTICELLO	3	00020	00049	00049	00049	00029	00028	00009

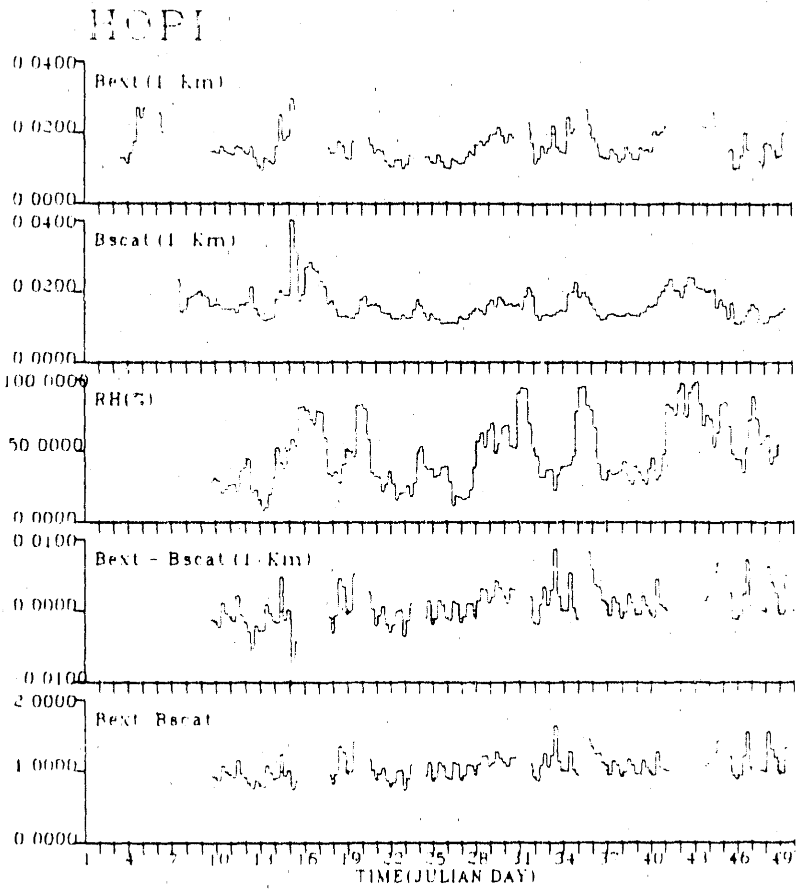

Figure 5.4: Time traces of optical data and relative humidity at Hopi Point.

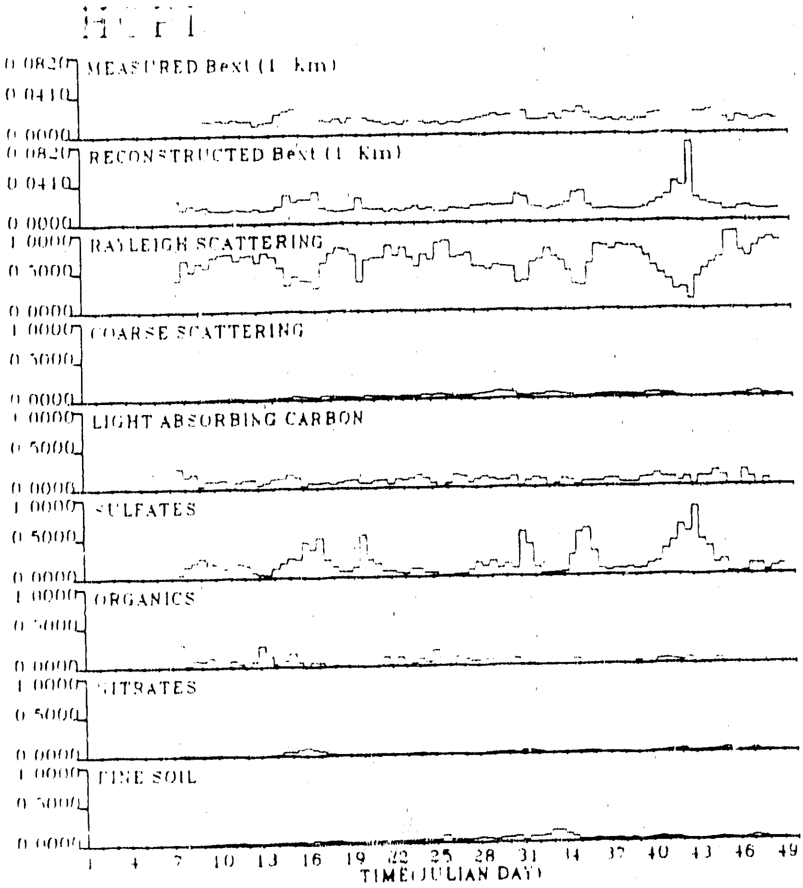

Figure 5.22: Measured and reconstructed 12-hour averaged extinction coefficients (Km^{-1}) and the fraction due to each component at Hopi Point. Extinction includes Rayleigh scattering.

Table 6.1: Regional emissions in units of tons/day from coal fired power plants, copper smelter, and large urban areas. These values are based on annual data for 1987.

SITE	LOCATION	SO_2	NO_x	PART
Apache	Cohise, AZ	5.5	7.4	3.8
Coronado	St. Johns, AZ	17.5	19.2	.27
NGS	Page, AZ	163	73	6.4
Springerville	Springerville, AZ	13.2	10.1	.5
Cholla	Joseph City, AZ	44.7	35.9	4.4
Cameo	Grand Junction, CO	8.2	9.6	•
Craig	Craig, CO	21.4	38.4	•
Hayden	Hayden, CO	40.5	23.0	•
Escalante	Preuritt, NM	2.7	7.9	.4
Four Corners	Fruitland, NM	105.5	227.7	2.8
San Juan	Waterflow, NM	115.6	93.2	•
North Valmy	Valmy, NV	11.5	15.9	3.3
Mohave	Mohave, NV	51.5	42.2	•
Carbon	Castledale, UT	15.6	12.0	•
Hunter	Castledale, UT	15.9	53.4	•
Huntington	Huntington, UT	32.6	58.1	•
Bridger	Point of Rocks, WY	145.9	90.1	12.3
Naughton	Kemmerer, WY	41.4	40.3	•
Asarco-Hayden	Hayden, AZ	92	•	•
Inspiration	Miami, AZ	54	•	•
Magma	San Manuel, AZ	480	•	•
Nacozari	Nacozari, Sonora	380	•	•
Cananea	Cananea, Sonora	240	•	•
	LA/Southern CA	•	•	•
	Phoenix, AZ	•	•	•
	Las Vegas, NV	•	•	•
	El Paso, TX	•	•	•
	Salt Lake City,UT	•	•	•

vapor concentrations or ozone concentrations were less than assumed, actual rates would be less than these calculations.

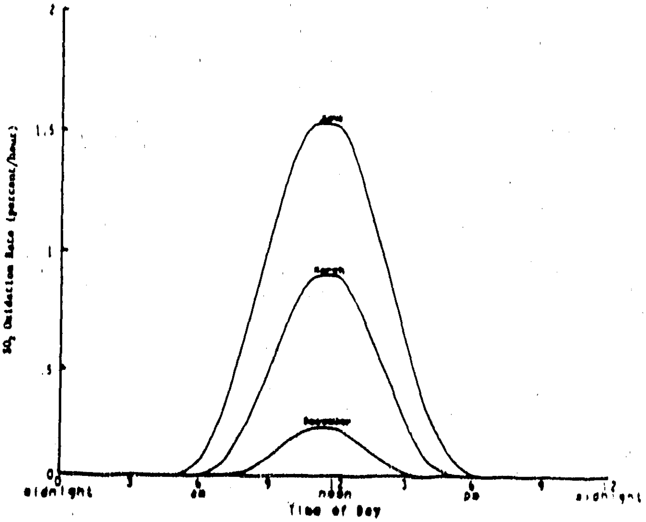

Figure 6.10: Calculated gas-phase SO_2 oxidation rates as a function of time of day and season (Source: Latimer et al., 1985).

Perhaps the most important conclusion from Figure 6.10 is that gas-phase reactions simply are not fast enough to explain the SO_2 oxidation rates on the order of 1 percent per hour suggested by WHITEX data. If one computes the 24-hour average SO_2 oxidation rate from Figure 6.10 for winter, one obtains a value of approximately 0.03 percent per hour, a factor of 30 too low. Even the maximum gas-phase oxidation rate of 0.2 percent per hour is too low by a factor of 5.

Thus, these high oxidation rates can only be explained by aqueous-phase oxidation reactions that occur within aerosols, or fog and cloud droplets. Theoretical calculations suggest that the higher rates observed during WHITEX are indeed plausible. Figure 6.11 shows the sulfur oxidation rates as a function of droplet pH as a result of reactions with ozone (O_3), hydrogen peroxide (H_2O_2), iron (Fe), manganese (Mn), carbon (C), nitrous acid (HNO_2), and nitrate nitrogen dioxide (NO_2). All reactions, except the one with hydrogen peroxide, are strong functions of pH. As the droplet becomes more acidic (from production of sulfuric acid), oxidation is dramatically slowed. However, the reaction with H_2O_2 remains rapid.

The reaction rates shown in Figure 6.11 are based on an assumed H_2O_2 concentration of 1 *ppb*. Although H_2O_2 concentrations were not measured during WHITEX, a series of measurements were made by Van Valin[51] during February 1987 along the 91.5 degree meridian from Iowa to the Gulf of Mexico. They found H_2O_2 concentrations varied inversely with latitude, with values in the range from <0.1 to 1.0 *ppb*. At the latitude of the Grand Canyon (36 degrees), they found H_2O_2 concentrations in the range from 0.1 to 0.6, centered on 0.3 *ppb*. They also found that H_2O_2

Table 6.10: Estimated age of the Navajo Generating Station plume (in hours) at various locations in the WHITEX study region, January–February 1987.

Notes

1. If numbers are not presented for given time and place, the NGS plume is not expected to be in the area.
2. If numbers are presented in parentheses (), the NGS plume would be present with minor modifications of winds.

WHITEX Study Period in 1987		Navajo Generating Station Plume Age (hours)					
Day	Hour	Page Arizona	Hopi Point	Canyonlands & Monticello	Bullfrog Marina & [illegible]	Green River Utah	Mexican Hat Utah
9	6	6-12					
9	17	6-12	12				
10	6	6-12					
10	17	6-36					
11	6	6-12	36-48				
11	17	6-12	58				
12	6	6-12	(6-72)				
12	17	6-12	(24)				
13	6	6-12	(48)				
13	17	6-12	(0-48)		6-38		
14	6	6-24	(6-48)				
14	17	6-12	(24-60)				
15	6	6-12	12-24				
15	17	6-12	24*				
16	6	6-12	29*				
16	17	6-12	60*				
17	6	6-12	36				
17	17	6-12	(36)				
18	7	6-12	(6)				
18	17	6-12			6-12	12	2
19	17	6-12	6-48		24		
20	6	6-12	6				
20	17	6-12	10-18				
21	6	6-24	24-30				
21	17	6-12	40-48		24-36		
22	6	6-24					
22	17	6-12			(0-36)		
23	6	6-12	64				
23	17	6-12	66				
24	6	6-60	24	48	48	48	[illegible]
24	17	6-12	36	20	6		
25	6	6-48		18	24	72	
25	17	6-12		24	24-36	64	
26	6	6-24		12	48	66	
26	17	6-44			[illegible]	[illegible]	18
27	6	6-12		72	72-84	[illegible]	18
27	17	6-12		60	[illegible]	[illegible]	18
28	6	6-36		96	72-120	132	48

*Based on Surface Winds

Table 6.10: cont.

WHITEX Study Period in 1987		Navajo Generating Station Plume Age (hours)					
Day	Hour	Page, Arizona	Hopi Point	Canyonlands & Monticello	Bullfrog Marina & Hite, Utah	Green River, Utah	Mexican Hat, Utah
28	17	6-12		(36)			
29	6	6-12	(12)	48	(48)		(48)
29	17	6-(72)	6-(54)	48-(120)			120
30	6	6-(120)	12-96				
30	17	6-12	60-120				
31	6	6-12					
31	17	6-12	(12)				
32	8	6-12	(132)				
32	17	6-(24)	(30)		12		24
33	6	6-(48)	(132)	40	6	24-30	48
33	17	6-(48)	(48-72)	48	48	48	60
34	6	6-60	84	60	72	20-48	72
34	17	6-(36)	96	72	24-(36)	30-(60) 84	
35	6	6-(48)	(24)	60-72	48-60	(60-72)	90
35	17	6-60	10-(60)	96	72	(72)	96
36	6	6-96	96-120				
36	17	6-(120)	6-120				
37	6	6-(120)	6-120				
37	17	6-12	2-(36)				
38	6	6-(24)	48-(132)				
38	17	6-(12)	36-60				
39	8	6-12	36-(48)				
39	17	6-12	(8)				
40	6	6-12	(24)				
40	17	6-12	(24-36)				
41	6	6-12					
41	17	6-12					
42	8	6-12	(18)				
42	17	6-12	(12-30)				
43	6	6-12	12				
43	17	6-(24)	30-(48)				
44	6	6-(120)	(96)	120	12-(96)	(132)	12-(96)
44	17	6-(120)	(48)	24-(96)	10-(120)	(132)	(96)
45	11	6-12					
45	17	6-12					
46	[illegible]	6-12					
46	8	6-12	12-(24)				
47	6	6-12					
47	[illegible]	6-12	6-12				
48	6	6-12					
48	17	6-24					
49	6	6-12	24-(30)				

Table 6.43: Time history of measured total sulfur ($\mu g/m^3$), NGS total sulfur ($\mu g/m^3$) and fraction of ambient total sulfur due to NGS based on DMB analysis for Hopi Point.

	Total Measured S			NGS Contribution to S			Fraction Due to NGS		
	Ambient	Uncertainties		NGS	Uncertainties			Uncertainties	
Julian Day	S Concent	due to K's	due to Measmt	S Concent	due to K's	due to Measmt	Ratio	due to K's	due to Measmt
13.8	0.25	0.04	0.04	1.40	0.47	0.18	5.63	1.90	1.28
14.3	1.50	0.11	0.11	3.31	1.12	0.31	2.21	0.75	0.24
14.8	0.71	0.05	0.05	0.66	0.38	0.11	0.93	0.53	0.17
15.3	0.38	0.05	0.05	1.39	0.44	0.13	3.65	1.16	0.66
15.8	0.33	0.04	0.04	0.76	0.38	0.28	2.34	1.18	0.93
16.2	0.59	0.04	0.04	0.77	0.42	0.11	1.30	0.71	0.20
16.7	0.78	0.05	0.05	0.57	0.37	0.04	0.72	0.47	0.06
17.2	0.57	0.04	0.04	0.57	0.47	0.17	1.01	0.83	0.42
17.7	0.34	0.04	0.04	0.40	0.37	0.14	1.20	1.11	0.47
18.2	0.20	0.04	0.04	1.23	0.42	0.24	6.13	2.12	1.90
32.2	0.08	0.03	0.03	0.06	0.10	0.01	0.78	1.26	0.76
32.7	0.07	0.03	0.03	0.22	0.17	0.09	2.90	2.23	2.52
33.2	0.09	0.03	0.03	0.05	0.10	0.01	0.57	1.10	0.38
33.7	0.12	0.03	0.03	0.15	0.16	0.10	1.24	1.36	0.84
34.2	1.01	0.06	0.06	0.09	0.11	0.02	0.09	0.11	0.02
34.7	0.50	0.04	0.04	0.12	0.06	0.09	0.24	0.11	0.19
35.2	4.42	0.33	0.33	0.59	0.29	0.10	0.13	0.06	0.03
35.7	0.61	0.05	0.05	1.24	0.39	0.29	2.05	0.64	0.53
36.2	0.91	0.07	0.07	0.16	0.23	0.01	0.17	0.26	0.02
36.7	1.33	0.10	0.10	1.66	0.57	0.46	1.25	0.43	0.16
37.2	0.75	0.06	0.06	1.08	0.37	0.11	1.43	0.49	0.14
37.7	0.71	0.06	0.06	0.72	0.24	0.13	1.02	0.35	0.22
38.2	0.55	0.05	0.05	0.24	0.31	0.02	0.43	0.56	0.06
38.7	0.24	0.03	0.03	0.26	0.24	0.07	1.10	0.98	0.35
39.2	0.34	0.04	0.04	0.11	0.11	0.07	0.31	0.31	0.22
39.7	0.55	0.04	0.04	0.19	0.07	0.24	0.35	0.12	0.43
40.2	0.79	0.06	0.06	0.10	0.07	0.04	0.13	0.09	0.06
40.7	0.65	0.05	0.05	0.10	0.06	0.08	0.16	0.08	0.13
41.2	0.49	0.04	0.04	0.20	0.06	0.14	0.42	0.13	0.40
41.7	0.27	0.04	0.04	0.69	0.21	0.41	2.60	0.78	1.67
42.2	0.54	0.04	0.04	0.93	0.39	0.14	1.71	0.71	0.29
42.7	0.46	0.04	0.04	0.98	0.29	0.43	2.12	0.63	0.79
43.2	0.40	0.04	0.04	1.22	0.38	0.12	3.05	0.98	0.41
43.7	0.25	0.04	0.04	0.46	0.27	0.21	1.79	1.06	0.40
44.2	0.16	0.03	0.03	0.02	0.01	0.03	0.12	0.09	0.21
44.7	0.15	0.03	0.03	0.17	0.10	0.05	1.14	0.70	0.50

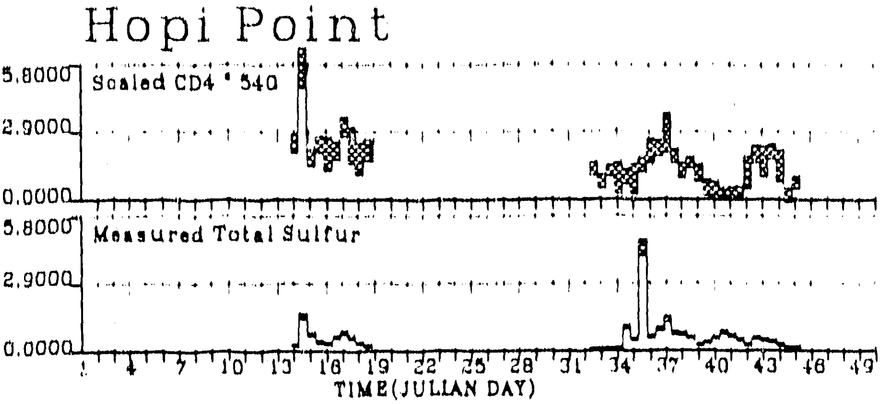

Figure 6.71 Time plot of predicted upper limit of NGS contribution to total sulfur at Hopi Point (540 × SCD_4) and measured total sulfur.

- 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

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

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

$$S_{T\,a} = [540]SCD_{4\,a} \qquad (6.10)$$

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 ± 0.03 $\mu g/m^3$. 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.

APPENDIX 6B: Tracer Mass Balance Model Regression (TMBR) Model and Tracer Mass Balance (TMB) Model

Overview

The Tracer Mass Balance Regression Model is a multiple regression based model which may be used to apportion an aerosol species of interest measured at a receptor site to the various contributing sources. It has been shown to be a special case of the General Mass Balance (GMB) Model. The actual regression analysis may be performed using the method of least squares. However, since the independent variables in this model are ambient concentrations of various aerosol components which are measured with error, the method of Orthogonal Distance Regression (ODR) is expected to give better estimates of the source contributions. A detailed discussion of the method of ODR may be found in the book by Fuller(1987).

Model Equations

The basic equation for TMBR model equation is

$$C_{ik} = \gamma_0 + \sum_{u=1}^{h} \gamma_{i_u} C_{i_u k} \varphi_{uk} \tag{1}$$

where:

C_{ik} = concentration of species i at the receptor for time period k. In the current application i refers to Sulfate Sulfur or SO2 sulfur.

$C_{i_u k}$ = concentration of trace element i_u which serves as a tracer for a group of one or more sources, for time period k.

γ_{i_u} = regression coefficient for trace element i_u which acts as a tracer for a group of one or more sources

γ_0 = intercept representing the mean background concentration of the species of interest, at the receptor.

h = number of groups of sources, each group being represented by a particular aerosol species which acts as a tracer for that group of sources.

ϕ_{uk} = a factor which is a function of field measurements, sampling period and possibly source type, chosen in such a way that the s coefficients in the model (1) are invariant with respect to the sampling period.

The model is known as the tracer mass balance (TMB) model when only a single trace element is used as a tracer for a particular source and all the remaining sources are accounted for by the intercept term in the model. When several trace elements are used in addition to the tracer for the distinguished source of interest, then the model is referred to as tracer mass balance regression (TMBR) model. The simplest versions of the TMBR model and the TMB model use $\phi_{uk} = 1$ for all time periods and source groups. In the current application we have used $\phi_{uk} = 1$ as well as $\phi_{uk} = RH_k$ where RH_k is the relative humidity at the receptor during sampling period k.

The use of RH_k as a linear factor in the above model was motivated by the following considerations. In apportioning a secondary aerosol, the constant $d_{i_u jk}$ derived from the GMB model had the form

$$d_{i_u jk} = \frac{r^*_{ijk}}{r_{i_u jk}} \frac{c_{ijk}}{c_{i_u jk}} \tag{2}$$

with

$$r^*_{ijk} = \frac{K_c(i^*,j,k)}{K_c(i^*,j,k) + K_d(i^*,j,k) - K_d(i,j,k)} \cdot$$

$$\{exp(-K_d(i,j,k)t_{jk}) - exp(-[K_c(i^*,j,k) + K_d(i^*,j,k)]t_{jk})\} \tag{3}$$

and

$$r_{i_u jk} = exp(-(K_c(i_u,j,k) + K_d(i_u,j,k))t_{jk}) \tag{4}$$

If the species i_u does not convert and its deposition rate is the same as that of the secondary aerosol species i being apportioned, then

$$r_{i_u jk} = exp(-K_d(i,j,k)t_{jk}) \tag{5}$$

so that the ratio $r^*_{ijk}/r_{i_u jk}$ reduces to $K_c(i^*,j,k)t_{jk}$ after using the approximation

$$exp(x) \approx 1 + x \text{ (when } x \text{ is sufficiently small)} \tag{6}$$

Recall that the full infinite series expansion for $exp(x)$ is given by

$$exp(x) = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \cdots$$

and we have used a first order approximation in (6). It is possible to use higher order approximations of $exp(x)$ in these derivations but this was not pursued here.

Assuming that $K(i^*, j, k)$ is proportional to RH_k with proportionality constant B, we obtain that the ratio $r^*_{ijk}/r_{i_u jk}$ is equal to $Bt_{jk} RH_k$ which gives

$$d_{i_u jk} = Bt_{jk} RH_k \frac{C_{ijk}}{C_{i_u jk}}$$

Defining

$$\gamma_{i_u k} = d_{i_u k}/\phi_{uk}$$

where $\phi_{uk} = RH_k$ and assuming that $\gamma_{i_u k}$ are constant for all sampling periods rather than the quantities $d_{i_u k}$ suggests the use of RH_k as a linear factor in the TMBR model equation (1).

For purposes of attributing total sulfur or sulfate sulfur to NGS, CD_4 is a unique NGS tracer. Furthermore, As was found to be below the detectible limit in samples gathered from within the NGS pluem (refer to Table [illegible]). Therefore, As is considered to be a unique tracer for emissions other than NGS and most probably associated with copper smelter emissions.

Therefore, in actual application of the TMBR model to WHITEX data, we have grouped the sources into 3 categories:

- NGS with CD4 serving as the tracer
- Sources with Arsenic (As) serving as a tracer, and,
- all remaining sources, if any.

In the application of the TMB model, there are only two categories, viz. NGS with CD4 as a tracer and all remaining sources.

The TMBR Model equations used in the application are

$$C_k = \gamma_0 + \sum_{u=1}^{h} \gamma_{i_u} C_{i_u k} \phi_{uk} \qquad (1)$$

where:

C_k = concentration of sulfate sulfur or total sulfur for time period k

$C_{i_u k}$ = concentration of trace element i_u for time period k

γ_{i_u} = regression coefficient associated with trace element i_u

γ_0 = intercept representing the mean background concentration of the species being apportioned due to all sources not accounted for explicitly

$\phi_{uk} = RH_k$, the relative humidity at the receptor during sampling period k, or 1, depending on the particular application

All of the cases considered may be written in the form

$$C_k = \gamma_0 + \sum_{u=1}^{I} \gamma_{i_u} A_{uk} \qquad (2)$$

where

A_{ik} = concentration of trace element t_i for time period k or concentration of trace element t_i multiplied by RH_k

The model is known as the tracer mass balance (TMB) model when the only trace element used is CD4 or scaled CD4 (SCD4). When other trace elements are used in addition to CD4, then the model is referred to as tracer mass balance regression (TMBR) model. Multiplication by RH, when included, is a surrogate for the RH dependent oxidation rate of SO2 to SO4.

Model Calculations and Uncertainties

The concentrations C_{ik} of sulfate sulfur or total sulfur associated with each trace element t_i for each time period are calculated by multiplying the measured values of A_{ik} for each trace element by the respective regression coefficients as follows.

C_{0k} would just be the intercept representing the contribution from all sources not explicitly accounted for by any of the reference species used in the TMBR model.

$$C_{ik} = s_{t_i} \cdot A_{ik} \tag{11}$$

The uncertainties for each of these concentrations are calculated by

$$\sigma_{C_{ik}} = \sqrt{A_{ik}^2 \sigma_{s_{t_i}}^2 + s_{t_i}^2 \sigma_{A_{ik}}^2 + \sigma_{s_{t_i}}^2 \sigma_{A_{ik}}^2} \tag{12}$$

The quantities $\sigma_{A_{ik}}$ are part of the WHITEX data base. The quantities s_{t_i} are obtained as outputs from the regression packages that were used. Errors in A_{ik} and the estimated regression coefficients have been assumed to be uncorrelated.

The total calculated sulfur C_k for each time period is the sum of the C_{ik}'s summed over all the reference aerosol species t_i and the intercept:

$$C_k = C_0 + \sum_{i=1}^{n} C_{ik} \tag{13}$$

The uncertainty associated with the total calculated sulfur concentration for each time period is

$$\sigma_{C_k} = \sqrt{\sigma_{C_0}^2 + \sum_{i=1}^{n} \sigma_{C_{ik}}^2} \tag{14}$$

assuming the covariance terms arising in the derivation are negligible. The sources assumed to be associated with each trace element are:

- CD4 or SCD4 — Navajo Generating Station (NGS)
- Selenium (Se) — All power plants including NGS
- Arsenic (As) — Copper smelters

- Intercept – Mean background concentration.

The estimated fraction of sulfur from each source for any given time period is equal to the sulfur associated with the trace element divided by the total calculated sulfur concentration

$$F_{uk} = \frac{C_{uk}}{C_k} \tag{15}$$

The uncertainty for each of these fractions is:

$$\sigma_{F_{uk}} = \sqrt{\frac{\sigma^2_{C_{uk}}}{C^2_k} + \frac{C^2_{uk}\sigma^2_{C_k}}{C^4_k}} \tag{16}$$

The mean fraction $\overline{F}_u$ of the sulfur attributed to each source is estimated by the mean sulfur concentration $\overline{C}_u$ for that source divided by the mean total calculated sulfur $\overline{C}$:

$$\overline{F}_u = \frac{\overline{C}_u}{\overline{C}} \tag{17}$$

where

$$\overline{C}_u = \frac{1}{s}\sum_{k=1}^{s} C_{uk} \tag{18}$$

and

$$\overline{C} = \frac{1}{s}\sum_{k=1}^{s} C_k \tag{19}$$

The uncertainties for $\overline{C}_u$ and $\overline{C}$ are calculated by

$$\sigma_{\overline{C}_u} = \frac{1}{K}\sqrt{\sum_{k=1}^{s} \sigma^2_{C_{uk}}} \tag{20}$$

and

$$\sigma_{\overline{C}} = \frac{1}{K}\sqrt{\sum_{k=1}^{s} \sigma^2_{C_k}} \tag{21}$$

The uncertainties associated with the mean fractions are calculated by

$$\sigma_{\overline{F}_u} = \sqrt{\frac{\sigma^2_{\overline{C}_u}}{\overline{C}^2} + \frac{\overline{C}^2_u\sigma^2_{\overline{C}}}{\overline{C}^4}} \tag{22}$$

The uncertainty formulas are all derived using propagation of error methods and assuming the covariances between various terms occurring in the derivation are negligible.

Model Assumptions.

The regression coefficients, including the intercept term, in the model have been assumed to be time independent. The aerosol species used in the model are assumed to be tracers for nonoverlapping groups of sources. In particular, none of the species other than the tracer associated with the source of interest can be emitted by that source unless there is an independent method such as CMB modeling to partition the ambient species concentrations into components attributable to the various groups of sources.

Potential Deviations from Assumptions.

It is highly unlikely that the regression coefficients are constant for all sampling periods. This will inflate the uncertainty in the final apportionments but the extent to which this inflation occurs will depend on how variable the regression coefficients are. We investigate below the possible effects of nonconstant regression coefficients in the TMB model. A similar investigation may be carried out for the more general TMBR model but the derivations are rather cumbersome and details are omitted here. For reasons of convenience, the notation in the subsequent subsection is entirely independent of the rest of the appendix but this need not cause any confusion.

Effect of nonconstant regression coefficients in the TMB model.

Suppose

y_t = pollutant concentration at the receptor at time t.
x_t = concentration of tracer at the receptor at time t.
w_t = pollutant concentration at the receptor attributable to the source under study.
z_t = pollutant concentration at the receptor attributable to other sources.

Then

$$y_t = w_t + z_t. \tag{23}$$

We define

$$m_t = w_t / x_t \tag{24}$$

so that

$$y_t = m_t x_t + z_t \tag{25}$$

It may be desirable to account for the fact that the actual measurements of $\{y_t\}$, $\{x_t\}$ involve measurement errors. Suppose the observed quantities are $\{Y_t\}$, $\{X_t\}$ where

$$\begin{aligned} Y_t &= y_t + S_t \\ X_t &= x_t + E_t\,, \end{aligned} \tag{26}$$

$\{S_t\}$, $\{E_t\}$ being the independent set of measurement errors with means equal to 0 and known standard deviations equal to σ_S, σ_E, respectively. An estimate of the average contribution of the pollutant by the source under study is given by

$$\overline{NGS} = \hat{\beta}\bar{X}, \tag{27}$$

where $\hat{\beta}$ is the slope of a structural regression line fit obtained by regressing $\{Y_t\}$ on $\{X_t\}$, while the estimated average fractional contribution, $\bar{f}$, of the source to the receptor, for the duration of the study, is

$$\bar{f} = \frac{\hat{\beta}\bar{X}}{\bar{Y}} \tag{28}$$

We now investigate how the estimated average pollutant concentrations due to NGS can differ from the actual value for the time period in question.

In the following discussion, a quantity such as $\beta\{y, x\}$ will refer to the slope of the least squares line fitted to $\{(y_t, x_t) \mid t = 1, \ldots, n\}$, with $\{y_t\}$ as observations on a dependent variable and $\{x_t\}$ as observations on an independent variable. A quantity such as $\bar{x}$ will represent $\frac{1}{n}\sum_{t=1}^{n} x_t$ and σ_x^2 will represent $\frac{1}{n}\sum_{t=1}^{n}(x_t - \bar{x})^2$.

The true average contribution of the pollutant from NGS to the receptor site is $\bar{w} = \frac{1}{n}\Sigma w_t$. The estimated average contribution is $\hat{\beta}\bar{x}$, where $\hat{\beta}$ is the slope of the regression line fitted to the data $\{(Y_t, X_t) \mid t = 1, \ldots, n\}$. At first we will consider the situation when $\hat{\beta}$ is the least squares estimate in which case we write $\hat{\beta}_{LS}$.

It is easily verified that

$$\begin{aligned} \Delta &= \hat{\beta}_{LS}\bar{X} - \bar{w} \\ &= \frac{(\bar{x} + \bar{E})(\beta\{w, x\} + \beta\{z, x\} + \beta\{S, x\} + \lambda\beta\{w, E\} + \lambda\beta\{z, E\} + \lambda\beta\{S, E\})}{1 + 2\beta\{E, x\} + \lambda} - \bar{w} \end{aligned} \tag{29}$$

where $\lambda = \sigma_E^2/\sigma_x^2$ and Δ is the difference between the estimated average NGS contribution and the true average NGS contribution. It seems reasonable to assume that the quantities

$$\bar{E}, \beta\{S, x\}, \beta\{w, E\}, \beta\{z, E\}, \beta\{S, E\}, \beta\{E, x\} \tag{30}$$

are all nearly zero because we expect measurement errors E_t averaged over n time periods to be nearly zero and because we expect measurement errors to be uncorrelated with the true values x, z and w.

To this degree of approximation,

$$\Delta \approx \frac{\bar{x}\beta\{w, x\} - \bar{w} + \bar{x}\beta\{z, x\} - \lambda\bar{w}}{1 + \lambda}. \tag{31}$$

If $\hat{\beta}$ is the estimate obtained using structural regression (or Orthogonal Distance Regression (ODR)), denoted by $\hat{\beta}_{ODR}$, we would obtain

$$\Delta \approx (\bar{x}\beta\{w, x\} - \bar{w}) + \bar{x}\beta\{z, x\} \tag{32}$$

since $\hat{\beta}_{ODR} \approx \hat{\beta}_{LS}(1 + \lambda)$, where Δ is the difference between estimated and actual average NGS contribution during the time period under study.

The quantity $\bar{x}\beta\{w,x\} - \bar{w}$ is zero if w_t/x_t is constant and will differ from zero if the least squares line fitted to the points $\{(w_t, x_t) \mid t = 1,\dots,n\}$ has a nonzero intercept. On the other hand, the quantity $\beta\{z,x\}$ is zero or nonzero depending on whether the least squares line fitted to the points $\{(z_t, x_t) \mid t = 1,\dots,n\}$ has a zero slope or not, i.e., whether or not z_t and x_t are "correlated". Ideally, if there was a constant background pollutant concentration $z_t \equiv \bar{z}$ and if the tracer release was directly proportional to emissions, and emissions were conservative, so that $m_t \equiv \bar{m}$, we would have $\Delta \approx 0$ and the reported estimated average NGS contribution should be a reliable estimate of the actual value for the time period in question.

Model Inputs.

The model requires the following quantities as inputs:

- The ambient concentrations of the aerosol species being apportioned, which is SO4 in our application.
- The ambient concentrations of the reference or tracer species, CD4 and As.
- Relative humidity at the receptor for each of the sampling periods, when $\phi_{uk} = RH_k$ is used in the model rather than $\phi_{uk} = 1$.
- The uncertainties in the above quantities, when ODR is used to estimate the γ coefficients, rather than OLS.

Model Outputs.

The model outputs include:

- Estimates of the actual amount of the contribution and the fractional contribution of the aerosol species of interest by the source or source type of interest to the receptor, along with the associated uncertainty estimates.
- Estimates of the average amount and the average fractional amount of the aerosol species of interest contributed by each source or source type of interest along with the associated uncertainty estimates.

Appendix 3:
CD_4 as an Air-Mass Tracer

Under proper conditions, CD_4 can be used as a reliable tracer of an air mass. It is the deuterated analogue to the common atmospheric trace gas methane (CH_4), and it is present in the unpolluted atmosphere at very low concentrations. The natural abundance of the ^2H isotope of hydrogen (deuterium) is only 0.015% of the total hydrogen (^1H + ^2H + ^3H), and the probability of four deuterium atoms combining in natural-formation processes with the same carbon atom to form CD_4 is very low. If a random association of the isotopes occurred in methane formation, only about 5 molecules in 10^{16} molecules of CH_4 would be expected to be CD_4. Background levels (2.7×10^{-4} ppt) reported in the NPS-WHITEX report are considerably higher than that expected from natural sources, but they are sufficiently low to make the use of CD_4 attractive as a tracer in field studies.

The deposition velocity of CD_4 is expected to be near zero. The tropospheric lifetime of CD_4 is determined by its rate of reaction with OH radicals. This rate coefficient is less than that of CH_4 at atmospheric temperatures, and hence, it is not destroyed measurably by chemistry in the troposphere during a tracer experiment, which lasts only a few days.

The CD_4 can be isolated from other non-CH_4 atmospheric trace gases using CH_4-enriched gas samples coupled with gas chromatographic techniques. The $CD_4 : CH_4$ ratio can be readily determined from the resulting fraction containing the separated CH_4 gases using mass spectrometric procedures. From this measured ratio and the known amount of CH_4 added to the mixture, the concentration of CD_4 in the original air sample can be estimated.

Appendix 4: Commission on Physical Sciences, Mathematics, and Resources

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