United States
Environmental Protection
Agency

Environmental Sciences Research
Laboratory
Research Triangle Park NC 27711

Research and Development

EPA-600/S3-83-085 Dec. 1983

EPA

Project Summary

The Chemistry, Physics, and Optical Properties of Plumes and Background Air in the Southwest United States

D.L. Blumenthal, L.W. Richards, E.S. Macias,
R.W. Bergstrom, and P.S. Bhardwaja

VISTTA (Visibility Impairment due to Sulfur Transport and Transformation in the Atmosphere) is a cooperative program involving numerous government agencies, private companies, and universities and is jointly sponsored by the U.S. Environmental Protection Agency and Salt River Project. During the summer and winter of 1979, plume measurement programs were conducted near the Navajo Generating Station (NGS), at Page, Arizona.

During VISTTA, ground and airborne measurements of aerosol size distribution, chemistry and optical properties, as well as trace gas concentrations, were made in the plume and in background air. Extensive regional and plume telephotometer measurements, airborne measurements along telephotometer sight paths, background meteorological measurements, and source aerosol and chemistry measurements were also made. Various types of visibility measurements were compared with one another and with calculations of light extinction made using aerosol and NO_2 data. The measured plume optical effects were compared to those predicted using the EPA-Systems Applications, Inc. plume visibility model (PLUVUE).

The data base collected during VISTTA can be used for plume visibility model evaluation. Specific data from 27 sight paths through the NGS plume on June 28, July 13, December 4, 7, and 15 have been tabulated and are available for model evaluation. These data include:

- Emission characteristics of the NGS.
- Meteorological data and sun-observer-plume geometry.
- Background trace gas, aerosol, and visibility data.
- Telephotometer measurements of the plume made from four sites.
- Aircraft measurements made along the telephotometer sight path, which include plume width, pollutant concentrations, and particle light scattering (b_{sp}).

The results of the study to date indicate that:

- For the NGS plume, under most lighting and viewing conditions, NO_2 dominates the blue light extinction and brown coloration due to the plume.
- For distances up to 100 km or more for power plants like NGS, secondary aerosol formation can be ignored in visibility models under the dry conditions studied.
- Widespread areas of elevated aerosol concentrations were documented in the Southwest due to long range transport from the Southern California area and wildfires. Other causes of regional haze are known to exist but were not documented in this study.
- Evaluation of the chemistry, aerosol growth, and optics components of the PLUVUE plume visibility model showed predictions to be in reasonable agreement with the

measurements. More uncertainty was encountered with the diffusion component. A set of nine reactions among NO, NO_2, O_3, O_2, SO_2, OH, H_2O, and O('D) was found to adequately simulate the plume chemistry for the clean dry background conditions at NGS.

This Project Summary was developed by EPA's Environmental Sciences Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

In 1977, the U.S. Congress amended the Clean Air Act to set as a national goal the "prevention of any future, and the remedying of any existing, impairment of visibility in mandatory class I Federal areas which impairment results from man-made pollution" (Section 169A). In order to accomplish this goal, an understanding of the effects of current and proposed emissions on visibility is necessary. In the southwestern U.S., visibility impairment is believed to be caused in large part by sulfur-emitting sources such as urban areas, smelters, and power plants. The percentage of the total sulfur emissions due to power plants is expected to increase in future years as more coal-fired plants are built and as sulfur emissions from smelters are further reduced by new controls. To develop the technical information required to understand the contribution of coal-fired power plants to visibility impairment in western pristine areas, the U.S. Environmental Protection Agency (EPA) initiated the VISTTA project (Visibility Impairment due to Sulfur Transport and Transformation in the Atmosphere).

The VISTTA project is a multiyear cooperative effort involving several government agencies, private companies, and universities, with the overall coordination of the program the responsibility of Meteorology Research, Inc.(MRI).*

The general goals of the VISTTA project are to:

- Determine the relationship between emissions of coal-fired power plants and their downwind optical effects.
- Document the current natural and anthropogenic contributors to visibility impairment in the southwestern U.S. and the relative contribution of the various sources, so that the contribution of power plants to the total can be determined.
- Provide data for evaluation of plume visibility models.

During the summers of 1977 and 1978, preliminary VISTTA experiments were performed using an instrumented aircraft to measure chemical and physical properties of selected point source plumes as well as regional haze in the southwestern U.S.

In 1979, two major field studies were conducted at and around the Navajo Generating Station (NGS) at Page, Arizona—one from June 26 to July 14 and the second from December 1 to 16. The specific objectives of the 1979 studies were to:

- Measure the chemical, optical, and physical properties of the NGS plume.
- Characterize the regional background aerosol and chemical environment near the power plant.
- Estimate the contributions of various sources to the regional haze using chemical element balance and extinction budget techniques.
- Analyze background and plume data to determine the effects of various plume components on plume optical effects and to evaluate EPA's PLUVUE visibility model.

This report summarizes the measurements and results to date of the June-July and December 1979 plume studies.

Procedures

During the 1979 field projects, ground and airborne measurements of aerosol size distribution, chemical and optical properties, as well as gaseous reactant concentrations, were made in both the NGS plume and background atmosphere. In-stack size distribution and aerosol chemistry measurements were made to characterize the emissions. Extensive regional and plume telephotometer measurements, airborne measurements along telephotometer sight paths, and meteorological data were collected.

The following types of specific experiments were performed:

- Plume chemistry flights. Sampling flights were made during which plume samples were collected for later chemical analysis. These flights consisted of a series of orbits (approximately one hour each) at fixed locations in the plume and in background air with one set of grab samples (filters, impactors, etc.) collected during each orbit. Plume samples were usually collected at two or three distances from the plant, ranging up to 100 km downwind. Samples were analyzed for $SO_4^=$, NO_3^-, HNO_3, NH_3, NH_4^+, C, and trace elements.
- Telephotometer sight path measurements. Sampling flights were made along numerous telephotometer sight paths both through the plume and through background air from the telephotometer to the target. Aerosol concentrations and size distribution as well as gas concentrations were measured along the path.
- Regional flights (summer only). Sampling flights were made by two aircraft to determine the composition and spatial variation of the regional haze. Aerosol size and chemistry as well as gaseous pollutants were measured. Regional flights were also made by one aircraft in the region upwind of Page on several days when the other aircraft was measuring plume chemistry.
- Ground based measurements of gases, aerosol chemistry and size distribution, and atmospheric optics. These measurements were made continually throughout the field programs to document the temporal and spatial variations in the background conditions, and to occasionally document plume characteristics at ground level.
- Regional light extinction and scattering measurements. Telephotometer and Integrating Nephelometer data were obtained continuously from several sites throughout the sampling region. These instruments provided supporting measurements of the temporal and spatial variations in visibility and provided an opportunity for intermethod comparisons.
- Method comparisons. Laboratory and field comparisons were performed between all the telephotometers used during the program, including commercial and research instruments to compare the results from telephotometers and Integrating Nephelometers. Comparisons were made between extinction from telephotometer data and calculations of extinction made by integrating

*In October 1982 this responsibility was transferred, along with the project scientists involved, to Sonoma Technology Inc., Santa Rosa, California

sight path aerosol data. Comparisons of several techniques for measuring sulfur aerosol and size distributions were made.

Throughout the program, all flights were supported by upper-air wind soundings every hour and temperature soundings every four hours in the Page vicinity. In addition, National Weather Service (NWS) surface and upper-air data were obtained for most of the Southwest for the period of the program. Two extra radiosonde measurements per day (total of four per day) were made at each of five NWS stations in the Southwest during the periods of the summer regional flights. Source measurements of aerosol size distribution and chemistry were made on several days. Emission rates, sulfur content, and other source operational parameters of NGS were made available by SRP for the duration of the program.

Results and Conclusions

As the report for which this summary is prepared is itself a summary of an extensive measurement and analysis program, a discussion of the experimental results is beyond the scope of this summary. In general, sufficient data were obtained to determine the quantity and variability of the aerosol and gas emissions, the size distribution of the aerosol emissions and plume aerosol, the formation rates in the plume of sulfates, nitrates, nitric acid, and fine particle aerosol, and the background aerosol composition for a few different synoptic situations. The optical properties of the plume were determined and compared to model predictions for 15 different case studies. The conclusions drawn from the data are presented below.

- For the NGS plume, under most lighting and viewing conditions within 50 km of the plant, NO_2 dominates the blue light extinction and brown coloration due to the plume. At distances less than 10 km, primary particles greater than 1 μm in diameter can dominate the light extinction at all visible wavelengths.The primary particle size distribution in the plume near the source has a small maximum under 0.1 μm diameter and a dominant maximum near 3.5 μm diameter. For modeling purposes, a mass median diameter of 3.5 μm should be used for NGS emissions.
- Sulfate formation rates in the NGS plume in both summer and winter under dry conditions were between 0 and 1% per hour. The NO_2 to HNO_3 conversion rate was substantially more rapid than the SO_2 to sulfate conversion rate, but the nitric acid remained in the gaseous state. The sulfate formed was largely ammonium sulfate. No particulate nitrates were measured in the plume. At distances up to 100 km in the plume, particle formation and growth were only detected in the size range below 0.1 μm and resulted in insignificant optical effects compared to those due to the background aerosol. Some aerosol probably was formed above 0.1 μm, but this formation was obscured by variations in the background aerosol concentrations. Gas-to-particle conversion was undetectable at night and while plume SO_2 concentrations were greater than about 100 ppb.
- The greatest causes of visibility impairment in the region during the 1979 summer study were widespread areas of elevated aerosol concentrations at different times due to:
  1. Long-range transport from the Southern California area 800 km away, and
  2. Wildfires.
- Although shown to be important by other studies, significant regional visibility impairment due to smelters or soil-derived elements (windblown dust) was not measured during the short 1979 summer VISTTA study.
- During this study, visibility impairment was generally caused by nonsoil aerosol. On these days, sulfates and organic carbon compounds dominated the fine particle aerosol composition. Fine particle chemical species contributed to light extinction approximately in proportion to their contribution to aerosol mass.
- Visibility reduction due to regional haze can equal or exceed the reduction caused by a plume from a nearby well-controlled power plant.
- In the NGS plume, NO_2 from primary emissions and the termolecular reaction can account for 3% to 6% of the measured NO_x near the source. For a given total amount of NO_x in any plume cross section, the NO_2 concentrations can be adequately modeled by assuming the photostationary-state relationship of NO, O_3, and NO_2. For dilute southwestern plumes (<100 ppb SO_2 at NGS), the reaction of NO_2 with OH represents a significant NO_2 loss mechanism, which should be accounted for in models.
- Evaluation of the chemistry, aerosol growth, and optics components of the EPA visibility model (PLUVUE) showed predictions to be in reasonable agreement with the measurements. More uncertainty was encountered with the dispersion component. The nine reactions used in PLUVUE adequately model the plume chemistry measured at NGS. For visibility modeling at power plants like NGS, for distances up to 100 km, secondary aerosol formation can be ignored under clean dry conditions.
- Comparisons between ground-based contrast telephotometer and Integrating Nephelometer data obtained during the program showed good agreement on days of regional homogeneity. The choice of targets was found to be important; the best correlations ($r > 0.9$) were for targets to the north. Inherent contrast changes in the targets with sun angle can substantially vary the correlation.
- Good agreement was found between the extinction coefficients determined by an Integrating Nephelometer on a sight path flight and the telephotometer viewing along the same sight path.
- Comparison and calibration of 12 multiwavelength contrast telephotometers showed an inherent error of about 1% or less in the contrast (ratio) mode and about 10% in the absolute radiance mode. Operator differences can increase the variation in contrast mode to 2% with a resulting variation in the calculated extinction coefficient of up to 15%.
- The SO_2 emission rate per BTU from NGS typically was found to vary less than 15%. Emission rates of NO_x and particulate matter per BTU, on the other hand, varied by about a factor of 2, complicating the prediction of visual impact in the definable plume.
- The chemical composition of the southwestern aerosol is substantially different for aerosol above and below about 1 μm diameter. For optimum separation of the coarse and fine aerosol, size-segregating samplers used in the southwestern U.S. should have a cut point near 1 μm diameter.

- The following findings suggest that NO_x and its oxidation products will be removed from the atmosphere more rapidly than SO_2 and its oxidation products, with the result that NO_x emissions have an impact over a smaller region than SO_2 emissions: (1) NO_x is oxidized to nitric acid (gas) several times more rapidly than SO_2 is oxidized to sulfate (particles); (2) gases are removed from the atmosphere more rapidly than particles; and (3) the air masses transported from Southern California contained easily measurable sulfate concentrations, but the nitrate concentrations were near the detection limit.
- The June-July and December 1979 VISTTA field programs provided an extensive data base for the evaluation of plume visibility models and of their individual components (e.g., dispersion, chemistry, and optics components). It is important to note, however, that the performance of a plume visibility model can vary according to the conditions considered. The VISTTA case studies presented in this report were obtained for a specific set of conditions (i.e., a power plant plume with particulate emission control in a relatively clean and dry atmospheric environment at downwind distances of less than 35 km). Further evaluation of plume visibility models could require the development of other data bases.

D. L. Blumenthal and L. W. Richards are presently with Sonoma Technology, Inc., Santa Rosa, CA; E. S. Macias is with Washington University, St. Louis, MO 63130; R. W. Bergstrom is with Systems Applications, Inc., San Rafael, CA 94903; and P. S. Bhardwaja is with the Salt River Project, Phoenix, AZ 85001.

***William E. Wilson, Jr.**, and **William D. Conner** are the EPA Project Officers (see below).*

The complete report, entitled "The Chemistry, Physics, and Optical Properties of Plumes and Background Air in the Southwest United States," (Order No. PB 83-261 768; Cost: $11.50, subject to change) will be available only from:

National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: 703-487-4650

The EPA Project Officers can be contacted at:

Environmental Sciences Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

☆U S GOVERNMENT PRINTING OFFICE 1983—759-015/7243

United States
Environmental Protection
Agency

Center for Environmental Research
Information
Cincinnati OH 45268

BULK RATE
U.S. POSTAG
PAID
Cincinnati, Oh
Permit No. G3

Official Business
Penalty for Private Use $300